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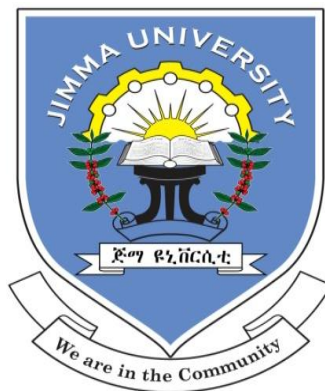**SCHOOL OF GRADUATE STUDIES**

DEPARTMENT OF CHEMISTRY

A THESIS ON:

KINETICS, EQUILIBRIUM AND THERMODYNAMICS STUDIES ON THE ADSORPTION OF METHYLENE BLUE AND CRYSTAL VIOLET FROM AQUEOUS SOLUTION USING ACTIVATED CARBON PREPARED FROM JACK FRUIT SEED

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OCTOBER, 2019

JIMMA, ETHIOPIA

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A THESIS SUBMITTED TO SCHOOL OF GRADUATE STUDIES JIMMA UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTERS OF SCIENCE (PHYSICAL CHEMISTRY)

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Declaration

This is to certify that this thesis entitled: (Kinetics, equilibrium and thermodynamics studies on the adsorption of methylene blue and crystal violet from aqueous solution using activated carbon prepared from jack fruit seed)**,** submitted to School of Graduate Studies, Department of Chemistry in partial fulfillment for the requirements of Master of Science Degree in Chemistry (Physical). I **Shiferaw Demissie** hereby declare that this M.Sc. thesis is my original work and has not been presented for a degree in any other University and that all source of materials used for the thesis have been duly acknowledged.

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A Thesis submitted to school of graduate studies Jimma University in partial fulfillment of the requirements for the degree of Master of Science in Chemistry (Physical)

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Approved by board of Examiners

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Jimma, Ethiopia

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Abbreviations and Acronyms

AC:-Activated carbon

JSAC: - Jackfruit seed activated carbon

CV: - Crystal violet

MB:-Methylene blue

R^2:- Correlation coefficient

ΔG: - Gibbs free energy change

ΔH: - Enthalpy change

ΔS: - Entropy change

ΔG^o:- Standard Gibbs free energy change

ΔH^o:- Standard enthalpy change

ΔS^o:- Standard entropy change

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Abstract

Dye removal from industrial effluents has become a significant issue in recent years. In this study Jackfruit (*Artocarpus heterophyllus*) seed activated carbon (JSAC) with zinc chloride ($ZnCl_2$) was used to investigate its potential as an adsorbent for the removal of two cationic dyes, methylene blue (MB) and crystal violet (CV) from aqueous solution. The dried Jackfruit seed powder/$ZnCl_2$ mixture was put on a crucible placed in an electrical furnace for carbonization. The heating rate of carbonization was 25 ºC/min and continues until the final temperature of 550 ºC was reached and it was kept at this temperature for 30 min. The absorbance for MB and CV solution was obtained using UV-Vis spectrophotometer. Experimental parameters such as contact time, medium pH, adsorbent dosage, dye concentration and temperature were studied to explore their effects on the adsorption of cationic dyes onto the adsorbent. Thermodynamics, isotherm models and kinetics were applied on the experimental data in order to further understand the adsorption process and mechanism. Kinetic studies of the data showed that the adsorption follows the pseudo-second-order kinetic model. Thermodynamic parameters, enthalpy change (ΔH), entropy change (ΔS) and Gibbs free energy change (ΔG) were also calculated for the uptake of MB and CV. This parameter showed that adsorption on the surface of JSAC was feasible, spontaneous in nature, and endothermic between temperatures of 25 and 45 ºC. The equilibrium data better fitted the Freundlich isotherm model for studying the adsorption behavior of MB and CV by JSAC. Maximum adsorption capacity of JSAC was observed to 1.82 mg/g for MB and 2.39 mg/g for CV at 25 ºC and 20 mg/L.

Keywords: Jackfruit seed activated carbon, Methylene blue, Crystal violet, Adsorption, Kinetic, Isotherm

1. Introduction

Dye removal from industrial effluents, such as textiles, leather, paper-making industries, plastics, printing, pharmaceutical, electroplating, jute, wool, dyestuff manufacturing, cosmetics and pharmaceuticals has become a significant issue in recent years [1,2,3]. Among these dyes, methylene blue (MB) and Crystal violet (CV) cationic dyes are carcinogenic, genotoxic, mutagenic, and teratogenic compared to anionic dye due to their synthetic origin and aromatic ring structure with delocalized electrons [4,5]. As most of these organic dyes in industrial effluents are damaging living aquatic organisms, therefore, it is very necessary to remove dyes from industrial effluents before it is discarded into the aquatic environment. Till now, the methods for the removal of ions and dyes from wastewater are adsorption [6,7,8], ionexchange [9], precipitation [10], electrochemical oxidation [11,12], ultra filtration [13], adsorption– photocatalytic degradation [14] etc. Among these techniques, adsorption is more promising than other available water treatment techniques for the removal of dyes from aqueous solutions, due to its flexible, more convenient, sample of design, clean, effective, and economical method[15,16].Therefore, several low-cost adsorbents have been used for dye treatment such as hen feather [17], coniferous pinus bark powder [18], bottom ash [16], red mud [17], ginger waste[2], bentonite [19,20], Hibiscus cannabinus fiber [21], vitreous tuff mineral [22], sawdust [23], and leaf powders [24,25].

The main aim of this research is to investigate the potential of Jackfruit seeds as low-cost adsorbent to remediate cationic dyes wastewater. Jackfruit (*Artocarpusheterophyllus*) tree is an evergreen tree that is found worldwide which include the South-East Asian nations, India, Florida, Central and Eastern African nations, Caribbean islands, Australia and most of the Pacific islands [26,27].The tree bears huge fruit with pungent fleshy yellow pulp and huge seeds. For most of the time, only the fleshy pulp is eaten while the seeds are considered as a by-product and are usually discarded which represented 8-15% of the total fruit weight[28]. The seeds are mainly consumed in the lower-income countries where the seeds can be roasted, boiled and steamed which produce aromatic and nutty taste. Locally, the seeds are usually diced and cook with curry; however, they are not popular cuisines due to the texture of seed and bland taste. The bland taste may be due to its high starch content which is approximate 93 to 95% [29]. On the other hand, starch-containing materials were reported to be effective in dye removal where corn starch and wheat starch removed approximately 37 and 39% of acid blue 193, respectively [30], and these results indicate that Jackfruit seed may be a good candidate for dye removal. This research will increase the value of *Artocarpusheterophyllus*.

In this study, the capabilities of Jackfruit seed as adsorbent was tested for the removal of two cationic dyes, MB and CV from aqueous solution. A series of experiments such as effects of contact time, pH, initial dye concentration, adsorbent dose, and temperature on the adsorption were investigated. The kinetics, isotherms of dyes, and thermodynamic studies were also performed.

1.1. Statement of the problem

Cationic dyes are considered as priority pollutants since they are harmful to organisms at low concentrations and many of them have been grouped as hazardous pollutants because of their potential to harm human health even in low concentration. They have been discharged into the environment as industrial wastes as mining, textile; petro-chemical, tannery and painting among others contaminate natural waters. Nowadays, to mitigate these toxic organic pollutants researchers' devised different conventional and advanced methods such as chemical precipitation and sludge separation, chemical oxidation or reduction, ion exchange, reverse osmosis membrane separation, electrochemical treatment and evaporation [31]. However, these methods face drawbacks as cost incompatibility, sludge production. Thus, the searches for low-cost adsorbents activated carbon like Jackfruit seeds have high surface area for adsorption capacities will be needed. Agricultural by-products have been widely studied for cationic dyes compounds removal from aqueous solutions. However, activated carbon is undoubtedly considered as universal adsorbent for the removal of diverse kinds of organic pollutants from aqueous solutions. Therefore, removing cationic dyes compounds from wastewater will an essential task to safe the water. Thus, the present research work can answer the following questions:

➢ What is the adsorptive removal efficiency of MB and CV using Jackfruit seed activated carbon?

➢ What are the factors that influence the adsorptive removal efficiency of the dyes using Jackfruit activated carbon?

➢ What is the adsorption isotherm model for experimental data to which the model fits?

➢ How Jackfruit activated carbon removes MB and CV dye from waste water?

➢ What is the reaction process?

1.2. Objectives of the study

1.2.1. General objective

➢ The general objective of this study is to evaluate the potential of activated carbon Jackfruit seeds for adsorption of MB and CV from aqueous solutions.

1.2.2. Specific objectives

➢ To prepare activated carbon from Jackfruit seed through chemical activation.
➢ To optimize parameters such as pH, mass of adsorbents, initial concentration, contact time and temperature on the adsorption efficiencies of adsorbent.
➢ To determine the appropriate adsorption isotherm models, kinetics and thermodynamics feasibility of adsorption for removal of MB and CV from aqueous solutions.

1.3. Significance of the study

Rapid industrialization and urbanization has resulted in the deterioration of water, air, and land quality [32]. Many industries discharge untreated or inadequately treated wastewater into waterways [33]. Large amount of wastewater having color is generated by many industries like textile, leather, paper, printing, plastic and so on [34]. Dyes are difficult to treat with municipal waste treatment operations as a result of their complicated chemical structures [35]. Cationic dyes are considered as toxic and carcinogenic when the amount of it above the limited concentration in tap water. Thus, removing MB and CV from aqueous solutions by Jackfruit seed is an economically feasible because of their relatively low investment and operational cost that is an important prior task to treat wastewater before discharging in to the environment.

2. Literature Review

2.1 History of synthetic dyes

Colorants (dyes and pigments) are important industrial chemicals. According to the technological nomenclature, pigments are colorants which are insoluble in the medium to which they are added, whereas dyes are soluble in the medium. The world's first commercially successful synthetic dye, named mauveine, was discovered by accident in 1856 by William Henry Perkin. These synthetic compounds can be defined as colored matters that color fibers permanently, such that they will not lose this color when exposed to sweat, light, water and many chemical substances including oxidizing agents and also to microbial attack [36,37].

By the end of the 19th century, over ten thousand synthetic dyes had been developed and used for manufacturing purposes. And an estimate was made in 1977 that approximately 800,000 tons of all recognized dyestuffs had been produced throughout the world [38].The expansion of worldwide textile industry has led to an equivalent expansion in the use of such synthetic dyestuffs, resulting in a rise in environmental pollution due to the contamination of wastewater with these dyestuffs [39].

The Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry (ETAD) was inaugurated in 1974 with the goals of minimizing environmental damage, protecting users and consumers and cooperating with government and public concerns in relation to the toxicological impact of their products [40].

A survey carried out by ETAD showed that of a total of approximately 4,000 dyes that had been tested, more than 90% showed LD_{50} values above 2×10^3 mg/kg, the most toxic being in the group of basic and direct diazo dyes [41].Thus, it appears that exposure to azo dyes does not cause acute toxicity, but with respect to systemic bioavailability, inhalation and contact with the skin by azo dyes is of concern, due to the possible generation of carcinogenic aromatic amines [42]. Of the approximately 10^9 kg of dyestuffs estimated to be manufactured annually throughout the World, the two most widely used in the textile industry are the azo and anthraquinone groups [43].

2.2 Chemistry of dye

Unlike most organic compounds, dyes possess color because they

1. absorb light in the visible spectrum (400–700 nm)
2. have at least one chromophore (color-bearing group)
3. have a conjugated system, i.e. a structure with alternating double and single bonds
4. exhibit resonance of electrons, which is a stabilizing force in organic compounds.

Since the effectiveness of a dying or printing process often hinges on the affinity between the dye and substrate, dyes are designed with a specific substrate in mind. In this regard, dyes must be designed that have a) greater affinity for the substrate than the medium (usually water) from which it is applied and b) a high degree of permanence under end-use conditions (e.g. stability to fading upon exposures to water (wet fast) and/or sunlight (light fast)[33].

2.3 Sources of dye contaminations

Contamination of water resources by dye pollutants is considered as an environmental important problem. Due to toxicity and unpleasant appearance, discharging the dye pollutants into surface water resources is undesirable [44]. In many industries such as food, textile, paper, rubber carpet, plastic and cosmetic, dyes are used in manufactures process [45]. Textile and dying industries are two main sources of dye wastewater production and treatment of this wastewater is difficult due to synthetic and complex structure of dye.

The main source of discharge of dyes is textile industries where they are used to color products. Today there are over 1,000,000 dyes for commercial use and around 700 tons of dyestuffs are produced annually [46].The types of dyes are mainly basic dyes, acid dyes, direct dyes, reactive dyes, mordant dyes, azo dyes, disperse dyes and sulphur dyes [47].

2.4 Toxicity of dye and mobility in the environment

Most of the dyes are toxic and have carcinogenic properties so they make water bodies inhibitory to aquatic systems. They don't fade by water or sunlight and owing to their complexity in structures; they can't be adequately treated in conventional treatment plants for waste waters. There are numerous harmful effects of dyes on ecosystem such as: they pose acute as well as chronic effects on most of the exposed organisms. These effects vary depending on the time of exposure and the concentration of dyes. They can absorb or reflect sunlight which enters the water bodies and thus affect the growth of bacteria and cause an imbalance in their biological. They are highly visible and even a minor amount may cause

abnormal coloration of water bodies which appears displeasing to eyes. They have complex molecular structures which makes them difficult to treat with common municipal treatment operations. They consume dissolved oxygen and affect aquatic ecosystem.

In addition, the effects caused by other pollutants in textile wastewater, and the presence of very small amounts of dyes (<1 mg/L for some dyes) in the water, which are nevertheless highly visible, seriously affects the aesthetic quality and transparency of water bodies such as lakes, rivers and others, leading to damage to the aquatic environment [48].

2.5 Types of dye

Synthetic dyes have many structural varieties, such as: acidic, basic, disperse, azo, diazo, anthroquinone based and metal complex dyes, that fall into either the cationic, nonionic or anionic type. Anionic dyes include the direct and the most problematic water-soluble acid and reactive dyes. Nonionic dyes refer to disperse dyes that do not ionize in aqueous medium and some of them have the ability of bioaccumulation. Whereas anthroquinone based dyes are the most resistant to degradation due to their fused aromatic ring structure [49].

The color of dye is combined effects of chromophores, delocalized electron system with conjugated double bonds, and auxochrome – electron withdrawing or electron donating substituent that enhance the color of chromophore by changing the overall energy of electron system. Some of the important chromophores are: $- N= N-$, $C= O$, $-NO_2$ and quinoid groups, and important auxochromes are: $-NH_3$, $-OH$, $-SO_3H$ and $-CO_2H$. Both chromophore and auxochrome increase the bathochromic effect – shifting adsorption bands to longer wavelength, on a conjugated system of dye. In addition to enhancing the chromophore in production of color, auxochromes are also responsible for the solubility of dye and increase its reactivity towards fibers [50].

The chromophores in anionic and non-ionic dyes are mostly azo groups or anthroquinone type. Toxic amines result when azo groups undergo reductive cleavage. Reactive dyes are azo-based chromopores that contain different types of reactive groups such as vinyl sulfone, chlorotriazine, trichloropyrimidine, diflurochloropyrimidine. In contrast to other classes of dyes, they form covalent bonds to the textile fibers such as cotton. The uses of reactive dyes are highly favored in the textile industries owing to their bright color, simple application techniques with low energy consumption and, thus reactive dyes are among the dyes most commonly in use today [51]. Reactive dyes are used primarily on cotton and rayon. They are highly soluble in water and with the help of large amount of salt; the exhaustion of the dyes is improved [36].

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2.5.1. Methylene blue

Methylene blue is a heterocyclic aromatic compound (a phenothiazine derivative) with the chemical formula $C_{16}H_{18}N_3SCl$. Its IUPAC name is 3,7-bis(Dimethylamino)- phenothiazin-5-ium chloride. The structure of methylene blue is shown in Scheme1. At room temperature it appears as a solid, odourless, dark green powder that yields a blue solution when dissolved in water. It shows maximum absorption of light around 681 nm. Methylene blue was first prepared as a stain in 1876 by German chemist Heinrich Caro. However, it was discovered to be an antidote to carbon monoxide poisoning and cyanide poisoning in 1932 by Matilda Moldenhauer Brooks [10].
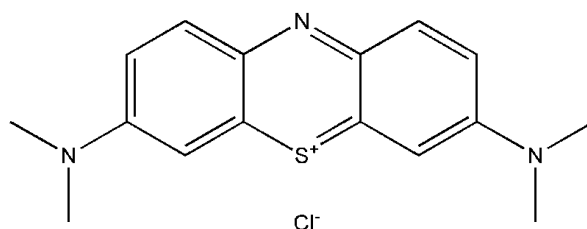
Scheme 1: Chemical structure of Methylene blue

2.5.2 . Crystal violet

Crystal violet belongs to triarylmethane group of dyes and has the chemical formula $C_{25}H_{30}N_3Cl$. Its IUPAC name is Tris(4-(dimethylamino) phenyl) methylium chloride. The structure of crystal violet is shown in Scheme 2.The dye has a violet colour with an absorbance maximum at 664 nm. The dye was first prepared by the German chemists Kern and Caro involved the reaction of dimethylaniline with phosgene to give 4,4′bis(dimethylamin o) benzophenone as an intermediate. This was then reacted with additional dimethylaniline in the presence of phosphorus oxychloride and hydrochloric acid [15].
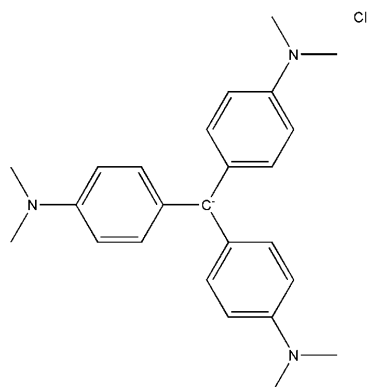
Scheme 2: Chemical structure of Crystal violet

2.6. Activated carbon

Activated carbon (AC) is an amorphous form of carbon that is specially treated to produce a highly developed internal pore structure and a large surface area; therefore, a reasonably cheap and excellent adsorbent is produced [52]. AC has a highly developed porosity, a large surface area (that can reach 3000 m^2 g^{-1}), variable surface chemistry characteristics, and a high degree of surface reactivity; therefore, it is considered a very effective adsorbent for the removal of a wide variety of organic and inorganic pollutants dissolved in aqueous media [53]. It is not truly an amorphous material but has a microcrystalline structure that starts to build up during the carbonization process. However, the activated carbon microcrystalline structure differs from that of graphite with respect to the interlayer spacing which is 0.335 nm in the case of graphite and ranges between 0.34 and 0.35 nm in activated carbon. Activated carbon is a fine black odorless and tasteless powder made from wood or other materials that have been processed to make it extremely porous and thus to have a very large surface area available for adsorption [54].

2.6.1. Applications of activated carbon

Applications of AC are enormous. Its important use is for gasoline vapor emission control canisters in automobile. AC can act as a filter material in air cleaning filters for removal of gases and vapors in the industrial environment. Especially impregnated grades are used in cigarette filters to adsorb some of the harmful components of tobacco, and as the catalyst or carrier of catalytically active substances. Cationic dyes ions such as MB and CV in drinking waters are very dangerous even in trace amount, and adsorption method for removing these ions can be essential for water and waste water contaminated by Cationic dyes ions. These ions cannot be removed from water with classic physical or chemical treatments completely [53]. Activated carbon can be used for removal of poisonous Cationic dyes ions from aqueous solutions. Adsorption in this case is due to the surface complex formation between in the Cationic dyes ions and the acidic surface function group of AC. The removal efficiency is influenced by various factors, such as solution concentration, solution pH, ionic strength, nature of adsorbate, adsorbent modification procedure, physical properties (surface area, porosity), and the chemical nature of AC [55,56].

2.6.2. Preparation of activated carbon

Any carboneous materials (animal, plant, or mineral origin) with a high concentration of carbon can be simply changed into activated carbon (using both chemical or gas activation

methods). The most common raw materials are wood, charcoal, nut shells, fruit pits, brown and bituminous coals, lignite, peat, bone and paper mill waste (lignin), synthetic polymers like PVC (Polyvinyl chloride), are used for manufacturing of activated carbon. Activated carbon obtained from hard wood is preferable for adsorption because charcoal obtained from soft wood, such as pinewood, is very unstable and readily crumbles. It has been reported that the best grades of AC are obtained from the coconut shell and apricot pits. Activated carbons are commonly prepared by a physical activation or chemical activation process. Physical activation consists of two steps: a carbonaceous material is carbonized under the oxygen-free atmosphere (carbonization process) and then activated with an activating gas such as CO_2 and H_2O (activation process).

In chemical activation, both carbonization and activation processes occur simultaneously at a lower temperature and a shorter time than that in physical activation. Therefore, it saves time and energy. Moreover, chemical activation is reported to give activated carbon with higher specific surface area and much better developed porosity than physical activation. Most studies concerning the removal of micro pollutants in aqueous solution by adsorption are carried out by using activated carbon. However, with the aim of implementing the technology at full scale application, studies of water and wastewater are the most significant. In chemical activation, several types of chemicals are used as the activating agent including $ZnCl_2$, H_3PO_4 and KOH. Different activating agents provide activated carbons with different properties. Hayashi and coworkers found that the greatest specific surface areas of activated carbons were obtained at the carbonization temperature of 600 ^{o}C with $ZnCl_2$ and H_3PO_4 activation. In contrast, the maximum surface areas of activated carbons are obtained at the carbonization temperature of 800°C with alkali metal (KOH, NaOH, K_2CO_3 and Na_2CO_3) activation [57].

2.7. Adsorption

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a film of molecules or atoms (adsorbate). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution [58].

2.7.1. Adsorption process

Adsorption arises as a result of the unsaturated and unbalanced molecular forces that are present on every solid surface. Thus, when a solid surface is brought into contact with a liquid or gas, there is an interaction between the fields of forces of the surface and that of the liquid or gas. The solid surface tends to satisfy these residual forces by attracting and retaining on its surface the molecules, atom, or ion of the gas or liquid. This results in a greater concentration

of the gas or liquid in the near vicinity of solid surface than in the bulk gas or vapor phase, despite the nature of gas or vapor. The process by which this surface excess is caused is called adsorption. The adsorption involves two types of forces as physisorption (characteristic of weak Van der Waals forces) or chemisorptions (characteristic of covalent bonding).

a. Physical adsorption: The adsorbate is bound to the surface by relatively weak Van der Waals forces, which are similar to the molecular force of cohesion and are involved in the condensation of vapors into liquids.

b. Chemical adsorption: Chemisorptions involves exchange or sharing of electrons between the adsorbate molecules and the surface of the adsorbent resulting in a chemical reaction. The bond formed between the adsorbate and the adsorbent is essentially a chemical bond and is thus much stronger than in the physisorption [58].

2.8. Adsorption kinetic studies

Adsorption is a time-dependent process and it is very important to know the rate of adsorption for design and evaluate the adsorbent in removing the MB and CV in wastewater. In many cases, the kinetics of adsorption based on the overall adsorption rate by the adsorbents is described by the first order Lagergren model and pseudo second-order[59].The first-order rate expression of Lagergrenis given as:

$$\frac{dq}{dt} = k_1(q_e - q_t) \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots (1)$$

where q_e and q_t are the amount of dyes adsorbed on adsorbent at equilibrium and time t, respectively (mg/g), and k_1 is the rate constant of the first order adsorption (min^{-1}). Integrating equation (1) for the boundary conditions t = 0 to t = t is the following:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k1}{2.303}\right)t \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots (2)$$

The plot of $\log(q_e - q_t)$ versus t will give a straight line and the value of k_1 can be obtained from the slope of the graph. The second-order kinetic model is expressed as:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots (3)$$

where, k_2 is the pseudo-second-order rate constant of adsorption (g mg^{-1}min^{-1}). The linearized integrated form of (3) is given as:

$$\frac{t}{q_t} = \frac{1}{k_2 qe^2} + \frac{1}{q_e t} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (4)$$

If the pseudo second-order kinetics is applicable to the system, then the plot of t/q_t versus t of equation 4 will give a linear relationship with 1/q_e and 1/$k_2q_e{}^2$ as a slope and intercept, respectively.

The values of q_e and k_2 can be determined from the slope and intercept and there is no need to know any parameters beforehand. The pseudo second-order kinetics model has been successfully applied to several biosorption systems as reported by [33,34].

2.9. Adsorption isotherms

There are several isotherm equations available for analyzing experimental adsorption equilibrium parameters, the most common being the Langmuir and Freundlich models. The Langmuir isotherm model is based on the assumption that there are a finite number of active sites which are homogeneously distributed over the surface of the adsorbent. These active sites have the same affinity for adsorption of a mono molecular layer and there is no interaction between adsorbed molecules [35].

A well-known linear form of the Langmuir equation can be expressed as

$$\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{q_m b_L} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (5)$$

where q_e is the amount of dye adsorbed (mg/g), c_e is the equilibrium concentration of the adsorbate (mg/L), and q_m and b_L are Langmuir constants related to the maximum adsorption capacity (mg/g) and energy of adsorption (L/mg).

According to equation 5, when the adsorption obeys the Langmuir equation, a plot of C_e/ q_e versus Ce should be a straight line with a slope of 1/ q_m and intercept 1/$q_m b_L$ [36]. This important characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless factor, R_L [37], which is defined as:

$$R_L = \frac{1}{1 + b_L C_o} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (6)$$

The R_L values indicate the type of adsorption as either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

The Freundlich isotherm model applies to adsorption on heterogeneous surfaces with interaction between the adsorbed molecules, and is not restricted to the formation of a

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monolayer.This model assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases and, correspondingly, the sorption energy exponentially decreases on completion of the sorption centers of the adsorbent. The well-known expression for the Freundlich model is given as [38]:

$$logq_e = logk_f + \frac{1}{nlogC_e} \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots (7)$$

Where q_e is the amount adsorbed at equilibrium (mg/g), K_f is the Freundlich constant, $1/n$ is the heterogeneity factor which is related to the capacity and intensity of the adsorption, and Ce is the equilibrium concentration (mg/L). The values of K_f and $1/n$ can be obtained from the slope and intercept of the plot of log q_e against log Ce. Value of $1/n$ ranges from 0 to 1 and the closer this value to zero, the more heterogeneous the adsorbent surface.

2.10. Thermodynamic study

Spontaneity of a process can be determined by thermodynamic parameters such as free energy change ($\Delta G°$) and entropy change ($\Delta S°$) [39].

The thermodynamic parameters can be determined by using the following equations.

$$lnk_c = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots (8)$$

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots (9)$$

where R (8.314 J/mol K) is the gas constant, T (K) the absolute temperature and Kc (L/g) is the standard thermodynamic equilibrium constant defined by q_e/c_e. By plotting a graph of lnk_c versus 1/T the values $\Delta H°$ and $\Delta S°$ can be estimated from the slopes and intercepts.

3. Materials and Methods

3.1. Chemicals and Materials

Hydrochloric acid (RIEDEL DEHAEN, 37% PURE), sodium hydroxide (MACRON FINE CHEMICALS,98% PURE), potassium hydroxide (BDH, England) solution (25% W/V), zinc chloride (CAS_7646-85-7] 98% PURE), phosphoric acid (H_3PO_4), acetic acid (LOBA CHEMIE, 99.5 PURE), sodium acetate (FINE, 99% PURE), methylene blue ($C_{16}H_{18}N_3SCl$, EK Industries–7443), crystal violet ($C_{25}H_{30}N_3Cl$,SKU: GENTIAN-1PERC-1OZ), electronic balance (ADAMAFP110L), pH meter (HANNA instruments, pH 215),oven (GENLAB WID NES, England), mechanical shaker, thermostatic water bath (Model Grant GLS400, England), UV-Vis spectrophotometer (JENWAY 6705,UV/Vis, England) electrical mill and electrical furnace (Model Nabertherm[R]).

3. 2. Preparation of adsorbent

Jackfruit was bought from local markets and the rind, fleshy pulps and seeds were separated. The seeds were washed with distilled water, diced into small pieces and dried in oven at 70 ^{o}C. After drying, the diced seeds were crushed using a blender and sieved to size less than 355 μm, and mixed with $ZnCl_2$ by [1:1] ratio, stirred and activated for 12 h at 25 ^{o}C, the mixture then dried at 105 ^{o}C in the oven. The dried Jackfruit seed powder/$ZnCl_2$ mixture then was put on a crucible placed in an electrical furnace for carbonization. The heating rate of carbonization was 25 ^{o}C/min and continues until the final temperature of 550 ^{o}C was reached and it was kept at this temperature for 30 min. The produced activated carbon was then cool down to room temperature.

The pyrolyzed samples were put into 0.1 M/L solution of HCl to be boiled for 20 min, and washed repeatedly with 0.1 M/L solution of HCl, later with distilled water until free of chloride ions. Once the activating agent was removed, the activated carbon sample was dried at 120 ^{o}C for 12 h and stored in desiccators until further use.

3. 3. Preparation of dye solution

An accurately weighted 1 gm of each dye was dissolved in 1000 mL of distilled water separately to prepare stock solution (1000 mg/L). The pH of each experimental observation was maintained with the use of 0.1M HCl or 0.1M NaOH.

3.4. Adsorption study

The adsorption study was carried out by contacting 0.2 g of the activated carbon with 25 mL of the dyes solution under different conditions for a period of time in a conical flask. The adsorption studies are conducted at 25 °C using mechanical shaker to determine the effect of pH, contact time and initial dyes concentration on the adsorption. The residual dyes were analyzed using UV-Vis spectrophotometer. All experiments were carried out in triplicate, and the concentrations given are average values. The initial dyes concentration in the test solution and the adsorbent dosage were varied to investigate their effect on the adsorption kinetics. The adsorption studies were carried out at different temperatures. This is used to determine the effect of temperature on the thermodynamic parameters. The amount of adsorption at time t, q_t (mg/g), was calculated using the following relation [47].

$$q_t = \frac{(C_o - C_t)v}{w} \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots (10)$$

Where C_t (mgL^{-1}) is the liquid phase concentrations of dyes at any time, C_0 (mgL^{-1}) is the initial concentration of the dyes in solution. V is the volume of the solution (L) and W is the mass of dry adsorbent (g).

The amount of equilibrium adsorption, q_e (mg /g), was calculated using

$$q_e = \frac{(C_o - C_e)v}{w} \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots (11)$$

Where Co and Ce (mgL^{-1}) are the concentrations of MB and CV initially and at equilibrium. The percentage adsorption of MB and CV solution was calculated by using the following equation.

$$\%adsorption = \frac{C_o - C_e}{C_o} \times 100 \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots (12)$$

where C_0 and C_e (mgL^{-1}) are the initial and equilibrium concentrations of the MB and CV solutions.

3.4.1 Effect of contact time on adsorption

A solution of MB and CV having each a concentration of 20 mg/L were prepared. 0.2 gm of activated carbon sample was taken in a 50 mL conical flask along 25 mL of the prepared dyes solution. This was then kept in a shaker at a temperature of 25° C (room temperature) and vibrating at 150 rpm. So 5 samples of above said concentration was prepared for each dyes in 50 mL taken in 5 different conical flasks. The contact time for 5 different conical flasks for each dyes were taken as 15, 30, 45, 60 and 75 min. The percent absorbance of UV at 681 nm was determined for MB and at 664 nm for CV solution.

3.4.2 Effect of pH on adsorption

The effect of pH on the adsorption of the dyes were done by contacting 0.2 g of activated carbon with 25 mL of 20 mg/L dyes solutions in 50 mL of conical flask within buffer solution ranging from pH 3 to 9. The conical flask containing the mixture were left in a mechanical shaker and shaken at 150 rpm and 25 ^{0}C for 45 min. The adsorbent was removed from the solution by filtration. The residual dyes concentration in the solution was analyzed. The optimum pH was determined as the pH with the highest adsorption of each dyes.

3.4.3. Effect of adsorbent dosage

The adsorption of dyes by JSAC at different adsorbent doses (0.1–0.3 g) and at the MB and CV concentration of 20 mg/L was investigated. This was done by weighing 0.1, 0.15, 0.2, 0.25 and 0.3 g of JFAC into each conical flask and 25 mL of 20 mg/L of MB and CV solutions at optimal pH and contact time. The conical flasks were left in a mechanical shaker and shaken at 150 rpm on 25 °C. The activated carbon was removed from the solution and the concentration of residual dyes in each solution was determined using UV-Vis spectroscopy.

3.4.4. Effect of initial concentration on adsorption

Batch adsorption study of MB and CV were carried out using a concentration range of 20 to 100 mg/L. This was done by introducing 0.2 g of the activated carbon into each of the conical flask employed and 25 mL of dyes solutions at optimal pH and contact time. The conical flasks were left in a mechanical shaker at 150 rpm and 25 °C. The activated carbon was removed from the solution and the concentration of residual dyes in each solution was determined using UV-Vis spectroscopy.

3.4.5. Effect of temperature on adsorption

The batch adsorption process was studied at different temperatures (25 – 45 °C) in order to investigate the effect of temperature on the adsorption process. This was done by contacting 0.2 g of activated carbon with 25 mL of 20 mg/L of dyes solutions at the optimal pH and contact time.

3.4.6. Statistical analysis

Triplicate measures were considered during the determination of MB and CV using UV-Vis spectroscopy. And it was analyzed by averaging the values. The curve fittings of the data obtained were performed using Origin 8.0 software.

4. Results and Discussions

In this study, batch adsorption experiment was carried out. Different parameters such as contact time, initial pH, adsorbent dose, effect of initial dye concentration and temperature were evaluated in order to determine the efficiency of adsorbent. The data obtained from these studied were used to describe responsible adsorption isotherm models, to assess the kinetics and thermodynamics of the adsorption of methylene blue and crystal violent onto Jackfruit seed activated Carbon.

4.1 Effect of contact time on dye removal

The dependence of adsorption on contact time was studied using fixed amount (0.2 g) of adsorbent (activated carbon) on 20 mg/L MB and CV solution in a fixed volume (25 mL).The percentage removal and the amount of dyes (MB and CV) adsorbed per unit mass of the adsorbent, q_t (mg/g) at JSAC was shown in Figure 1 A and B. From the Figure 1, the removal efficiency of MB and CV and adsorption capacity were found to increase with contact time. Initially within first 15 min increase in adsorption was reflected till maximum slope reached in next 30 min. There after a steady state equilibrium was obtained. The initial fast reaction may be due to the increased number of vacant sites available at the initial stage; as a result there exist increased concentration gradient between adsorbate in solution and adsorbate in the adsorbent and the CV removal capacity increased from 1.45 mg/g to 2.39 mg/g and also the MB removal capacity increased from 1.6 mg/g to 2.3 mg/g.

Maximum percentage of MB and CV removal occurs at 45 min, after that the percentage adsorption remains uniform. The maximum percentage removal of MB and CV at this time was found to be 92% and 95.6% in 20 mg/L of solution, respectively. Based on this experimental result the optimum contact time for adsorption on JSAC was fixed to be 45 min.
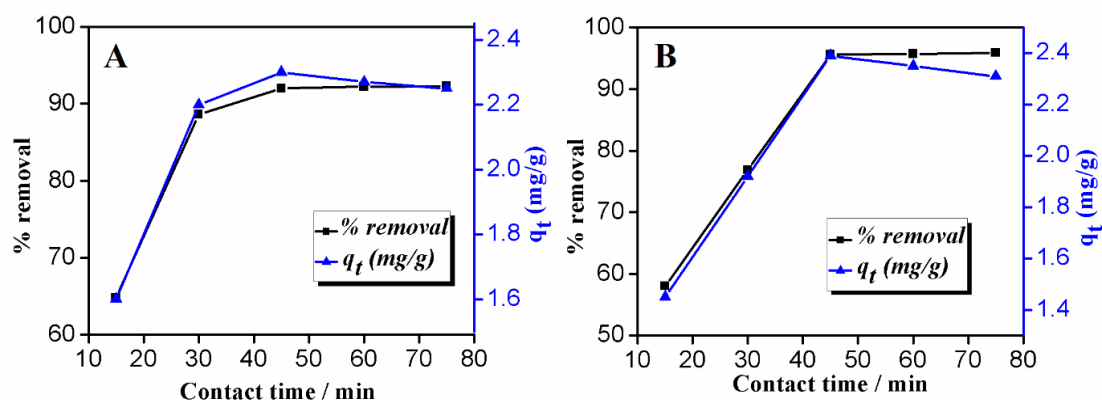

Figure 1.Effect of contact time for adsorption of A) MB and B) CV

4.2 Effect of initial pH on dye removal

The pH medium plays a significant role in adsorption process. In order to study the effect of pH on uptake, the solution pH was varied from 3 to 9 at a temperature of 25°C and 20 mg/L concentration of MB and CV aqueous solution. The contact time has been fixed as 45 min. Figure 2 shows the effect of pH on adsorption percentage of CV and MB by JSAC. It was found that adsorption of MB and CV from aqueous solution was strongly pH dependent.

For MB and CV adsorption increases with increasing pH from 3 to 5, further increase in pH of solution leads to decline in percent adsorption. At pH 9 the adsorption was reasonably low around 42% for MB and 55% for CV. The maximum adsorption percentage obtained were 97.7% at pH 5 for MB and 95.6 for CV. At low pH, H_3O^+ exist into the solution and it compete with positive ions for active binding sites on the surface of JSAC, which leads to fewer binding sites being available to bind MB and CV resulting lower adsorption efficiency. As the pH increases, there were fewer numbers of H_3O^+ available; the surface became negative resulting greater electrostatic attraction between MB, CV ions and the surface of JSAC. Thus, the adsorption efficiency was increased between pH 3 to 5. So, all the batch experiments were conducted in slightly acidic medium of pH 5.
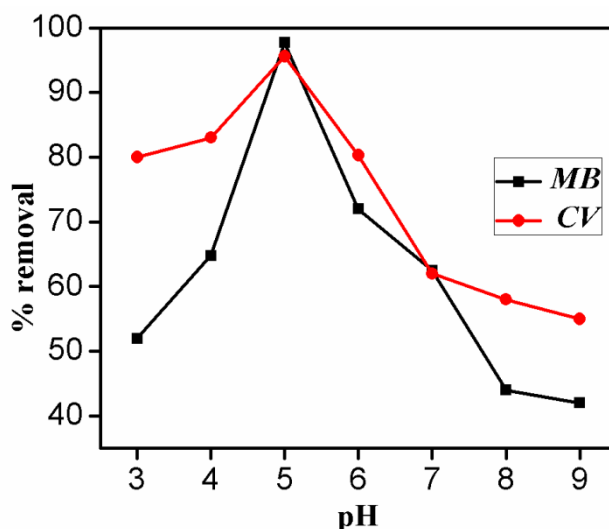
Figure 2. Effect of pH for adsorption of MB and CV

4.3 Effect of adsorbent dosage on dye removal

The variation of the adsorbent dosage experiments is an important part of the study, because it determines the capacity of an adsorbent for a given initial concentration of the adsorbate at the operating conditions. The effect of adsorbent dosage between 0.1 and 0.3 g on MB and CV at 25 ^{o}C is investigated. Figure 3 showed the effect of adsorbent dosage on the percentage removal and the amount of dyes (MB and CV) adsorbed, q_e (mg/g). The percent adsorption

increases from 77 to 98.9% for MB, 83 to 98.89% for CV with an increase in the dose of JSAC from 0.1 to 0.2 g and remained nearly constant at adsorbent quantities higher than 0.2 g. This is due to the greater availability of adsorption sites of adsorbent and thus making easier penetration of the MB and CV to the adsorption sites. After an adsorbent dosage of 0.2g MB and CV adsorption was not observed to increase significantly. On the other hand, the adsorption capacity decreases from 3.88– 1.65 for MB and 4.156 − 1.646 for CV as dosage increase. The decrease in the adsorption capacity is due to the increased solid dose for the fixed solute load resulting in a lower availability of the dyes per unit mass of adsorbents [60].
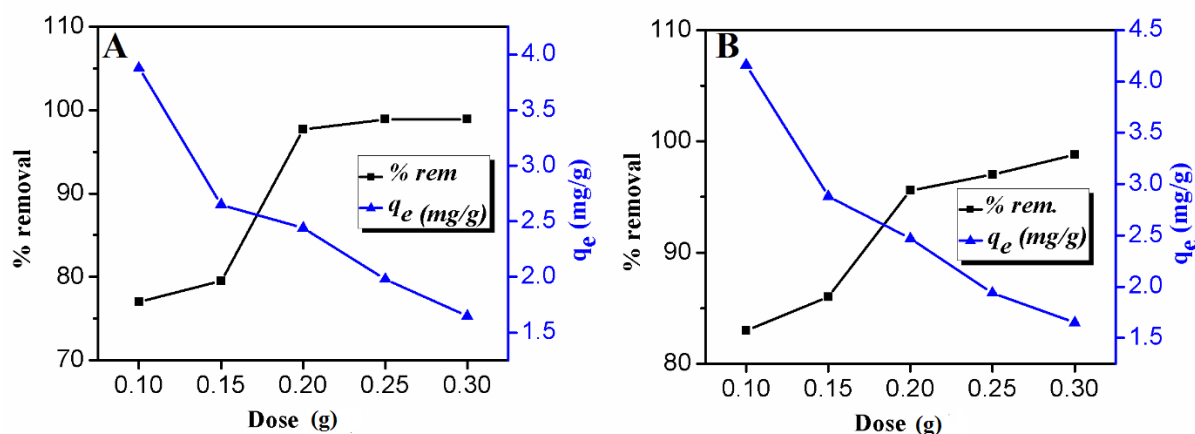

Figure 3. Effect of adsorbent dose on A) MB and B) CV removal efficiency and adsorption b
capacity by JSAC.

4.4 Effect of dye concentration on dye removal

The adsorption of MB and CV onto the JSAC was studied for different concentrations 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L and 100 mg/L of MB and CV solution (Figure 4 A and B). The experiment was conducted at optimum condition 0.2 g adsorbent dosage, 25 °C and pH 5 for contact time of 45 min. The adsorption efficiency decreased from 72.7 to 64.1% for MB and from 95.6 to 71% for CV with increases initial concentration from 20 to 100 mg/L. Maximum dye removal occurred for low initial concentration of MB and CV that showed gradual reduction when initial concentration of dye was raised. It could be ascribed to fixed concentration of adsorbent dosage. With increase in initial dye concentration the adsorption sites were fixed and achieved saturation at low dye concentration. Hence with increase in dye concentration no further adsorption could be achieved and resulted in reduced removal of dye with increase in dye concentration [60].
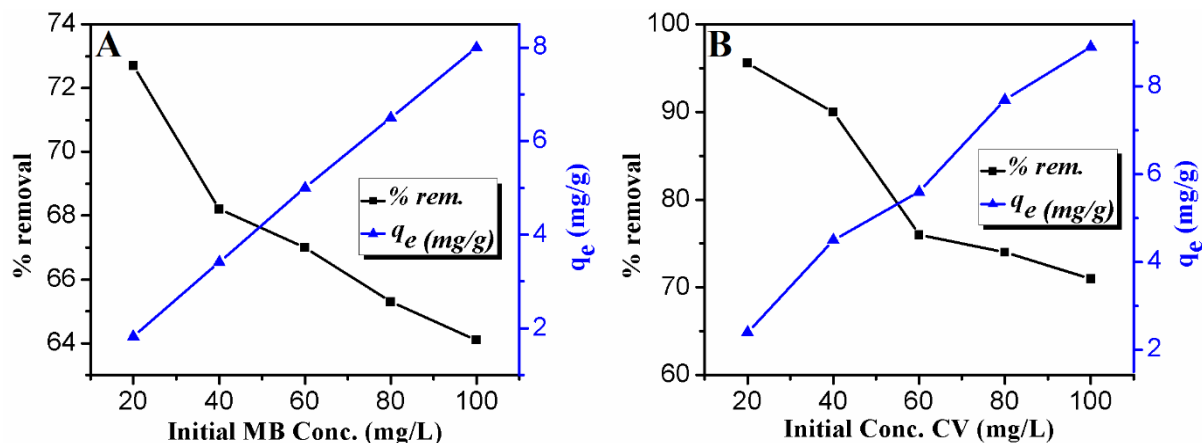
Figure 4. Effect of initial A) MB and B) CV concentration on MB and CV removal efficiency and adsorption capacity

4.5 Effect of temperature

Temperature is a highly significant parameter in the adsorption process. Experiments were performed at different temperatures (25 ^{o}C, 30 ^{o}C, 35 ^{o}C and 45 ^{o}C) at optimum pH and contact time. It was observed that the percentage of adsorption increases from 93 to 98.9% for MB and 90.9 to 98.8 for CV with the rise in temperature from 25 to 45 ^{o}C. The results are evident from Figure 5. The results revealed the endothermic nature of the adsorption process which were later utilized for determination of changes in standard Gibbs free energy (ΔG^{o}), standard heat of adsorption (ΔH^{o}), and standard entropy (ΔS^{o}) of the adsorption of MB and CV from aqueous solutions. The increase in adsorption with the rise in temperature because, this adsorbent is not homogenous, implying the active energy of adsorption sites is different. Therefore, at low temperature, the adsorption sites with lower active energy were first occupied, and the other sites with higher active energy were occupied as the increase of temperature [61].

The rise of the adsorption capacity increases with temperature because of the rise of the kinetic energy of adsorbent particles. Thus, the collision frequency between adsorbent and adsorbate increases, which results in the enhanced adsorption onto the surface of the adsorbent. Secondly, at high temperature due to bond rupture of functional groups on adsorbent surface there more, be an increase in number of active adsorption sites, which may also lead to enhanced adsorption with the rise in temperature [60].
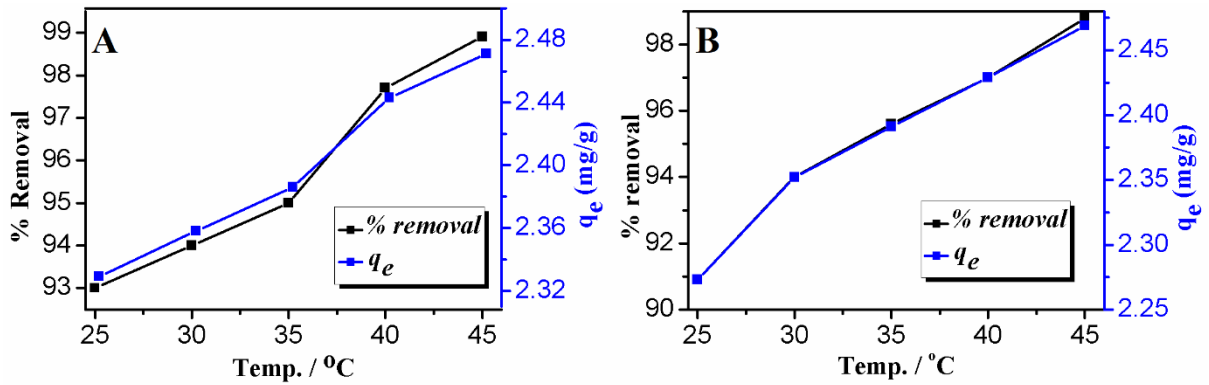
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Figure 5. Effect of Temperature A) MB and B) CV removal efficiency and adsorption capacity

4.6 Adsorption isotherms

Isotherms give an equilibrium relationship between the amounts of adsorbate adsorbed on the adsorbent surface and its concentration in the solution at a constant temperature. Numerous adsorption models are available in the literature to fit the experimental adsorption data. In this study, the data were fitted using Langmuir and Freundlich models. Each of these models makes use of a parameter q_e (i.e. adsorption capacity per unit mass of the adsorbent at equilibrium) in mg/g

$$q_e = \frac{(C_o - C_e)V}{X} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (13)$$

C_o=Initial concentration of solution (mg/L)

C_e=Equilibrium concentration of solution in (mg/L)

V=Volume of solution in L

X=Amount of adsorbent used in g

The linear form of Langmuir expression:

$$C_{e/q_e} = C_{e/}Q_o + \frac{1}{bQ_o} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (14)$$

Where C_e is the equilibrium concentration of dye solution (mg/L), q_e is the equilibrium capacity of dye on the adsorbent (mg/g), Q_o 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. Langmuir model was fitted to the experimental data as shown in the Table 1 below. The activated carbon was taken as 0.2 g for different concentration of dyes. The solution inside the conical flask was maintained around pH 5 and it was kept in shaker for 45 min.

Table 1, show that the adsorption of MB and CV on JSAC fits well with the Freundlich model. The fact that the Freundlich model is a good fit to the experimental adsorption data suggests physical adsorption as well as a heterogeneous distribution of active sites on the JSAC surface. The observed correlation coefficients for Freundlich isotherms were 0.992 for MB and 0.909 for CV. The other Freundlich constant, n, is a measure of the deviation of the adsorption from linearity. If the value of n is equal to unity, the adsorption is linear. If the value of n is below unity, it implies that the adsorption process is unfavorable, and if the value of n is above unity, adsorption is favorable [62]. In the present study, the values of the dimensionless factor, R_L, were between 0 and 1. This also suggested a favorable adsorption between JSAC and MB and CV.

Table 1. Results of isotherm models for the adsorption of MB and CV by AC at 25 $^{\circ}$C

Isotherm models	Parameters	MB	CV
Langmuir isotherm	q_m (mg/g)	1.831	2.412
	b_L (L/mg)	-0.3496	-0.6592
	R^2	0.909	0.327
Freundlich isotherm	K_f	1.295	2.69
	1/n	0.401	1.0
	R^2	0.992	0.94
	R_L at 100 mg/L	0.0294	0.0154

4.7. Adsorption kinetic studies

For any adsorption system, study of chemical kinetics is very important so as to determine the rate constants for the reaction and to know how quickly or slowly the reaction is proceeding. In order to evaluate the kinetic parameters, Pseudo first order and Pseudo second order models were implemented to analyze the experimental data. The pseudo first order equation can be expressed as:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.203}\right)t \quad \text{.......................................} (15)$$

where, q_e and q_t represent the amount of adsorbed (mg/g) at equilibrium and at any time t, k_1 is the first order rate constant (min^{-1}). From the plots of log (q_e-q_t) versus t in Figure 4(A), k_1 can be calculated from the slope and theoretical q_e can be obtained from intercepts. Pseudo second order equation can be given by:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e 2} + \frac{1}{q_e}t \quad \text{...} (16)$$

where, k_2 is the rate constant of second order adsorption. The linear plots of t/q_t versus t determine $1/q_e$ as slope and $1/k_2q_e^2$ as intercepts. The linear plots of pseudo first and pseudo second order model are shown in Figure 6(A) and 6(B).

The correlation coefficient, R^2 of pseudo first order kinetics was 0.893 for MB and 0.846 for CV but the calculated q_e (mg/g) values obtained from Pseudo first order kinetics did not agree well with the experimental (mg/g) values were shown in Table 2. Thus, it can be concluded that it is not appropriate to use the Pseudo first order kinetic model to predict the adsorption kinetics for MB and CV onto AC for the entire adsorption period.

On the contrary, the correlation coefficient, R^2 for the pseudo second order kinetic model were almost equal to unity for all the concentrations signifying the applicability of the model. Moreover, the calculated q_e (mg/g) values obtained from Pseudo second order kinetics were in good agreement with the experimental (mg/g) values (Table 2). Thus, it appeared that the system under study is more suitably described by pseudo second order kinetics which was based on the assumption that the rate limiting step may be chemisorptions concerning valances forces through sharing and exchange of electrons. The pseudo second-order kinetics model has been successfully applied to several adsorption systems as reported by [33,34].
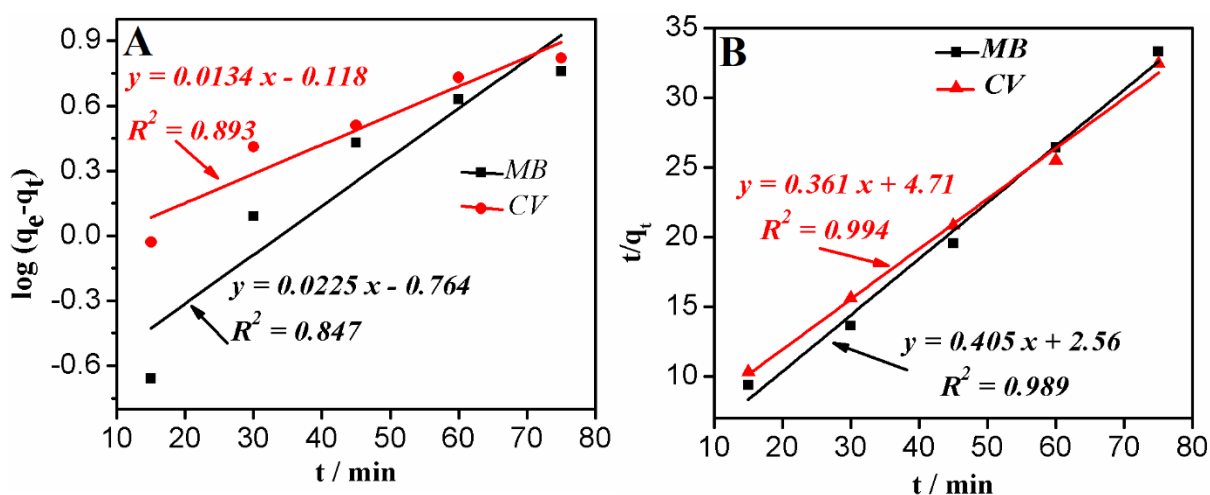

Figure 6. A) Pseudo-first-order kinetics plot and B) Pseudo-second-order kinetics plot for the adsorption of MB and CV.

Table 2: Kinetics Parameters for the Adsorption of MB and CV on AC at 25 °C

Kinetic models	Parameters	MB	CV
Pseudo-first order	$q_{e\,exp.}$ (mg/g)	8	8.9
	$q_{e\,cal.}$ (mg/g)	7.3	10.7
	k_1(x 10^{-3} min^{-1})	0.678	0.893
	R^2	0.846	0.893
Pseudo-second order	q_{ecal} (mg/g)	8.1	10.5
	k_2(x 10^{-3} min^{-1})	2.76	4.07
	R^2	0.999	0.989

exp: experimental result; cal: calculated result

4.8. Thermodynamic study

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

$$\Delta G^o = -RTln K_c \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (17)$$

where R is the gas constant (8.314 J/ mol. K), T is the absolute temperature in Kelvin, and Kc (L/g) is the standard thermodynamic equilibrium constant defined by qe/C_e. Similarly, the enthalpy change (ΔH^o) from 298.2 to 318.2 K was computed from the following equation:

$$ln K_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots. (18)$$

ΔH^o (kJ.mol^{-1}) and $\Delta S^{\,o}$(kJ.mol^{-1}.K^{-1}) were calculated from the slope and intercept of the linear plot of $ln K_c$ versus 1/T. However, the calculated values of thermodynamic parameters are listed in Table 3. The positive value of enthalpy change confirms the endothermic nature of the adsorption process. The enthalpy value for adsorption process may be used to distinguish between chemical and physical adsorption. For chemical adsorption, values of enthalpy change range from 83 to 830 kJ/ mol, while for physical adsorption they range from 8 to 25 kJ/ mol. The low values of ΔH give clear evidence that the interaction between MB, CV and AC was weak. On this basis we concluded that MB and CV adsorption by JSAC is a physical adsorption process. The positive value of entropy, ΔS° represents an increase in the degree of freedom of the adsorbed species. The positive value of ΔS° also reflects that some

changes occur in the internal structure of AC during the adsorption process. The magnitude of Gibbs free energy change, ΔG° obtained is negative demonstrating that the adsorption is rapid and spontaneous. The negative value of ΔG° ensures the feasibility of the process. Generally, ΔG° values range from 0 to −20 KJ/mol for physical adsorption and −80 to −400 KJ/mol for chemical adsorptions. In this study, the ΔG° values ranged from −5.717 to − 9.942 KJ/mol, indicating that adsorption is mainly physical.

Table 3: Thermodynamic parameters for the adsorption of MB and CV on AC at different temperatures.

Dyes	T(K)	Lnkc	ΔG(kJ/mol)	ΔH(KJ/mol)	ΔS(KJ/mol.K)	R(KJ/mol.K)
MB	298.2	3.761	-9.324	8.821	31.97	8.314×10^{-3}
	308.2	3.045	-7.802			
	318.2	3.758	-9.942			
CV	298.2	2.306	-5.717	9.31	33.45	8.314×10^{-3}
	308.2	3.084	-7.646			
	318.2	3.542	-9.370			

4.9 Comparison of MB and CV adsorption with different adsorbents

The adsorption capacity of the adsorbents for the adsorption of MB and CV has been compared with those of others reported in the literature and the values of adsorption capacity as presented in Table 4. The experimental data of the present investigation were compared with reported values. Results of our investigation revealed that JSAC has the highest percent adsorption and adsorption capacity.

Table 4: Comparison of adsorption capacity of different adsorbents for the adsorption of MB and CV

Adsorbent	Dye	Adsorbent capacity (mg/g)	Reference
Avocado seed powder	Crystal violet	1.98	[63]
Bamboo leaves	Methylene blue	1.17	[64]
Biochar-palm bark	Methylene blue	1.66	[65]
Biochar-eucalyptus	Methylene blue	1.06	[66]
Carbon slurry	Methylene blue and Crystal violet	1.26 2.11	[67]
Cotton stalk	Methylene blue	1.47	[68]
Eucalyptus sheathiana bark	Methylene blue	1.24	[69]
Hevea brasiliensis seed shell	Crystal violet	2.31	[70]
Longan shell	Methylene blue	1.41	[71]
Jack fruit seed	Methylene blue and Crystal violet	1.82 2.39	This work

5. Conclusions and Recommendation

5.1 Conclusions

This study investigated the adsorption of MB and CV from aqueous solution using activated carbon prepared from Jackfruit (*Artocarpus heterophyllus*) seed by chemical activation method. The experiments were carried out at initial pH of 5 for MB and CV of the solution to ensure true adsorption. The adsorption was found to be strongly influenced by pH, contact time and temperature. Based on the experimental findings of this work the enthalpy value for adsorption process, ΔH and the magnitude of Gibbs free energy change, ΔG were shown that the adsorption of MB and CV on JSAC is a physical adsorption process. Equilibrium attained very quickly within 45 min for MB and CV. Both Freundlich and Langmuir models were used to fit the data and estimate model parameters but the overall data is better fitted by Freundlich isotherm at the studied temperature range reflecting surface heterogeneity of JSAC. The pseudo-second order kinetic model was found to be a better fit for the adsorption of MB and CV by JSAC. Thermodynamic studies predict that the adsorption is feasible, spontaneous and endothermic in nature at temperatures of 298.2, 308.2 and 318.2 K. As negative values of standard change in Gibbs free energy (ΔG^o), positive values of standard enthalpy change (ΔH^o) and positive values of standard entropy change (ΔS^o) are suggested.

5.2 Recommendations

As it is known specific surface area is the primary factor for adsorption so that it has to be studied in the future work. The future studies should also be focused on applicability of the adsorbent to the real situation where large volume of waste effluent is being discharged. Moreover, desorption experiments should be carried out in order to recover methylene blue and crystal violet from the adsorbed surface. The impact of other ions on the removal efficiencies should also be studied as the real waste effluents composed of a number of other ions.

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