

**Adsorption of Crystal Violet on Commercial Activated Carbon and
Activated Carbon Obtained from Bagasse**

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**A Thesis Submitted in Partial Fulfillment of the Requirements for
the Degree of Master of Science in Physical Chemistry
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ชื่อวิทยานิพนธ์	การดูดซับสีย้อม Crystal Violet บนถ่านกัมมันต์ทางการค้าและถ่านกัมมันต์ที่เตรียมจากชานอ้อย
ผู้เขียน	นางสาวเมมุน ชัตตารีย์
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บทคัดย่อ

ศึกษาลักษณะเฉพาะทางกายภาพของถ่านกัมมันต์ทางการค้า (CAC) และถ่านกัมมันต์ที่เตรียมจากชานอ้อย (BAC) และการดูดซับสารละลายสีย้อม Crystal Violet บน CAC และ BAC ปัจจัยที่มีผลในการดูดซับ คือ เวลาที่เข้าสู่สมดุลของการดูดซับ ความเข้มข้นเริ่มต้นของสารละลายสีย้อม Crystal Violet ปริมาณตัวดูดซับ pH และอุณหภูมิ จากผลการทดลองพบว่ารูปแบบการดูดซับของถ่านกัมมันต์ทั้งสองชนิดสอดคล้องกับสมการของ Langmuir isotherm โดยปริมาณการดูดซับสีย้อม Crystal Violet สูงสุด (Q_m) บน CAC คือ 0.86, 0.95, 1.06 และ 1.30 mmol g^{-1} และปริมาณการดูดซับสีย้อม Crystal Violet สูงสุด (Q_m) บน BAC คือ 0.83, 0.84, 0.85 and 0.87 mmol g^{-1} ที่อุณหภูมิ 30, 40, 50 และ 60 °C ตามลำดับ และจากข้อมูลทางเทอร์โมไดนามิกส์ค่าเอนทัลปีของการดูดซับ (H_{ads}) มีค่าเป็นบวกแสดงให้เห็นว่าการดูดซับที่เกิดขึ้นเป็นกระบวนการแบบดูดความร้อนและจากค่า Separation factor (R_L) ซึ่งมีค่าในช่วง $0 < R_L < 1$ แสดงว่าการดูดซับเกิดขึ้นได้ดี อีกทั้ง BAC ดูดซับ สารละลายสีย้อม Crystal Violet ได้ประมาณ 80 - 90% จึงสามารถนำถ่านกัมมันต์จากชานอ้อย (BAC) ที่เตรียมจากของเสียทางการเกษตรมาใช้แทนถ่านกัมมันต์ทางการค้า (CAC) ได้

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ABSTRACT

A commercial activated carbon (CAC) and activated carbon obtained from bagasse (BAC) were characterized some physical properties and tested for their efficiency in adsorption of Crystal Violet. The parameters affect the adsorption had been studied such as contact time, initial dye concentration, weight of activated carbon, pH and temperature. Langmuir isotherm model was applied to the equilibrium data. The maximum adsorption (Q_m) obtained from the Langmuir isotherm plots were 0.86, 0.95, 1.06, and 1.30 mmol g⁻¹ for CAC, and 0.83, 0.84, 0.85, and 0.87 mmol g⁻¹ for BAC at 30, 40, 50, and 60°C, respectively. The positive values of the heat of adsorption (H_{ads}) indicate the endothermic nature of adsorption. The range of dimensionless separation factor (R_L) values is $0 < R_L < 1$ reveal that the adsorption is favorable. The adsorption efficiency of Crystal Violet on BAC is about 80-90%. Therefore, BAC which is agricultural waste can be used in place of commercial activated carbon for removal of dyes from waste.

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CHAPTER 1

INTRODUCTION

1.1 Introduction

General industry uses large quantity of water. Water is used for cleaning the equipment and the plant area will become waste water that flow into the river. Some industries may have the remaining materials from industrial productions combined with the waste water. From all this reason, the river is wasted, bad smelling and full of toxic substances which make the environment become pollute.

The problems which have come from dye in waste water from the industrial factory are that it affects to the beauty of scenery and degradable organic dye makes the quantity of oxygen dissolving decrease which affect the living things in water and obstruct the light expedition that necessary for the photosynthesis. Also, some dyes are carcinogen. From all above, it brings about the improper water condition for the living things in water.

Thus, before waste water from dye factory is released to the river, it has to be treated to remove some substances including residual colors. There are various treatment methods but the interesting one is the adsorption by using activated carbon which is efficient for dye adsorption. Its capacity will be increased by the quantity of activated carbon's porosity.

Synthetic dyes are extensively used for dyeing and printing in a variety of industries. Over 10,000 dyes with an annual production over 7×10^5 metric tones world wide are commercially available and 5-10% of the dye stuff is lost in the industrial effluents. Therefore there is a need to remove dyes before effluent is discharged into receiving water bodies. Crystal violet is a well-known dye that is used in a variety of ways: as a biological stain; dermatological agent; veterinary medicine; additive to poultry feed to inhibit propagation of mold, intestinal parasites, and fungus; etc. It is also extensively used in textile dyeing and paper printing.

The removal of color from dye-bearing effluents is a major problem because of the difficulty in treating such wastewaters by conventional treatment methods. Adsorption is a widely used method for the treatment of industrial wastewaters containing colors, heavy metals and other inorganic and organic impurities. The advantages of adsorption are its simplicity of operation, low costs (compared to other separation processes), and absence of sludge formation. Textile industries are the major consumers of water, and they release a fair amount of color in their effluents. Liquid-phase adsorption has been used effectively for the removal of dye from wastewater. Activated carbon is the most widely used adsorbent for this purpose because of its extensive surface area, microporous structure, high adsorption capacity, and high degree of surface reactivity. In the present study removal of crystal violet from aqueous solution using activated carbon as an adsorbent was investigated.

1.2 Preliminary knowledge and theoretical section

1.2.1 Evolution of Dyes

There is no clear evidence in the history of dye that who was the founder of dye but most historian has assumed that the origin of dye might happen among the far-east country. Dyeing is the art that has been with the human culture for a long time. Thousand years ago, China was the first country that the evidence of dyeing was appeared (since 3,000 B.C.). Moreover, there were other nations that using dye such as European during the Metal Age (2,500 – 800 B.C.), Indian (2,500 B.C.) and Egyptian (1,450 B.C.). During the ancient time, people made dye by dipping the natural color into water until it was rusty. Then, they brought cotton drown into it or if cotton was dyed in the rust, it will turn into red-brown. This natural color was come from some parts of plants as its body, its seed or its tuber, some insects and some shells. For example, black was from ebony due to its black resin. Yellow was from resin of Chrome. Golden or dark yellow was from one type of ixora called Modder or indigo was from one kind of plants called Indigo. During 1856 after World War I, the young German chemist named William Perkin discovered and produced synthetic color for the first time. He discovered it by chance due to his attempt to synthesize

quinine for curing malaria. Since then, the second period of dye was begun which was the important point to separate the age of dye from Natural Dye Age to Synthetic Dye Age. Due to William Perkin's discovery, the new colors were increased by more than 500 colors during 1900. England, Germany and France were the countries that developed synthetic color most. In this second period, synthetic color was used broadly taking place to the natural color. Synthetic dye has been able to dye some Cellulose Fibers as cotton and some Protein Fibers from animals as silk worm and fur. Until during 1920, synthetic fiber, which was the product from oil industry such as Nylon and Polyester, has been discovered. Synthetic dye that was used at that time was not able to dye this new synthetic fiber. Afterward, the dye that can dye synthetic fiber called Disperse Azo has been discovered and used so far. Mostly, it uses for dye Polyester. During 1950s, Reactive Dye, which is the color that has highly cohesion with fiber by using chemistry bond, was discovered. It makes the dye be permanent and bright.

Dye is one type of colors that can be used to dye some materials or textiles. It can be organic or inorganic substances, crystal or powder that is able to absorb light by put it on or in the surface of material until it was diffused into the material structure for making the color appeared. Some dyes can be dissolved but some cannot except in organic solvent. During dyeing process, the molecule of dye was adsorbed into the molecule of fiber and was destroyed the crystal structure of that material for a time which may have ionic bond or covalent bond with the material that need to dye directly. The color of dye comes from electron in double bond which is in dye's molecule that can absorb the energy in different wavelength between 400 – 700 nm. The difference of dye's molecule structure will make the difference in absorption of light energy in different wavelength, so the different tone of color in dye's molecule will appear us in different color.

Classification of dyes

The first human-made (synthetic) organic dye, mauveine was discovered by William Henry Perkin in 1856. Many thousands of synthetic dyes have since been prepared.

Synthetic dyes quickly replaced the traditional natural dyes. They cost less, they offered a vast range of new colors, and they imparted better properties to the dyed materials. Dyes are now classified according to how they are used in the dyeing process.

- (1) **Acid dyes** are water-soluble anionic dyes that are applied to fibers such as silk, wool, nylon and modified acrylic fibers using neutral to acid dye baths. Attachment to the fiber is attributed, at least partly, to salt formation between anionic groups in the dyes and cationic groups in the fiber. Acid dyes are not substantive to cellulosic fibers. Most synthetic food colors fall in this category.
- (2) **Basic dyes** are water-soluble cationic dyes that are mainly applied to acrylic fibers, but find some use for wool and silk. Usually acetic acid is added to the dye bath to help the uptake of the dye onto the fiber. Basic dyes are also used in the coloration of paper.
- (3) **Direct or substantive dyeing** is normally carried out in a neutral or slightly alkaline dyebath, at or near boiling point, with the addition of either sodium chloride (NaCl) or sodium sulfate (Na₂SO₄). Direct dyes are used on cotton, paper, leather, wool, silk and nylon. They are also used as pH indicators and as biological stains.
- (4) **Mordant dyes** require a mordant, which improves the fastness of the dye against water, light and perspiration. The choice of mordant is very important as different mordants can change the final color significantly. Most natural dyes are mordant dyes and there is therefore a large literature base describing dyeing techniques. The most important mordant dyes are the synthetic mordant dyes, or chrome dyes, used for wool; these comprise some 30% of dyes used for wool, and are especially useful for black and navy shades. The mordant, potassium dichromate, is applied as an after-treatment. It is important to note that many mordants, particularly those in the heavy metal category, can be hazardous to health and extreme care must be taken in using them.
- (5) **Vat dyes** are essentially insoluble in water and incapable of dyeing fibres directly. However, reduction in alkaline liquor produces the water soluble alkali metal salt of the dye, which, in this leuco form, has an affinity for the textile

fibre. Subsequent oxidation reforms the original insoluble dye. The color of denim is due to indigo, the original vat dye.

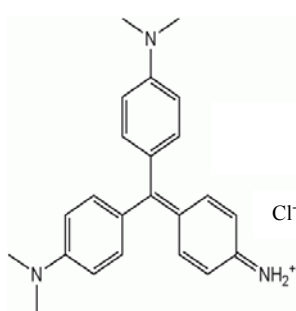
- (6) **Reactive dyes** utilize a chromophore attached to a substituent that is capable of directly reacting with the fibre substrate. The covalent bonds that attach reactive dye to natural fibers make them among the most permanent of dyes. “Cold” reactive dyes, such as Procion MX, Cibacron F, and Drimarene K, are very easy to use because the dye can be applied at room temperature. Reactive dyes are by far the best choice for dyeing cotton and other cellulose fibers at home or in the art studio.
- (7) **Disperse dyes** were originally developed for the dyeing of cellulose acetate, and are water insoluble. The dyes are finely ground in the presence of a dispersing agent and sold as a paste, or spray-dried and sold as a powder. Their main use is to dye polyester but they can also be used to dye nylon, cellulose triacetate, and acrylic fibres. In some cases, a dyeing temperature of 130 °C is required, and a ressurized dyebath is used. The very fine particle size gives a large surface area that aids dissolution to allow uptake by the fibre. The dyeing rate can be significantly influenced by the choice of dispersing agent used during the grinding.
- (8) **Azoic dyeing** is a technique in which an insoluble azo dye is produced directly onto or within the fibre. This is achieved by treating a fibre with both diazoic and coupling components. With suitable adjustment of dyebath conditions the two components react to produce the required insoluble azo dye. This technique of dyeing is unique, in that the final color is controlled by the choice of the diazoic and coupling components.
- (9) **Sulfur dyes** are two parts “developed” dyes used to dye cotton with dark colors. The initial bath imparts a yellow or pale chartreuse color; this is after treated with a sulfur compound in place to produce the dark black we are familiar with in socks for instance. Sulfur Black 1 is the largest selling dye by volume.
(<http://en.wikipedia.org/wiki/dye>)

Methyl violet

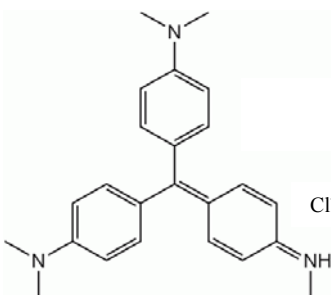
Methyl violet is a family of organic compounds that are used as dyes. Depending on the amount of attached methyl groups, the color of the dye can be

altered. Its main use is as a purple dye for textiles and to give deep violet colors in paint and ink.

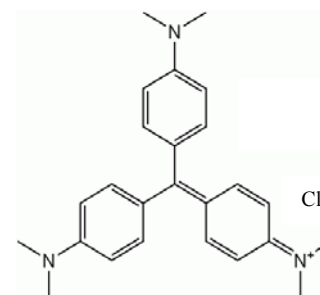
The term methyl violet encompasses three compounds that differ in the number of methyl groups attached to the amine functional group. They are all soluble in water, ethanol, diethylene glycol and dipropylene glycol.



Methyl Violet 2B



Methyl Violet 6B



Methyl Violet 10B

Methyl Violet 2B

Methyl violet 2B is the tetramethyl derivative. Solid samples appear lustrous and blue-green in color; melting at 137 °C (279 °F). It is used as a pH indicator, with a range between 0 and 1.6. The protonated form (found in acidic conditions) is yellow, turning blue-violet above pH levels of 1.6.

Methyl Violet 6B

Methyl violet 6B contains five methyl groups. It is a darker blue than 2B.

Methyl Violet 10B or Crystal Violet

Methyl violet 10B has six methyl groups. It is known in medicine as Gentian violet (or crystal violet) and is the active ingredient in a Gram stain, used to classify bacteria. Gentian violet destroys cells and can be used as a disinfectant. Compounds related to methyl violet is potential carcinogens. 10B also inhibits the growth of many Gram positive bacteria, except streptococci. When used in conjunction with nalidixic acid (which destroys gram-negative bacteria), it can be used to isolate the streptococci bacteria for the diagnosis of an infection. Methyl violet also binds to DNA. This means it can be used in cell viability assays in biochemistry. However,

this binding to DNA will cause replication errors in living tissue, possibly leading to mutations and cancer.

The structure of Crystal Violet in aqueous solution is displayed below.

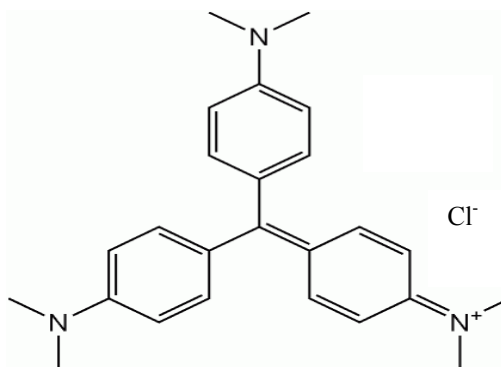


Figure 1 Structure of Crystal Violet.

IUPAC name: 4-[(4-dimethylaminophenyl)-phenyl-methyl]-N, N-dimethyl-aniline

Other name: Methyl Violet 10B, Gentian Violet, Aniline Violet, Viola Crystallina

Characteristics of Crystal Violet

Molecular formula: C₂₅H₃₀ClN₃

Molar mass: 407.979

Appearance: violet

Melting point: 215 °C (Decomposes)

Classification of dye: basic dye

Crystal violet is often used as a bactericide and an antifungal agent, the primary agent used in the Gram stain test, perhaps the single most important bacterial identification test in use today, and it is also used by hospitals for the treatment of serious heat burns and other injuries to the skin and gums. Typically prepared as a weak (e.g. 1%) solution in water, it is painted on skin or gums to treat or prevent fungal infections. Gentian violet does not require a doctor's prescription (in the US), but is not easily found in drug stores. Tampons treated with gentian violet are sometimes used for vaginal applications.

1.2.2 Definition of activated carbon

Activated carbon, also called activated charcoal or activated coal is a form of carbon that has been processed to make it extremely porous and thus to have a very large surface area available for adsorption or chemical reactions.

The word *activated* in the name is sometimes replaced with *active*. Due to its high degree of microporosity, just one gram of activated carbon has a surface area in excess of 500 m², as determined typically by nitrogen gas adsorption. Sufficient activation for useful applications may come solely from the high surface area, though further chemical treatment often enhances the adsorbing properties of the material.

Activated carbon mainly consists of elementary carbon in graphite alike structure. It can be produced by heat treatment, or “activation”, of raw materials such as wood, coal, peat and coconut shell. During the activation process, the unique internal pore structure is created, and it is this pore structure which provides activated carbon its outstanding adsorption properties.

Activated carbons are complex products which are difficult to classify on the basis of their behaviors, surface characteristics and preparation methods. However, some broad classification is made for general purpose based on their physical characteristics (Chuenchom, 2004).

Classification

(1) Powdered activated carbon (PAC)

Traditionally, active carbons are made in particular form as powders or fine granules less than 1.0 mm in size with an average diameter between 0.15 and 0.25 mm. Thus they present a large surface to volume ratio with a small diffusion distance. PAC is made up of crushed or ground carbon particles, 95 – 100% of which will pass through a designated mesh sieve or sieve. Granular activated carbon is defined as the activated carbon being retained on a 50 mesh sieve (0.297 mm) and PAC material as finer material, while ASTM classifies particle sizes corresponding to an 80 mesh sieve (0.177 mm) and smaller as PAC. PAC is generally added directly to other process units, such as raw water intakes, rapid mix basins, clarifiers, and gravity filters. In this research, particle sizes of both activated carbons 140 - 170 mesh sieve which are PAC.

(2) Granular activated carbon (GAC)

Granular activated carbon are irregular shaped particles with sizes ranging from 0.2 to 5 mm which has a relatively larger particle size compared to powdered activated carbon and consequently, presents a smaller external surface. Granulated carbons are used for water treatment, deodorization and separation of components of flow system. This type is used in both liquid and gas phase applications.

(3) Extruded activated carbon (EAC)

Extruded activated carbon combines powdered activated carbon with a binder, which are fused together and extruded into a cylindrical shaped activated carbon block with diameters from 0.8 to 130 mm. These are mainly used for gas phase applications because of their low pressure drop, high mechanical strength and low dust content.

(4) Impregnated carbon

Porous carbons containing several types of inorganic impregnant such as iodine, silver, cation such as Al, Mn, Zn, Fe, Li, Ca have also been prepared for specific application in air pollution control especially in museums and galleries. Due to antimicrobial/antiseptic properties, silver loaded activated carbon is used as an adsorbent for purifications of domestic water. Drinking water can be obtained from natural water by treating the natural water with a mixture of activated carbon and flocculating agent $\text{Al}(\text{OH})_3$. Impregnated carbons are also used for the adsorption of H_2S and thiols (mercaptans). Adsorption rates for H_2S as high as 50% by weight have been reported.

(5) Polymers coated carbon

This is a process by which a porous carbon can be coated with a biocompatible polymer to give a smooth and permeable coat without blocking the pores. The resulting carbon is useful for hemoperfusion. Hemoperfusion is a treatment technique in which large volumes of the patient's blood are passed over an adsorbent substance in order to remove toxic substances from the blood.

([http://en.wikipedia.org/wiki/Activated carbon](http://en.wikipedia.org/wiki/Activated_carbon))

Utilities of activated carbon

Activated carbon, the common factor in hundreds of different applications just a grab from the numerous applications: decolourisation of sugar and sweeteners, drinking water treatment, gold recovery, production of pharmaceuticals and fine chemicals, catalytic processes, off gas treatment of waste incinerators, automotive vapour filters, colour/odour correction in wines and fruit juices, additive in liquorice, etc.

In its numerous applications, activated carbon represents a number of different functionalities:

Adsorption: the most well-known mechanism, through chemisorption or physical adsorption (Van der Waals forces)

Reduction: e.g. removal of chlorine from water is based on chemical reduction reactions.

Catalysis: activated carbon can catalyse a number of chemical conversions, or can be a carrier of catalytic agents (e.g. precious metals).

Carrier of biomass: supported material in biological filters.

Carrier of chemicals: e.g. slow release applications colourant, activated carbon's function in decolourizing (Chuenchom, 2004).

1.2.3 The activation process of activated carbon

Activation refers to the development of the adsorption properties of carbon. It can be produced by one of the following processes:

(1) Physical activation: The precursor is developed into activated carbons using gases. This is generally done by using one or a combination of the following processes:

Carbonization: Material with carbon content is pyrolyzed at temperatures in the range 600–900 °C, in absence of air (usually in inert atmosphere with gases like argon or nitrogen)

Activation/Oxidation: Raw material or carbonized material is exposed to oxidizing atmospheres (carbon dioxide, oxygen, or steam) at temperatures above 250 °C, usually in the temperature range of 600–1200 °C.

(2) **Chemical activation:** One of the key steps in the production of activated carbon is chemical activation through the impregnation of the raw material with chemicals such as phosphoric acid, potassium hydroxide, zinc chloride. These additives are known to enhance carbonization, resulting in improved development of the pore structure. Chemical activation is usually limited to woody precursors. Among the activating agent used for the production of activated carbon from carbonaceous material, zinc chloride has been proven to be one of the most effective impregnants. Zinc chloride acts as a dehydration agent, influencing the decomposition of carbonaceous material during the pyrolysis, thus restricting the formation of tar and increasing the carbon yield. The degradation of cellulose material and the aromatization of the carbon skeleton upon zinc chloride treatment result in the creation of the pore structure. These pores are the interstices left vacant upon the removal of zinc chloride from the carbon matrix by intensive washing. The studies have clearly demonstrated that the amount of zinc chloride used during chemical activation significantly impacts the structure characteristics of the carbons (http://en.wikipedia.org/wiki/Activated_carbon)

1.2.4 Porosity: definition

Based on the experience of adsorption chemistry, total porosity is classified into three groups. The origins and structure of porosities are elaborated upon below. IUPAC classifies porosities as follows:

- Micropores width less than 2 nm
- Mesopores width between 2 and 50 nm
- Macropores width greater than 50 nm

It has also been useful to classify micropores further into ultra-(< 0.5 nm width) and super- (1.0 – 2.0 nm) micropores, these definitions being relevant when considering adsorption behavior. Micropores are considered as being about the size of adsorbate molecules and accommodate one, two or perhaps three molecules. Mesoporosity is wider than micropores. Macroporosity has little interest for the surface chemist. They are transport pores to the interior of particles and are considered as external surface. Some activate carbons contain all of these sizes of porosity associated with the botanical composition of the material. The pore size distribution is highly important for the practical application; the best fit depends on the compounds of interest, the

matrix (gas, liquid) and treatment condition. The desired pore structure of an activated carbon product is attained by combining the right raw material and activation conditions (Chuenchom, 2004).

1.2.5 Adsorption

Adsorption is the adhesion of molecules of gas, liquid, or dissolved solids to a surface. This process creates a film of the *adsorbate* (the molecules or atoms being accumulated) on the surface of the *adsorbent*. It differs from *absorption*, in which a fluid permeates or is dissolved by a liquid or solid. The term sorption encompasses both processes, while desorption is the reverse of adsorption.

Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent, or metallic) of the constituent atoms of the material are filled by other atoms in the material. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbates. The exact nature of the bonding depends on the details of the species involved, but the adsorption processes are two different types:

- (1) **Physisorption**, where the adsorbates were held by physical (i.e., Van der Waals) forces. These forces can be eliminated (removal of molecules from surface of adsorbent) when increasing temperature. Therefore, physisorption can be called reversible process.
- (2) **Chemisorption**, where there is direct chemical bond between the adsorbate and the surface. This bond cannot be broken by only increased temperature. This behavior is usually irreversible process.

Chemisorption and physisorption are usually distinguishable from each other without any great difficulty. Table A summarizes the main criteria.

Table A Criteria for distinguishing between chemisorption and physisorption. (Bond, 1987)

Criteria	Chemisorption	Physisorption
Enthalpy of adsorption or heat of adsorption (H_{ads})	> 40 kJ/mol usually around 600-700 kJ/mol	0 – 40 kJ/mol
Activation energy, E_a	Usually small	Zero
Increasing temperature	Irreversible	Reversible

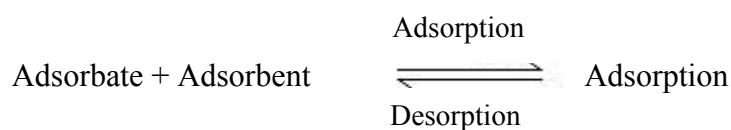
The adsorption characteristics in solution phase between the adsorbent and adsorbate were explained by the adsorption isotherm models in general. Several models can be used to describe adsorption data. The two most frequently used for dilute solutions are the Langmuir and Freundlich isotherms (Chuenchom, 2004).

Adsorption isotherm

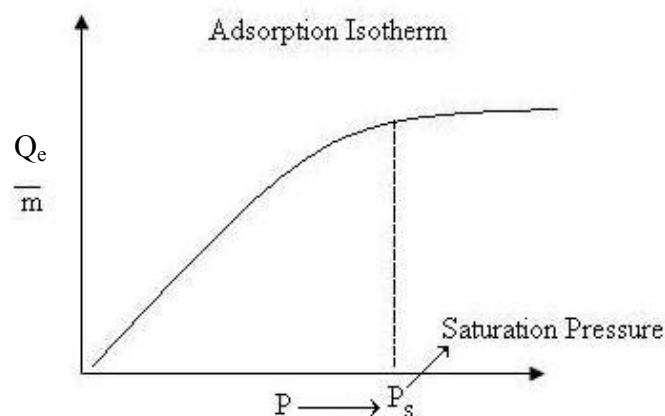
The process of Adsorption is usually studied through graphs which are known as adsorption isotherm. It is the graph between the amounts of adsorbate (Q_e) adsorbed on the surface of adsorbent (m) and pressure at constant temperature. Different adsorption isotherms have been Freundlich, Langmuir and BET theory.

Basic adsorption isotherm

In the process of adsorption, adsorbate gets adsorbed on adsorbent.



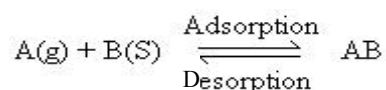
According to Le-Chatelier principle, the direction of equilibrium would shift in that direction where the stress can be relieved. In case of application of excess of pressure to the equilibrium system, the equilibrium will shift in the direction where the number of molecules decreases. Since number of molecules decreases in forward direction, with the increases in pressure, forward direction of equilibrium will be favored.



From the graph, we can predict that after saturation pressure P_s , adsorption does not occur anymore. This can be explained by the fact that there are limited numbers of vacancies on the surface of the adsorbent. At high pressure a stage is reached when all the sites are occupied and further increase in pressure does not cause any difference in adsorption process. At high pressure, adsorption is independent of pressure.

Langmuir adsorption isotherm

In 1916 Langmuir proposed another adsorption isotherm known as Langmuir Adsorption isotherm. This isotherm was based on different assumptions one of which is that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.



Where A (g) is unadsorbed gaseous molecule, B(s) is unoccupied surface and AB is adsorbed gaseous molecule.

Based on his theory, he derived Langmuir Equation which depicted a relationship between the number of active sites of the surface undergoing adsorption and pressure.

$$Q_e = \frac{Q_m b C_e}{1 + b C_e} \quad (\text{Nonlinear form}) \quad (1)$$

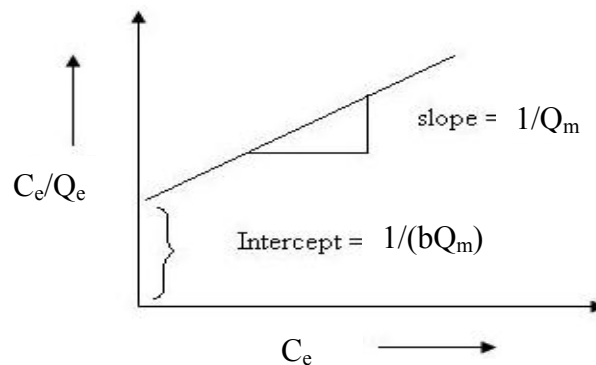
Where Q_e represents the amount of solute adsorbed per unit weight of adsorbent (mmol g^{-1}); Q_m is the amount of solute adsorbed per unit weight of adsorbent required for monolayer coverage of the surface, also called the monolayer capacity (mmol g^{-1}); C_e is the concentration of adsorbate in solution at equilibrium

conditions (mmol L^{-1}); and b is an equilibrium constant related to the heat of adsorption, $b = e^{(H_{\text{ads}}/RT)}$ (Adamson and Gast, 1997)

Equation (1) is usually linearized by inversion to obtain the following form

$$\frac{C_e}{Q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m} \quad (\text{Linear form}) \quad (2)$$

Many researchers have usually used equation (2) to analyse batch equilibrium data by plotting C_e / Q_e versus C_e , which yields a linear if data conform to the Langmuir isotherm.



Once b is considered, this parameter can be rewritten as

$$b = b' e^{H_{\text{ads}}/RT} \quad (3)$$

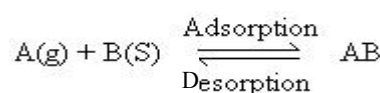
Where H_{ads} is enthalpy or heat of adsorption, R is the universal gas constant, T is the temperature in Kelvin and b' is pre-exponential factor constant.

The heat of adsorption (H_{ads}) can be determined from slope of the observed linearity from the plot of $\ln b$ (or $\log b$) versus $1/T$ that leads to heat process involved in adsorption at monolayer coverage.

Assumptions of Langmuir isotherm

Langmuir proposed his theory by making following assumptions.

1. Fixed number of vacant or adsorption sites are available on the surface of solid.
2. All the vacant sites are of equal size and shape on the surface of adsorbent.
3. Each site can hold maximum of one gaseous molecule and a constant amount of heat energy is released during this process.
4. Dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.



Where A (g) is unadsorbed gaseous molecule, B(s) is unoccupied surface and AB is adsorbed gaseous molecule.

5. Adsorption is monolayer or unilayer.

Limitations of Langmuir adsorption equation

1. The adsorbed gas has to behave ideally in the vapor phase. This condition can be fulfilled at low pressure conditions only. Thus Langmuir equation is valid under low pressure only.
2. Langmuir equation assumes that adsorption is monolayer. But, monolayer formation is possible only under low pressure condition. Under high pressure condition the assumption breaks down as gas molecules attract more and more molecules towards each other. *BET theory* proposed by Brunauer, Emmett and Teller explained more realistic multilayer adsorption process.
3. Another assumption was that all the sites on the solid surface are equal in size and shape and have equal affinity for adsorbate molecules i.e. the surface of solid is homogeneous. But we all know that in real solid surfaces are heterogeneous.
4. Langmuir equation assumed that molecules do not interact with each other. This is impossible as weak force of attraction exists even between molecules of same type.
5. The adsorbed molecules has to be localized i.e. decrease in randomness is zero ($\Delta S = 0$). This is not possible because on adsorption liquefaction of gases taking place, which results into decrease in randomness but the value is not zero.

From above facts we can conclude that, Langmuir equation is valid under low pressure conditions.

Freundlich adsorption isotherm

Freundlich proposed another adsorption isotherm known as Freundlich adsorption isotherm or Freundlich adsorption equation or simply Freundlich isotherm. The Freundlich adsorption equation is perhaps the most widely used for the description of adsorption in aqueous systems. The Freundlich equation is of the form

$$Q_e = K_F C_e^{1/n} \quad (\text{Non linear form}) \quad (4)$$

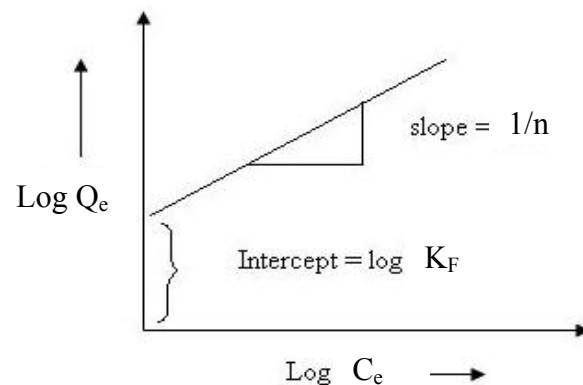
Where Q_e and C_e have definitions as previously presented for the Langmuir isotherm. K_F is the so-called unit capacity factor that shows adsorption capacity and n is the empirical parameter that represents the heterogeneity of the site energies and also is indicative of the intensity of adsorption.

The logarithm of equation (4) given below is usually used to fit data as

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \quad (\text{Linear form}) \quad (5)$$

The above equation is comparable with equation of straight line, $y = mx + c$ where, m represents slope of the line and c represents intercept on y axis.

Plotting a graph between $\log Q_e$ and $\log C_e$, we will get a straight line with value of slope equal to $1/n$ and $\log K_F$ as y -axis intercept.



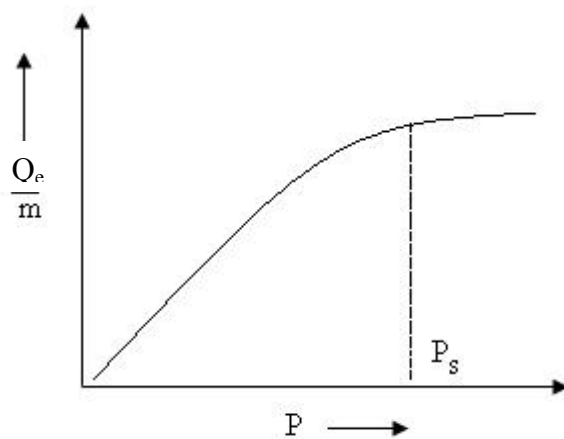
Limitation of Freundlich adsorption isotherm

Experimentally it was determined that extent of adsorption varies directly with pressure till saturation pressure P_s is reached. Beyond that point rate of adsorption saturates even after applying higher pressure. Thus Freundlich adsorption isotherm failed at higher pressure.

Type of adsorption isotherm

Five different types of adsorption isotherm and their characteristics are explained below.

Type I Adsorption isotherm

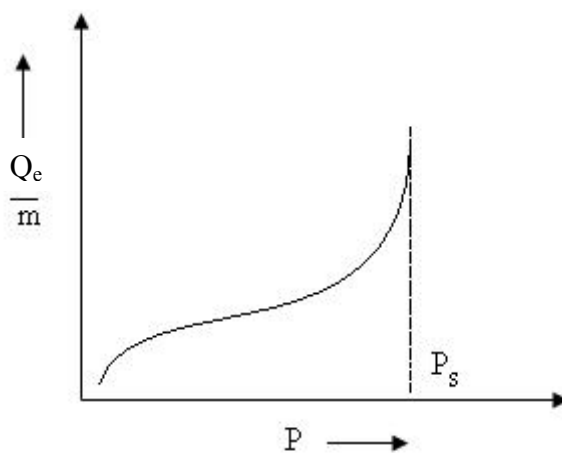


The above graph depicts monolayer adsorption.

This graph can be easily explained using Langmuir adsorption isotherm.

Examples of type I adsorption are adsorption of nitrogen (N_2) or hydrogen (H) on charcoal.

Type II Adsorption isotherm

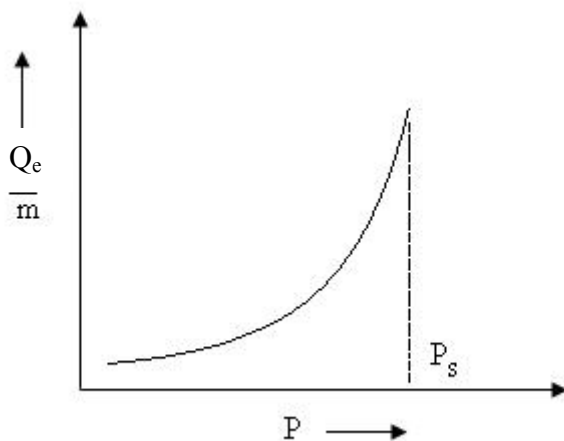


Type II adsorption isotherm shows large deviation from Langmuir model of adsorption.

The intermediate flat region in the isotherm corresponds to monolayer formation.

Examples of type II adsorption are nitrogen (N_2 (g)) adsorbed on iron (Fe) catalyst and nitrogen (N_2 (g)) adsorbed on silica gel.

Type III Adsorption isotherm



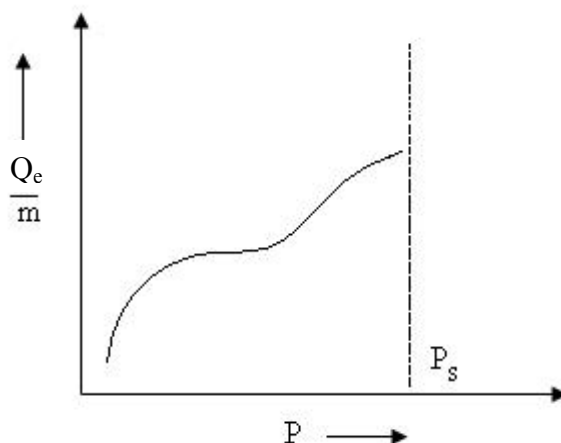
Type III adsorption isotherm also shows large deviation from Langmuir model.

This isotherm explains the formation of multilayer.

There is no flattish portion in the curve which indicates that monolayer formation is missing.

Examples of type III adsorption isotherm are bromine (Br_2) on silica gel or iodine (I_2) on silica gel.

Type IV adsorption isotherm

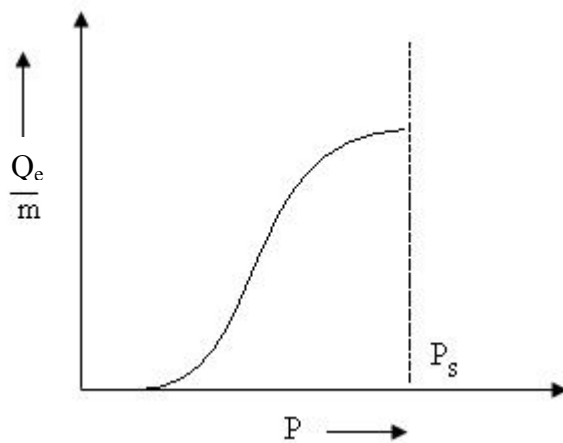


At lower pressure region of graph is quite similar to type II. This explains formation of monolayer followed by multilayer.

The saturation level reaches at a pressure below the saturation vapor pressure. This can be explained on the basis of a possibility of gases getting condensed in the tiny capillary pores of adsorbent at pressure below the saturation pressure (P_s) of the gas.

Examples of type IV adsorption isotherm are of adsorption of benzene on iron oxide (Fe_2O_3) and adsorption of benzene on silica gel.

Type V adsorption isotherm



Explanation of type V graph is similar to type IV.

Example of type V adsorption isotherm is adsorption of water (vapors) on charcoal.

Type IV and V shows phenomenon of capillary condensation of gas.

Heat (enthalpy) of adsorption consideration

If the isotherm of adsorption can be fitted with Langmuir model adequately, the heat of adsorption process at monolayer coverage can be investigated from equation (3).

There is another propose that is usually used to explain heat of adsorption. The adsorption data obtained at different temperatures are used to estimate the isosteric heat of the process. Consequently, enthalpy changes associated with adsorption processes can be estimated using the Clausius-Clapeyron equation. The heat of

adsorption was calculated by applying the Clausius-Clapeyron equation to the adsorption isotherm as follows (Alberty and Silbey, 1992 and Sirichote, et al., 2002)

$$\frac{dP}{dT} = \frac{P}{RT^2} \frac{H_{vap}}{RT} \quad (6)$$

Where P is the equilibrium pressure of gas, T is the absolute temperature, ΔH_{vap} is the heat of vaporization, and R is the gas constant. On rearrangement equation (6) becomes

$$\frac{dP}{P} = \frac{H_{vap}}{RT^2} dT \quad (7)$$

The equation (7) can be rewritten as follows

$$d \ln \frac{P}{P_0} = \frac{H_{vap}}{RT^2} dT \quad (8)$$

Where P_0 is the standard pressure used. Replacement of P by $C_e RT$ and P_0 by $C^0 RT$ from ideal gas law where C_e is the equilibrium concentrations (mmol L^{-1}) and C^0 is the standard value of the concentration (mmol L^{-1}) equation (8) becomes

$$d \ln \frac{C_e}{C^0} = \frac{H_{vap}}{RT^2} dT \quad (9)$$

For adsorption in solution the ΔH_{vap} is replaced by ΔH_{ads} which is the heat of adsorption. Integrating on the assumption that the ΔH_{ads} is independent of temperature and concentration and since the term $\ln C^0$ is equal to zero, equation (9) yields

$$\begin{aligned} d \ln C_e &= \frac{H_{ads}}{R} \frac{1}{T^2} dT \\ \ln C_e &= \frac{H_{ads}}{RT} + c \end{aligned} \quad (10)$$

Where C_e is the equilibrium concentrations (mmol L^{-1}), H_{ads} is the isosteric heat of adsorption (kJ mol^{-1}), R is the universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) and c is the integration constant. Plot of $\ln C_e$ versus $1/T$ should give a straight line of slope is $-(\Delta H_{ads}/R)$. The plots of applied Clausius-Clapeyron equation to adsorption isotherm in equation (10) as $\ln C_e$ versus $1/T$

1.3 Review of literature

There have been many researches concern in the adsorption of metal ions and dyes on activated carbon surface. This interest is based on the importance of the following process: surface chemistry, water chemistry, analytical chemistry, chemical engineering and environmental studies. Many researchers have studied adsorption of metal ions and dye on activated carbon such as:

Jia, et al., (1998) introduced various types of oxygen functional groups onto the surface of coconut shell derived activated carbon by oxidation using nitric acid. Fourier-transform infrared spectroscopy (FT-IR), temperature programmed desorption (TPD) and selective neutralization were used to characterize the surface oxygen functional groups. The oxidized carbons were also heat treated to provide a site of carbons where the oxygen functional groups of various thermal stabilities were varied progressively. The adsorption of cadmium ions was enhanced dramatically by oxidation of the carbon. The ratio of released protons to adsorbed cadmium ions on oxidized carbon was approximately 2, indicating cations exchange was involved in the process of adsorption. Na^+ exchange studies with the oxidized carbon gave a similar ratio. After heat treatment of the oxidized carbons to remove oxygen functional groups, the ratio of H^+ released to adsorbed Cd^{2+} and the adsorption capacity decreased significantly. Both reversible and irreversible processes were involved in cadmium ion adsorption with reversible adsorption having higher enthalpy. The irreversible adsorption resulted from cation exchange with carboxylic acid groups, whereas the reversible adsorption probably involved physisorption of the partially hydrated cadmium ion.

Jia, et al., (2002) investigated effects of nitrogen surface functional groups to metal ions adsorption. A commercially available coconut-shell-derived active carbon was oxidized with nitric acid and both the original and oxidized active carbons were treated with ammonia at 1073 K to incorporate nitrogen functional groups into the carbon. An active carbon with very high nitrogen content (9.4 wt%) was also prepared from a nitrogen-rich precursor, polyacrylonitrile (PAN). These nitrogen-rich carbons had points of zero charge (pH_{pzc}) similar to H-type active carbons. X-ray adsorption

near-edge structure (XANES) spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, and temperature-programmed desorption (TPD) were used to characterize the nitrogen functional groups in the carbons. The nitrogen functional groups present on the carbon surface were pyridinic, pyrrolic (or indolic), and pyridonic structures. The adsorption of transition metal cations Cd^{2+} , Ni^{2+} , and Cu^{2+} from aqueous solution on the site of active carbons showed that adsorption was markedly higher for carbons with nitrogen functional groups present on the surface than for carbons with similar pH_{pzc} values. In contrast, the adsorption characteristics of Ca^{2+} from aqueous solution were similar for all the carbons studied. Flow microcalorimetry (FMC) studied showed that the enthalpies of adsorption of Cd^{2+} (aq) on the active carbons with high nitrogen contents were much higher than for nitric acid oxidized carbons studied previously, which also had enhanced adsorption characteristics for metal ion species. The enthalpies of adsorption of Cu^{2+} were similar to those obtained for Cd^{2+} for specific active carbons. The nitrogen functional groups in the carbons act as surface coordination sites for the adsorption of transition metal ions from aqueous solution. The adsorption characteristics of these carbons were compared with those oxidized carbons.

Sirichote, et al., (2002) studied the adsorptions of Fe^{3+} from aqueous solution at room temperature on activated carbons obtaining from bagasse, pericarp of rubber fruit and coconut shell. The activated carbons were prepared by carbonization of these raw materials and followed by activation with ZnCl_2 . The adsorption behavior of Fe^{3+} on these activated carbons could be interpreted by Langmuir adsorption isotherm as monolayer coverage. The maximum amounts of Fe^{3+} adsorbed per gram of these activated carbons were 0.66, 0.41, and 0.18 mmol g^{-1} , respectively. Study of the temperature dependence on these adsorptions has revealed them to be exothermic processes with the heats of adsorption of about -8.9, -9.7 and -5.7 kJ mol^{-1} for bagasse, pericarp of rubber fruit and coconut shell, respectively.

Meikap, et al., (2006) studied the adsorption onto activated carbons which is a potent method for the treatment of dye-bearing effluents because it offers various advantages. In this study, activated carbons, prepared by a new technique from low-

cost rice husk by sulfuric acid and zinc chloride activation, were used as the adsorbent for the removal of crystal violet, a basic dye, from aqueous solutions. The effects of various experimental parameters, such as adsorbent dosage and size, initial dye concentration, pH, contact time, and temperature, were investigated in batch mode. The kinetic data were well fitted to the Lagergren, pseudo-second-order, and intraparticle diffusion models. It was found that intraparticle diffusion plays a significant role in the adsorption mechanism. The isothermal data could be well described by the Langmuir and Freundlich equations. The maximum uptakes of crystal violet by sulfuric acid activated (RHS) and zinc chloride activated (RHZ) rice husk carbon were found to be 64.875 and 61.575 mg g⁻¹ of adsorbent, respectively. The results indicate that RHS and RHZ could be employed as low-cost alternatives to commercial activated carbon in wastewater treatment for the removal of basic dyes.

Sirichote, et al., (2008) reported activated carbons prepared from bagasse, oil palm shell and pericarp of rubber fruit were used to study the adsorption of phenol from aqueous solution. The obtained activated carbons were characterized for iodine number, BET surface area, surface functional groups, and point of zero charge (pH_{pzc}). The values of BET surface area of bagasse, pericarp of rubber fruit and oil palm shell were 1076, 877, 770 m² g⁻¹, respectively. Adsorption of phenol in aqueous solution at pH 2 and pH 12 were determined by UV-Visible spectrophotometer at 30°C. The adsorption data were fitted to Freundlich isotherm. The adsorption capacity of phenol of the different types of activated carbon was approximately the same. The adsorption capacity of phenol at pH 2 is greater than at pH 12 because of pH 2 the surfaces of activated carbons are protonated and have acidic surfaces with positive charges. Phenol behaves as a weak base that interacts with the acidic surface of activated carbons by dispersion electron donor-acceptor interaction.

Pattabhi, et al., (2009) studied activated carbon prepared from *Ricinus Communis* Pericarp (RCP) was used to remove a crystal violet dye from aqueous solution by an adsorption technique under varying conditions of agitation time, dye concentration, adsorbent dose and pH. The removal of dye increased with increasing carbon dosage and attained a maximum (100%) at a particular carbon dosage.

Adsorption is influenced by pH, dye concentration, carbon concentration and contact time. Equilibrium was attained within 60 min. The kinetic data were well fitted to the Lagergren model. Adsorption followed both Langmuir and Freundlich isotherm models. The Langmuir constant were $Q_m = 106.95 \text{ mg g}^{-1}$ and $b = 0.4770 \text{ L mg}^{-1}$ of the dye. The Freundlich constants were $K_F = 53.3676$ and $n = 5.6980$ for 25 mg L^{-1} of the dye. Desorption studies reveals that recovery of dye from adsorbent was possible. The percent desorption increased with increasing CH_3COOH concentration in the aqueous medium and attained a maximum desorption at $0.8 \text{ N CH}_3\text{COOH}$ solutions.

1.4 Objectives

- 1.4.1 To characterize some physical and chemical properties of the commercial activated carbon and activated carbon obtained from bagasse.
- 1.4.2 To study the dependence of variable parameters on the adsorption of Crystal Violet on commercial activated carbon and activated carbon obtained from bagasse.
- 1.4.3 To study the adsorption isotherm of Crystal Violet on commercial activated carbon and activated carbon obtained from bagasse.

CHAPTER 2

METHOD OF STUDY

2.1 Chemicals and materials

1. Commercial activated carbon (CAC); Sigma – Aldrich, USA
2. Crystal Violet; BDH, Chemical.Ltd. POOLE, UK
3. Sodium chloride, NaCl; A.R., Assay 98%, Merck, Germany
4. Sodium hydroxide, NaOH; A.R., Assay 99%, Lab Scan, Ireland
5. Hydrochloric acid, HCl; A.R., 37%, Merck, Germany
6. Potassium bromide, KBr; IR grade, Merck, Germany

2.2 Equipments and Instruments

2.2.1 Department of Chemistry, PSU

1. Centrifuge; MSE, HOMOGENISER, UK
2. Analytical balance; AB 204 – S, METTLER TOLEDO, Switzerland
3. pH meter; WTW Inolab pH level 1, Germany
4. Oven; UFE 500, Memmert, Germany
5. Hotplate and stirrer; Heidolph MR 3001, Jenway, UK
6. Thermostat shaker water bath; Memmert, Germany
7. Test sieve and lid receiver; 100 – 140, 140 - 170 and 170 - 200 mesh U.S., Endecotts
8. UV-Vis spectrophotometer; SHIMADZU UV-160A, Japan
9. Fourier-transform infrared spectrophotometer and diffuse reflectance accessory, FT-IR and KBr techniques; Spectrum GX, Perkin Elmer, U.S.

2.2.2 Scientific Equipment Center, PSU

Scanning electron microscope (SEM; JSM-5800 LV, JEOL: Attached with energy dispersive X-ray spectrometer (EDS; Oxford ISIS 300)

2.2.3 Department of Chemical Engineering, PSU

Surface area and pore size analyzer; SA 3100, Coulter

2.3 Methods

2.3.1 Preparation of activated carbon obtained from bagasse (BAC)

The production processes of activated carbon from bagasse were carbonization and chemical activation with ZnCl_2 . Bagasse was dried in the sun and cut into small pieces approximately 1 inch and placed into stainless steel box with cover.

The carbonization was then conducted in a in a muffle furnace at 400°C for 1 h. After carbonization the residual char was grounded in a laboratory jar mill to pass between 140-170 mesh sieves. Then, the chemical activation was performed by mixing the grounded char with concentrated solution of ZnCl_2 at ratio 1:2. The sample was activated at 600°C for 3 h in the muffle furnace (Sirichote et al., 2002). The obtained activated carbon was washed with 1% HCl. In the next step, it was soaked in hot water for five minutes and subsequently the water was drained off through a Buchner funnel. This step was repeated two more times to obtain a neutral pH value. Finally, it was dried in the oven at 110°C for 24 h. The obtained activated carbon was kept in a dessicator (Sirichote et al., 2008). (The BAC was prepared by bachelor's degree student in chemistry project at Department of Chemistry, PSU.)

2.3.2 Characterization of activated carbon surfaces

2.3.2.1 Surface area and pore size analysis

Nitrogen adsorption isotherms at 77 K carried out with Coulter model SA 3100 apparatus were used to determine specific surface areas (BET surface areas) and micropore volumes of activated carbons by using Brunauer-Emmett-Teller (BET) and

t-plot equations, respectively. The pore size distribution was calculated by using the Barrett-Joyner-Halenda (BJH) model (program for calculation these parameters is already in this apparatus). Prior to the nitrogen adsorption experiments, for maintaining the integrity of the chemical surface properties, all samples were degassed for 1 hour at 120 °C. (The measurement was conducted at Department of Chemical Engineering, PSU.)

2.3.2.2 Scanning electron microscopy (SEM)

A scanning electron microscope JSM-5800 LV located at Scientific Equipment Center, PSU was used to analyze the porosity of activated carbon samples.

2.3.2.3 Fourier-transform infrared spectrophotometry (FT-IR)

Activated carbon samples were studied spectroscopically with Fourier-transform infrared spectrophotometry, FT-IR. The transmission IR spectra of the carbon samples were obtained using KBr technique. The KBr disks were prepared by activated carbon-KBr mixtures in a ratio about 1:300 which were finely ground by pestle in an agate mortar and then dried at 120°C in oven and finally pressed in a hydraulic press (KBr pellet presser). Before the spectrum of a sample was recorded, the background line was obtained arbitrarily and subtracted. The spectra were recorded from 4000 to 400 cm^{-1} at a scan rate of 0.2 cm s^{-1} , and for the best resolution, the numbers of interferogram at a nominal resolution of 4 cm^{-1} was scanned more than 10 times.

2.3.2.4 Point of zero charge measurements (pH_{pzc})

By using the pH drift method (Jia, et al., 2002), the pH at the potential zero charge (pH_{pzc}) of various activated carbons was measured. The pH of a solution of 0.1 M NaCl was adjusted between 2-12 by using 0.01 mol L^{-1} HCl or NaOH. Activated carbon sample (0.2000 and 0.6000 g) was added into 100 mL of NaCl solution in 250 mL flask. The flasks were sealed, to eliminate any contact with air and then left at ambient temperature. The final pH was recorded after the pH had stabilized (typically after 24 h). The point at which initial pH and final pH were the same value was

determined by using the graph of final pH versus initial pH. This was taken as the pH_{pzc} of the activated carbon.

2.3.3 Adsorption studies

2.3.3.1 Adsorbate (dye solution)

A basic dye, Crystal Violet was used in the experiments. Chemically, crystal violet is known as hexamethyl pararosaniline chloride. Its molecular weight is $407.979 \text{ g mol}^{-1}$. The dye was supplied by BDH. Chemical. Ltd. POOLE, UK.

A stock solution of Crystal Violet (1000 mg L^{-1}) was prepared by dissolving in distilled water. Then the stock solution was diluted with distilled water to obtain series of standard solutions with concentrations ranging from $250\text{-}500 \text{ mg L}^{-1}$.

2.3.3.2 Effect of variable parameters

Weight of activated carbon

The various doses of the activated carbon were mixed with the dye solutions and the mixtures were agitated in a mechanical thermostat shaker at 30°C . The adsorption capacities for different doses were determined at definite time intervals by keeping initial concentration of dye, contact time, and pH constant

Initial concentration of dye

Experiments were conducted with different initial concentrations of dyes ranging from $250 - 500 \text{ mg L}^{-1}$. Weight of activated carbon, contact time, and pH were kept constant.

Contact time

The effect of contact time on the adsorption of dye by the adsorbent in a single cycle was determined by keeping particle size of activated carbon, pH and initial concentration of dye constant.

Temperature

The adsorption experiments were performed at $30, 40, 50$ and 60°C in a thermostat - attached water bath shaker.

pH

The pH of Crystal Violet solution of 300 mg L⁻¹ was adjusted between 2 - 13 by using 0.01 mol L⁻¹ HCl or 0.01 mol L⁻¹ NaOH. Activated carbon sample (0.03 g and 0.05 g for commercial activated carbon (CAC) and bagasse activated carbon (BAC), respectively) was added to 50 mL of dye solution. The contents were then shaken at 30°C in the thermostat shaker water bath. After the equilibrium was obtained (more than 8, 12 h for CAC, BAC), about 2 mL was transferred to test tube and centrifuge. The supernatant was decanted and analyzed for the concentration of Crystal Violet.

2.3.3.3 Adsorption isotherm studies of Crystal Violet on activated carbons

By adding 0.03 g of CAC and 0.05 g of BAC to 50 mL of Crystal Violet solution, adsorption equilibrium studies of Crystal Violet on CAC and BAC were carried out in a batch process at 30, 40, 50 and 60 °C. The concentrations of solutions at pH 5 were varied in the range of 250 – 500 mg L⁻¹. The contents were centrifuged after gentle shaking for 8 h and 12 h for CAC and BAC, respectively, in a thermostat shaker water bath. Crystal Violet concentrations before and after adsorption were then determined by UV-Vis spectrophotometer at a wavelength 591 nm. The amounts of Crystal Violet adsorbed were calculated based on the difference between the Crystal Violet concentration in aqueous solution before and after adsorption. The amount adsorbed was calculated from the equation.

$$Q_e = \frac{V(C_0 - C_e)}{W} \quad (11)$$

where Q_e is the amounts of dye adsorbed onto activated carbon (mg g⁻¹), V is the volume of the solution (L), C_0 is the initial liquid- phase concentration of dye (mg L⁻¹), C_e is the equilibrium liquid- phase concentration of dye (mg L⁻¹), and W is the weight of the adsorbent (g). The amount of dye adsorbed on to activated carbon was calculated based on the previously determined calibration curve.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Characterization of activated carbons surfaces

3.1.1 Scanning electron microscopy (SEM)

In Figure 2, the scanning electron micrographs of the external structures of two activated carbon, CAC 140 – 170 mesh and BAC 140 – 170 mesh, are shown. From micrographs, it can be seen that both the samples are full of holes with diameters ranging from around 9.5 – 19.5 μm and 5 - 10 μm , respectively. These holes are defined as macropore of the activated carbon ($>50\text{ nm}$). Both the micropore and mesopore are not resolved by scanning electron microscopy even at higher magnification because of the limit of detection of instrument.

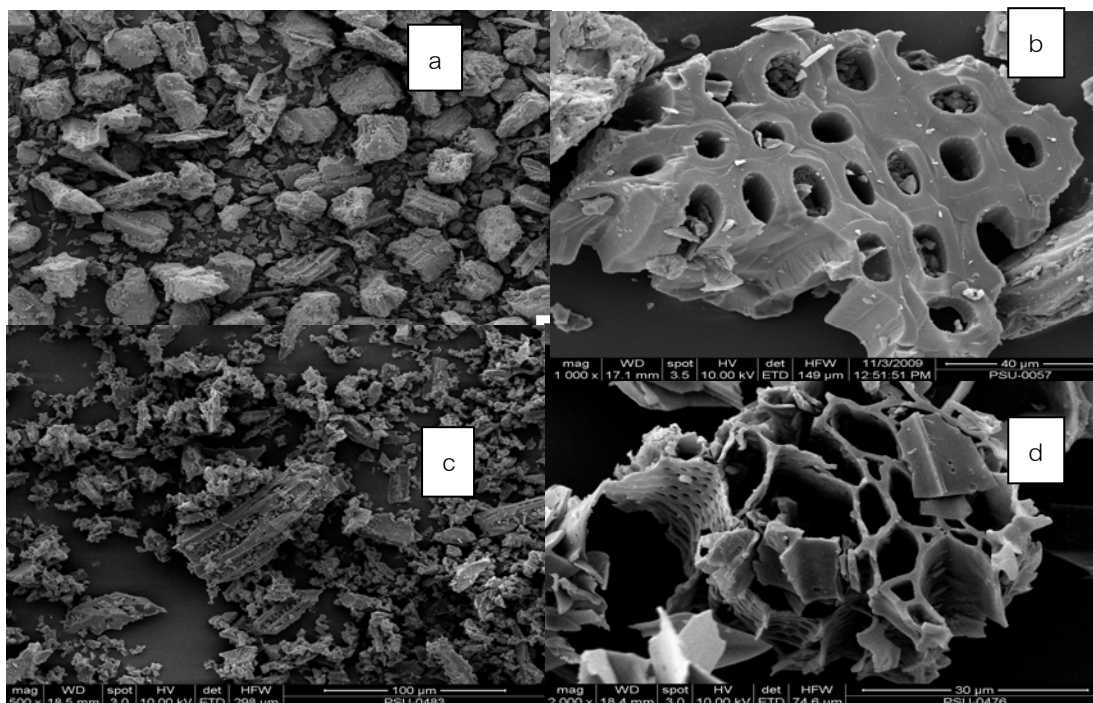


Figure 2 SEM micrographs of (a) CAC-140-170 (150), (b) CAC- 140-170 (1000), (c) BAC- 140-170 (500), and (d) BAC- 140-170 (2000) activated carbons.

3.1.2 Surface area and pore size analysis (physical or porous texture characterization)

By the construction of N₂ adsorption isotherms, an understanding of the surface area and porosity of an adsorbent can be achieved. The adsorption volume of adsorbent was measured over a wide range of relative pressures at constant temperature (77 K). Nitrogen adsorption isotherms measured for CAC and BAC activated carbon were shown in Figure 3. It is evident that all isotherms can be classified into two types.

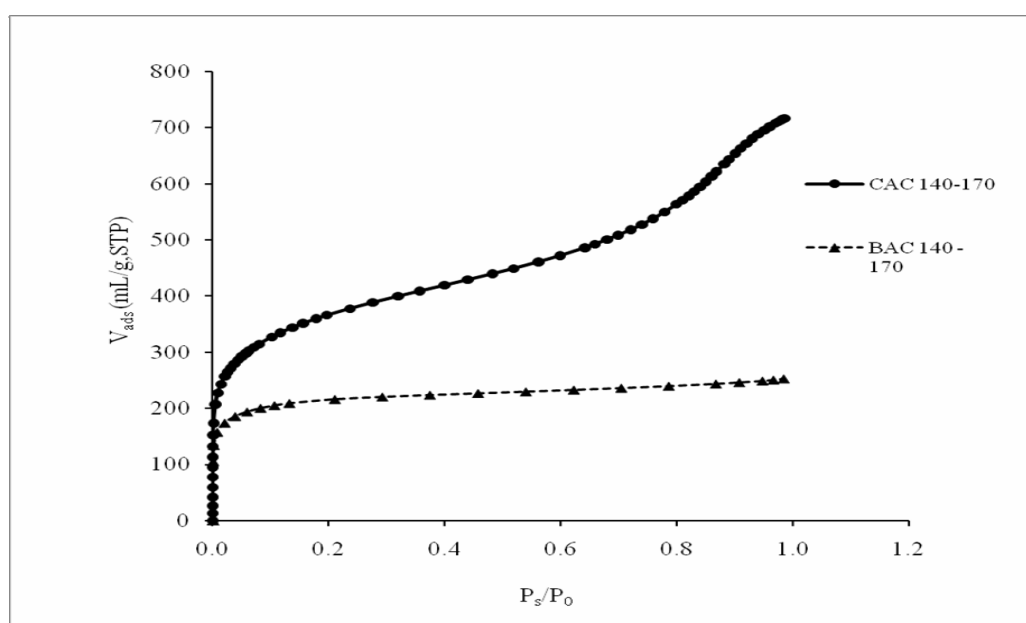


Figure 3 Adsorption isotherms of N₂ at 77 K for the CAC and BAC (P_s/P_0 is relative pressure).

In the case of BAC, the sample is approximately type I according to IUPAC classification (Hu and Vansant, 1995) since most of the adsorbed volume is contained in the micropores. Its isotherms shows the steep rise of the initial part of the isotherms where micropores is filled by nitrogen molecule completely at $\sim 0.2 P/P_0$. After 0.2 P/P_0 , the isotherms become plateau. It is now widely accepted that the initial part of the type I isotherm represented micropore filling and that the slope of the plateau at high relative pressure is due to multilayer adsorption on the nonmicroporous structures, such as in mesopores, in macropores, and on the external surface. It can be assumed that its material have significant micropores if nitrogen adsorption isotherm

of any porous material can be fitted with type I isotherm. Thereby, BAC have the contents largely of micropore. On the other hand, isotherms of CAC belong to a mixed type in the IUPAC classification (Juang, et al., 2002). In the initial parts it is type I, with an important uptake at low relative pressures. It is type II at intermediates and high relative pressures. The steep rise of the initial part of the isotherms evidences the presence of micropores. However, the present samples do not reach a clear plateau unlike other activated carbons. This indicated that CAC and BAC are mainly micro- and mesoporous in character with a minor presence of wider pores where capillary condensation occurred.

Table 1 BET and micropore surface areas of CAC and BAC.

Samples	BET surface areas ($\text{m}^2 \text{g}^{-1}$)	Micropore surface areas ($\text{m}^2 \text{g}^{-1}$)	Micropore fractions (%)	Micropore volumes (mL g^{-1})
CAC 140-170	1,308.83	458.76	35.05	0.19
BAC 140-170	786.24	573.86	72.99	0.24

From Table 1, further understanding in porous characters of all carbons can be observed. The results show that all of the samples possess a well-developed porous structure. CAC and BAC exhibit different BET surface areas. The difference among BET surface area of both samples is about 40%. Hence, BET surface areas may affect the adsorption efficiency in this study.

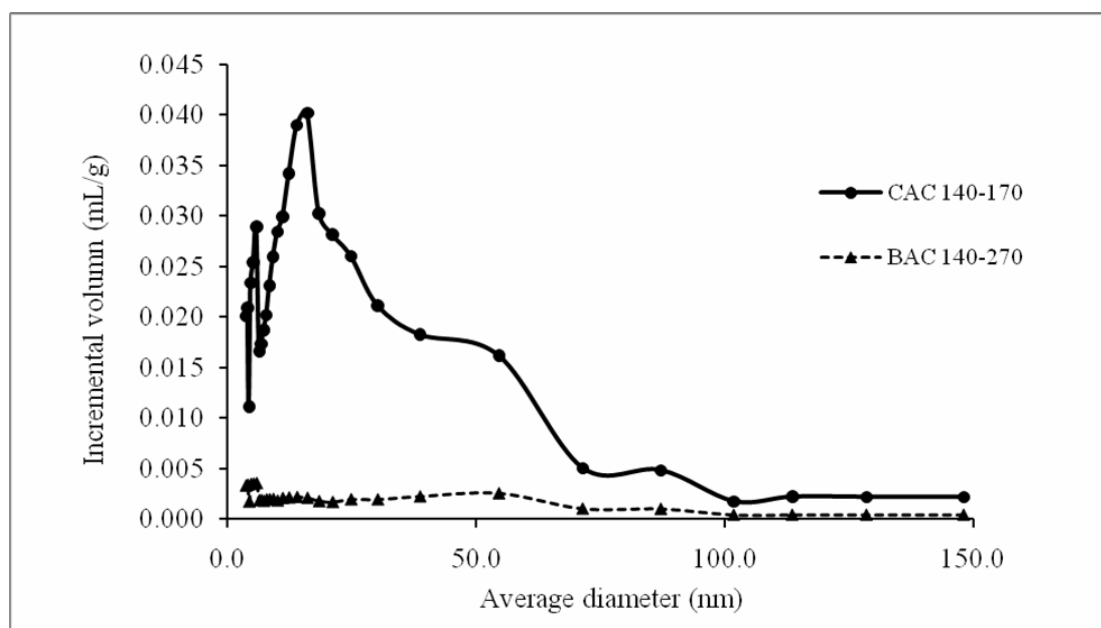


Figure 4 BJH pore size distribution of CAC and BAC

Generally, the pores of activated carbon are classified into three groups, micropore (< 2 nm), mesopore (2-50 nm) and macropore (> 50 nm). In this study, however, pore size distribution in the micropore region cannot be measured due to the limitation of instrument. There are many methods of pore size distribution in the micropore region. Methods based on the potential theory of Dubinin, t-plot method, α plot or MP methods (Strelko and Malik, 2002) are widely used for micropore evaluation. This research has used t-plot method for determining micropore surface area, micropore fraction and micropore volume but this method cannot be used for determination of the distribution of micropore. Pore size distribution above 2 nm, however, can be assessed accurately using the method of Barrett, Joyner and Halenda (BJH) model (Barrett, et al., 1951).

It can be seen from Table 1 that BAC possesses more micropore surface areas and percentages of micropore fraction ((micropore surface area/ BET surface area) $\times 100$) around 73% which is more than the CAC. Noticeably, CAC has more BET surface areas than BAC but CAC shows less micropore fraction. From Figure 4, CAC remarkably has more incremental pore volume of mesopore than BAC. Therefore, the

physical characteristics of raw materials seem to be important factor for porous nature of activated carbon.

Figure 4 shows the meso- and macropore nature (>2 nm) of all activated carbon. BAC does not have significant mesopores and macropores. In contrast, CAC possesses a significant amount of mesopore with a maximum at 6 nm and 16 nm. BAC also shows the evidence of the presence of mesopores and macropores. The presence of mesopores and macropores of CAC may affect to reduction of micropores while its BET surface area is highly remained.

3.1.3 Fourier-transform infrared spectrophotometry (FT-IR)

The assignment of a specific wave number to a given functional group is not possible although numerous FT-IR spectroscopic studies have been conducted on various forms of carbon because the characteristic bands of various functional groups overlap and shift, depending on their molecular structures and environments (Fuente, et al., 2003). Nonetheless, a consensus in the assignment of band frequencies to different functional groups is possible to a certain extent.

In Figure 5, the spectra of two activated carbons are shown. The strong band appears at about $3,400\text{ cm}^{-1}$ is mainly assigned to O-H stretching vibrations. The band observed at about $2,900\text{ cm}^{-1}$ which is ascribed to symmetric and asymmetric C-H stretching vibrations in aliphatic CH, CH₂ and CH₃ groups are detected. The bands at about $1,600\text{ cm}^{-1}$ is C=C stretching vibration in aromatic rings. Many bands because of hydrogen, oxygen, and nitrogen functional groups are observed in the range $1,400 - 400\text{ cm}^{-1}$ which is difficult to assign each simple motion of specific functional groups except the strong band at about $1,020\text{ cm}^{-1}$ can be attributed to C-O stretching vibrations. The both activated carbon samples show very similar spectra (Buczek, et al., 1999).

As mentioned above, all activated carbon samples have similar spectra. It does not mean chemical nature of activated carbons will not be different. Unfortunately, FT-IR can be used only to characterize functional groups on the carbon surfaces qualitatively. Quantitative analysis by using this method is difficult to distinguish the nature of carbons. It is necessary to employ other methods for clear chemical characterizations.

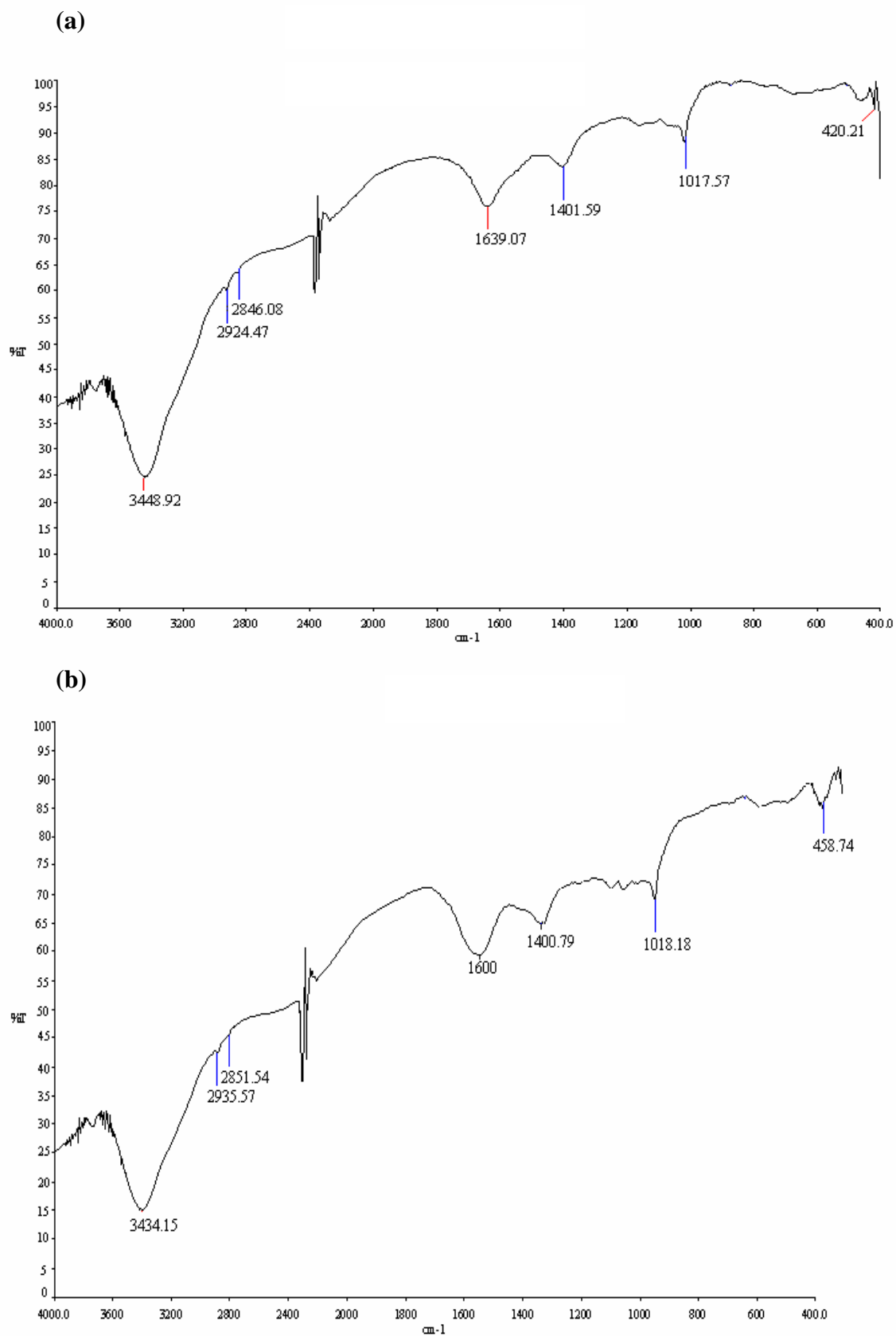


Figure 5 FT-IR Spectra of (a) CAC, and (b) BAC

3.1.4 Point of zero charge measurements (pH_{pzc})

In Figure 6, the graphs of final pH versus initial pH obtained by using pH drift method (Jia, et al., 1998) for all activated carbon samples. The results show that pH_{pzc} of CAC and BAC is 3.5 and 4.5, respectively, which indicating the acidic surface nature of both activated carbons. The graph of final pH (pH_f) versus initial pH (pH_0) is used to determine the points at which initial pH and final pH values were equal. This point is taken as the pH_{pzc} of the activated carbon.

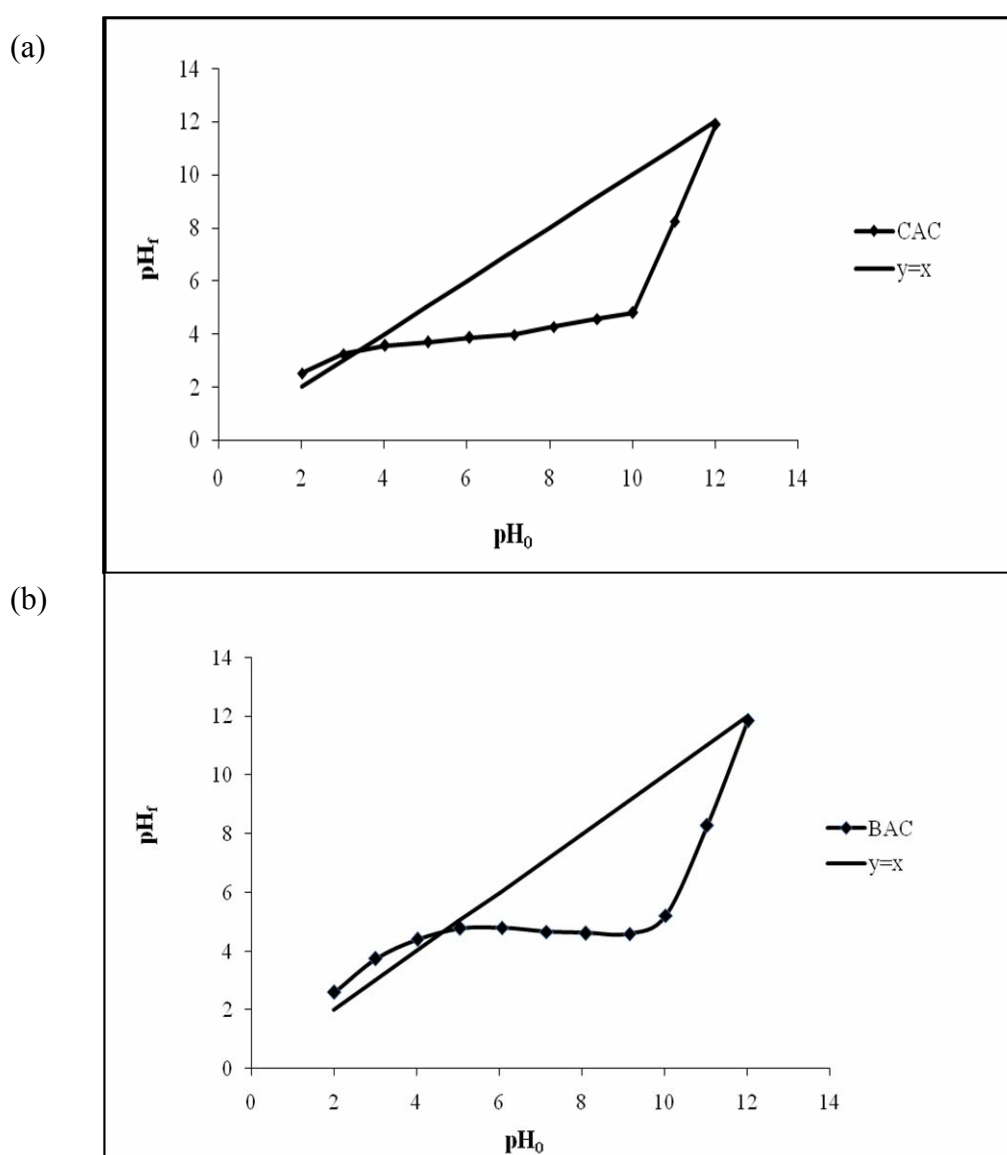


Figure 6 Graphs of final pH versus initial pH for determination the point of zero charge (pH_{pzc}) of CAC – 140 – 170 (a) and BAC – 140 – 170 (b).

The amphoteric character of surface oxides S-CO₂ where S represents the activated carbon surface can be explained as follows (Kadirtvalu, et al., 2000).

For pH < p*H*_{pzc}, the dominant reaction is:



The release of hydroxyl ions induces an increase of pH and a protonated surface of activated carbon.

For pH > p*H*_{pzc}, the following reaction takes place:



The activated carbon surface is deprotonated and the release of protons induces a decrease in pH.

The pH and acid-base values of the activated carbon give a good indication of the surface oxygen complexes and the electrical surface changes undergone by them. These surface changes arise from the interaction between the carbon surface and the aqueous solution. The complexes on the carbon surfaces are generally classified as acidic, basic, and neutral groups.

3.2 Adsorption studies

3.2.1 Spectroscopy of Crystal Violet

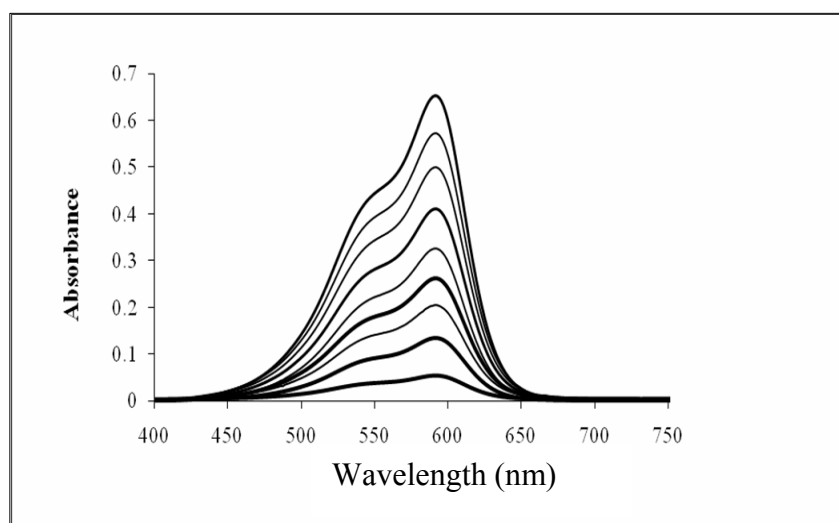


Figure 7 Spectra of 0.4 – 3.6 mg L⁻¹ Crystal Violet.

Figure 7 shows the concentration of Crystal Violet in aqueous solution as determined by UV-Vis spectrophotometer at maximum wavelength of 591 nm.

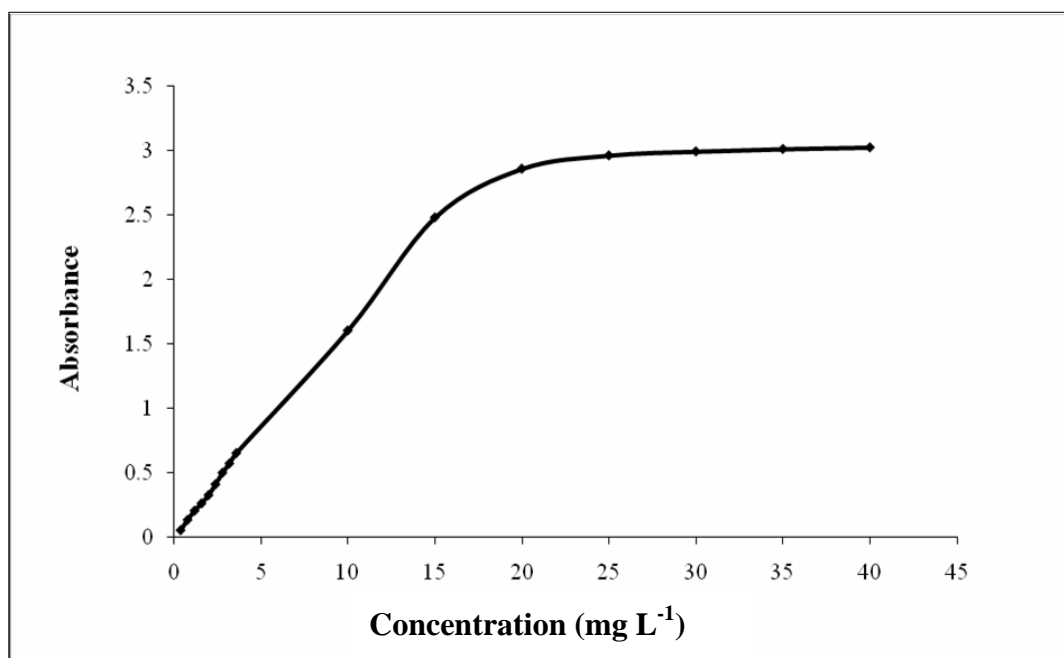


Figure 8 Relation of absorbance with 0.4 – 40 mg L⁻¹ Crystal Violet (at $\lambda_{\text{max}} = 591$ nm, room temperature)

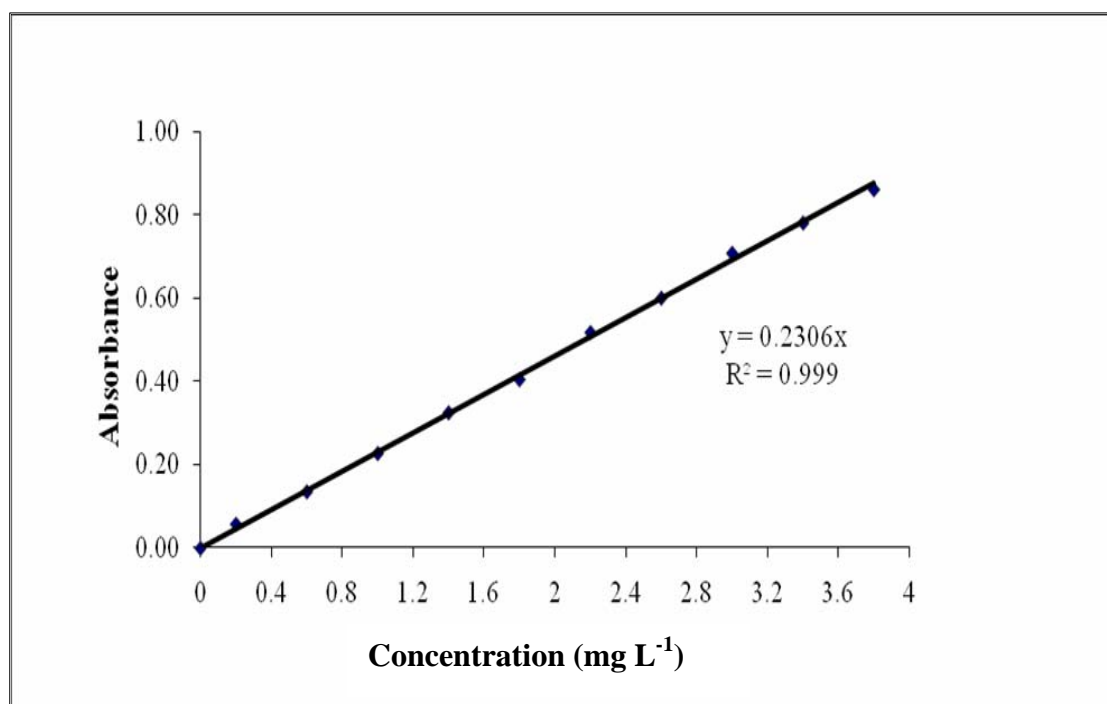
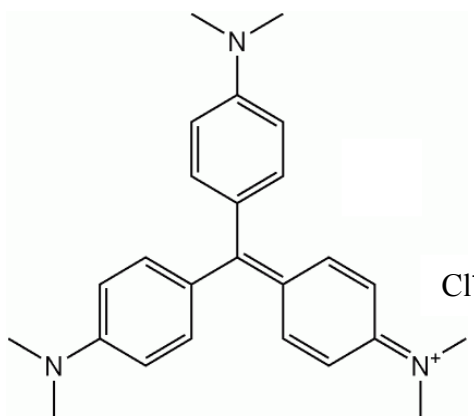


Figure 9 Standard curve of Crystal Violet solutions (0 – 3.8 mg L⁻¹, at $\lambda_{\text{max}} = 591$ nm)

3.2.2 Adsorbate dye solution

Concentration range of Crystal Violet was used in this study is 250 to 500 mg L⁻¹, which is completely dissolved in water.

The structure of Crystal Violet in aqueous solution is shown below.



3.2.3 Effect of various parameters

3.2.3.1 Weight of activated carbon

The adsorption of Crystal Violet onto the 140 – 170 mesh CAC and BAC (Meikap, et al., 2006) were studied by varying the weights of activated carbon in the ranges of 0.015 - 0.040 g/ 50 mL and 0.02 – 0.07 g/50 mL for 300 mg L⁻¹ of dye concentration, respectively, at pH 5 which is pH nature of dye solution. The percentage of adsorption increased with increasing weight of both activated carbons as shown in Figure 10 and Figure 11, respectively. Effect of weight of activated carbon was attributed to the increase of surface area and availability of more adsorption sites (Namasivayam, et al., 1996). In this study, the appropriate weight of CAC and BAC is 0.03 and 0.05, respectively for adsorption of Crystal Violet.

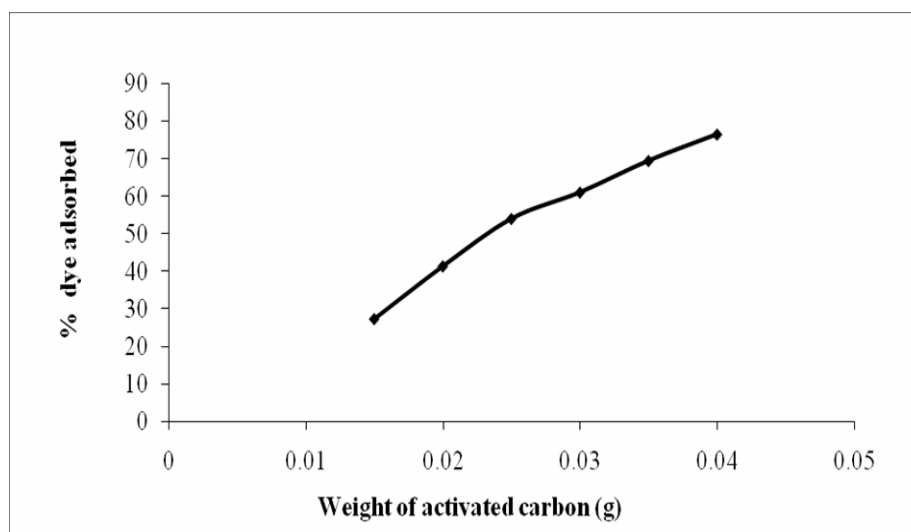


Figure 10 Effect of weight of CAC (140 – 170 mesh), 0.015 – 0.040 g/50 mL at 30°C pH = 5 and dye concentration 300 mg L⁻¹.

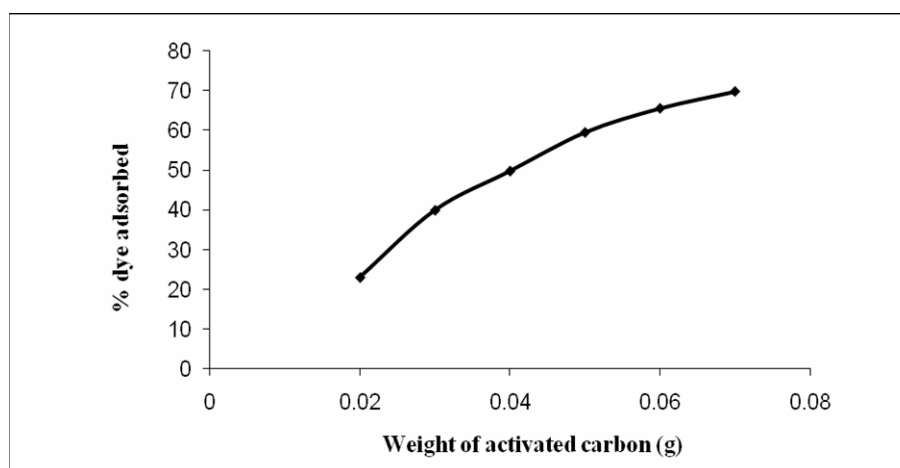


Figure 11 Effect of weight of BAC (140 – 170 mesh), 0.02 – 0.07 g/50 mL at 30° C pH = 5 and dye concentration 300 mg L⁻¹.

3.2.3.2 Effect of contact time and initial dye concentration

The adsorption of Crystal Violet onto the CAC and BAC were studied in order to assess the time required for equilibrium to be achieved. In most adsorption isotherm studies, the results showed that equilibrium was achieved within around 8 h. and 12 h. for CAC and BAC as shown in Figure 12 and Figure 13, respectively. However, the solutions were left longer than equilibrium time to ensure complete equilibration.

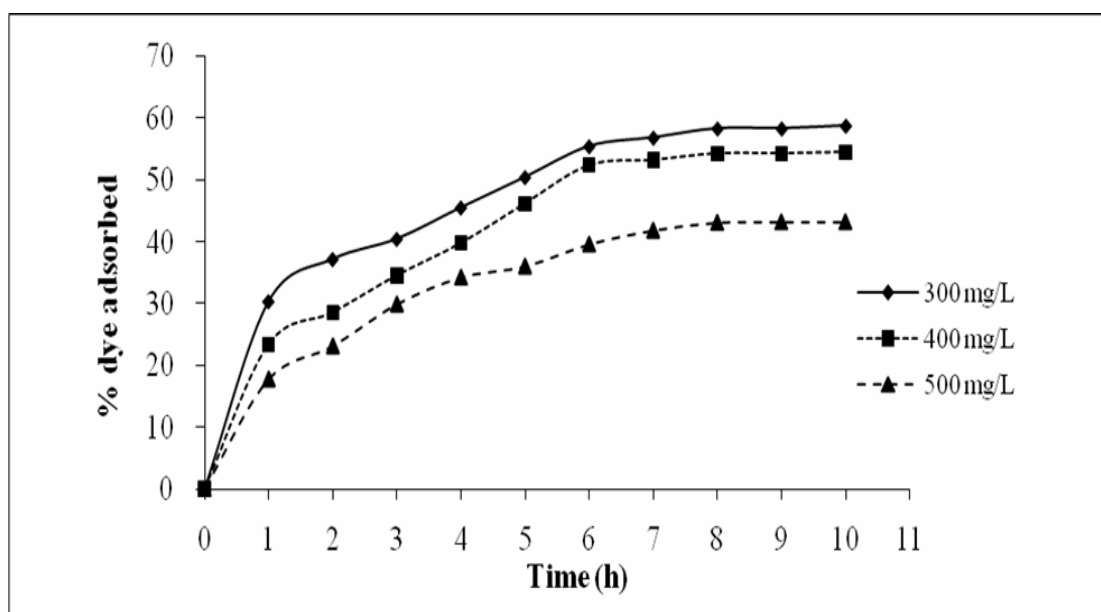


Figure 12 Equilibrium time of 300, 400 and 500 mg L⁻¹ Crystal Violet on CAC at 30°C and pH = 5.

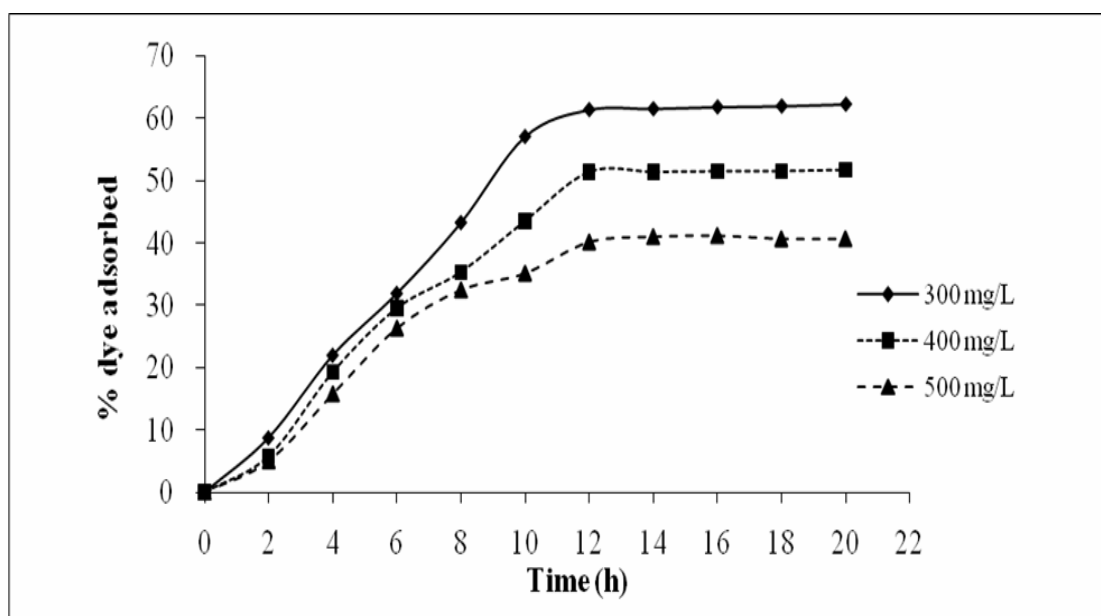


Figure 13 Equilibrium time of 300, 400 and 500 mg L⁻¹ Crystal Violet on BAC at 30°C and pH = 5.

3.2.3.3 Effect of pH

The pH of Crystal Violet solution decreased with increasing concentration of Crystal Violet as shown in Table 2 due to the increasing in amount of proton which release from Crystal Violet.

Table 2 The pH of aqueous solution Crystal Violet at various concentrations.

Concentration (mg L ⁻¹)	pH
50	5.68
300	5.48
500	5.28
1000	5.12

Effect of pH on adsorption of Crystal Violet on activated carbon

In Figure 14, it shows the effect of solution pH values on the adsorption of Crystal Violet on all of the activated carbons. Crystal Violet displays a general trend of slightly increased adsorption on all the activated carbons with the increase of solution pH values. At pH higher than 2, the adsorption amount of Crystal Violet on CAC and BAC slightly increased with the increase of solution pH values. In addition, at low pH there is competition for the surface sited of activated carbon between protonation (H⁺ adsorption on the carbon surface) and adsorption of Crystal Violet. Since the surface of CAC and BAC are negative at pH > p_H_{pzc} (3.5) for CAC and pH > p_H_{pzc} (4.5) for BAC. When pH of solution increase with increasing amount of adsorbed because the increase of solution pH values, the electrical repulsion force become weaker and the Crystal Violet may be transported to the surface of the activated carbons and become to attach on the surface due to the action of other factors such as less competitive from protonation.

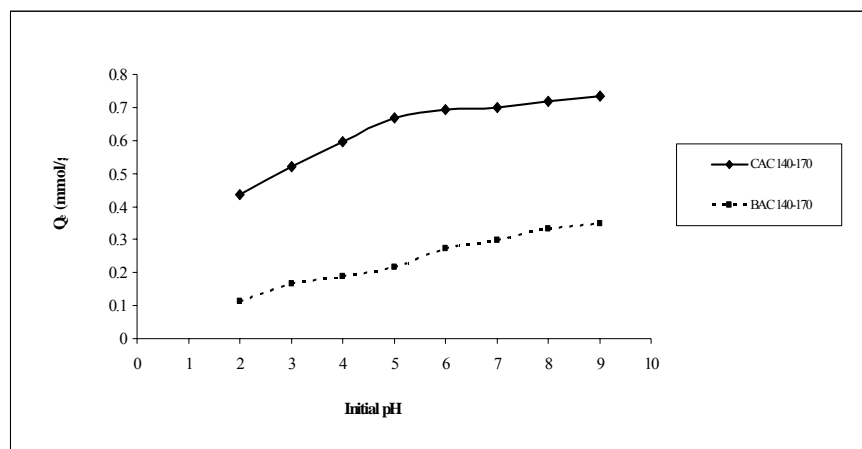


Figure 14 Adsorption of Crystal Violet on CAC (a) and BAC (b) with pH range 2 – 13 and dye concentration 300 mg L⁻¹.

3.2.3.4 Effect of temperature

The adsorption capacity of the adsorbent increased with increase in the temperature of the system from 30 - 60 °C as shown in Table 3 for CAC and Table 4 for BAC. The percentage of adsorption increases with increasing the temperature. It indicates that the adsorption process is endothermic.

Table 3 Equilibrium parameters for the adsorption of Crystal Violet 0.6 – 1.2 mmol L⁻¹ onto CAC 0.03 g.

C ₀ (mmol L ⁻¹)	Temperature (°C)							
	C _e (mmol L ⁻¹)				% dye adsorbed			
	30	40	50	60	30	40	50	60
0.6	0.0903	0.0659	0.0510	0.0383	85	89	92	94
0.7	0.1276	0.1074	0.0925	0.0765	82	85	87	89
0.9	0.1743	0.1658	0.1977	0.1488	80	81	76	83
1.0	0.2817	0.2583	0.2051	0.1818	71	74	78	81
1.1	0.3795	0.3486	0.3316	0.2838	65	68	70	74
1.2	0.4655	0.4486	0.4347	0.4167	62	64	65	66

Table 4 Equilibrium parameters for the adsorption of Crystal Violet 0.6 – 1.2 mmol L⁻¹ on BAC 0.05 g.

C ₀ (mmol L ⁻¹)	Temperature (°C)							
	C _e (mmol L ⁻¹)				% dye adsorbed			
	30	40	50	60	30	40	50	60
0.6	0.2062	0.1701	0.1371	0.0978	66	72	77	84
0.7	0.2828	0.2679	0.2349	0.1403	60	63	68	81
0.9	0.3873	0.3316	0.2881	0.1945	55	61	66	77
1.0	0.5293	0.4666	0.3986	0.3338	47	52	59	66
1.1	0.6384	0.5761	0.5261	0.4018	42	47	52	63
1.2	0.7588	0.6994	0.6431	0.5070	39	43	48	59

3.2.4 Adsorption isotherm studies of Crystal Violet on activated carbons

The adsorption of Crystal Violet on the CAC and BAC were studied in order to assess the time required for equilibrium to be achieved. In most adsorption studies, the results showed that equilibrium was achieved within around 8 h and 12 h for CAC and BAC, respectively. However, the solutions were left for 16 h and 24 h for CAC and BAC, respectively, to ensure complete equilibration.

According to the Langmuir equation the equilibrium concentration of dye over the adsorbed amounts of dye (C_e/Q_e , g L⁻¹) were plotted against the equilibrium concentrations of dye (C_e) at various temperatures as shown in Figure 15 for CAC and Figure 16 for BAC. For each temperature the graph was fitted to a straight line. Then the maximum amount of dye adsorption, Q_m (mmol g⁻¹) was calculated from the slope ($= 1/Q_m$) and equilibrium constant related to the heat of adsorption, b (L mmol⁻¹) was calculated from the intercept ($= 1/(bQ_m)$). The values of Q_m and b including the correlation coefficients, R^2 , are tabulated in Table 5

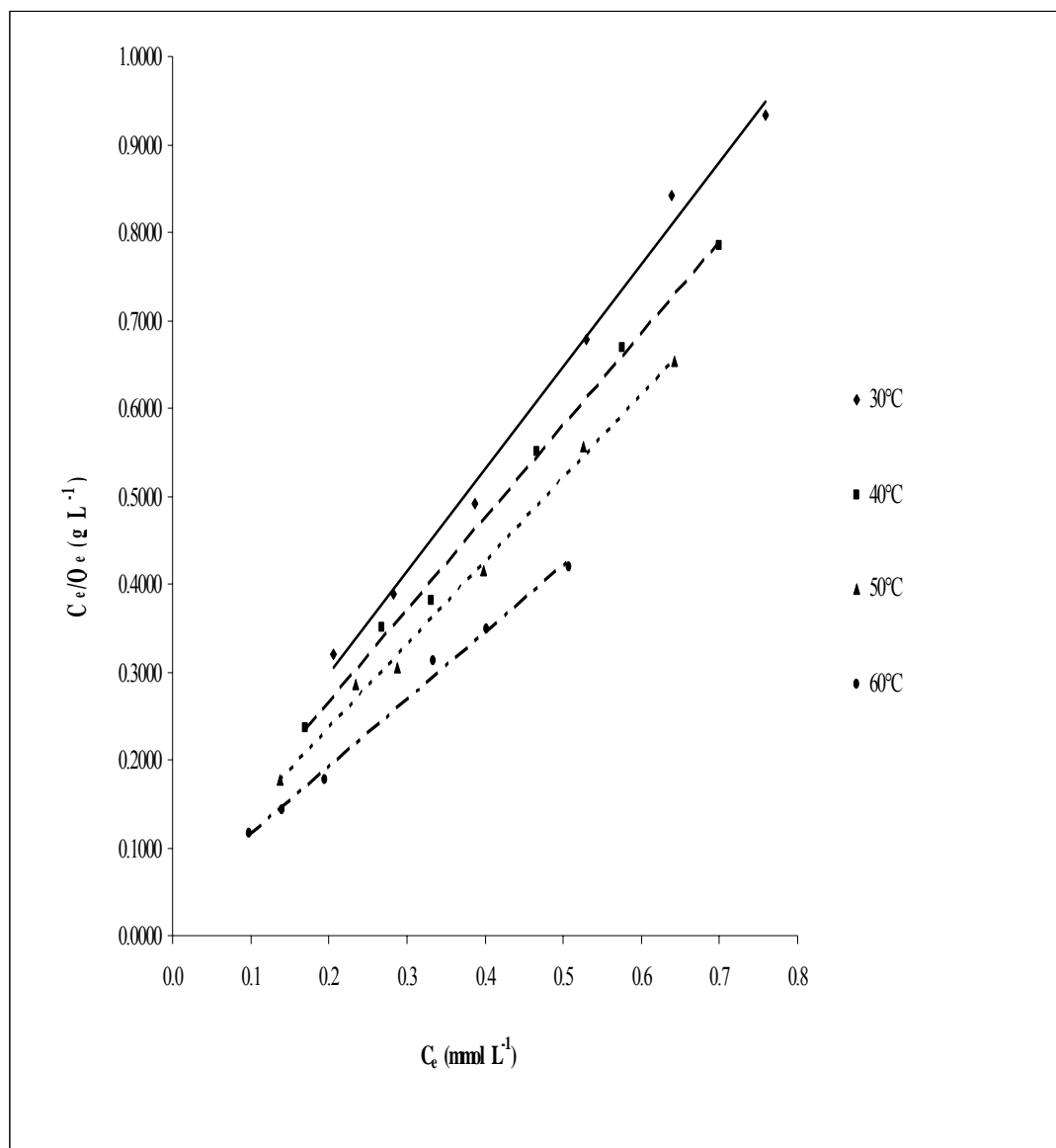


Figure 15 Langmuir adsorption isotherms for linear form of Crystal Violet on CAC (0.03 g) at 30 °C, 40 °C, 50 °C and 60 °C, dye concentrations 250-500 mg L⁻¹ and pH = 5.

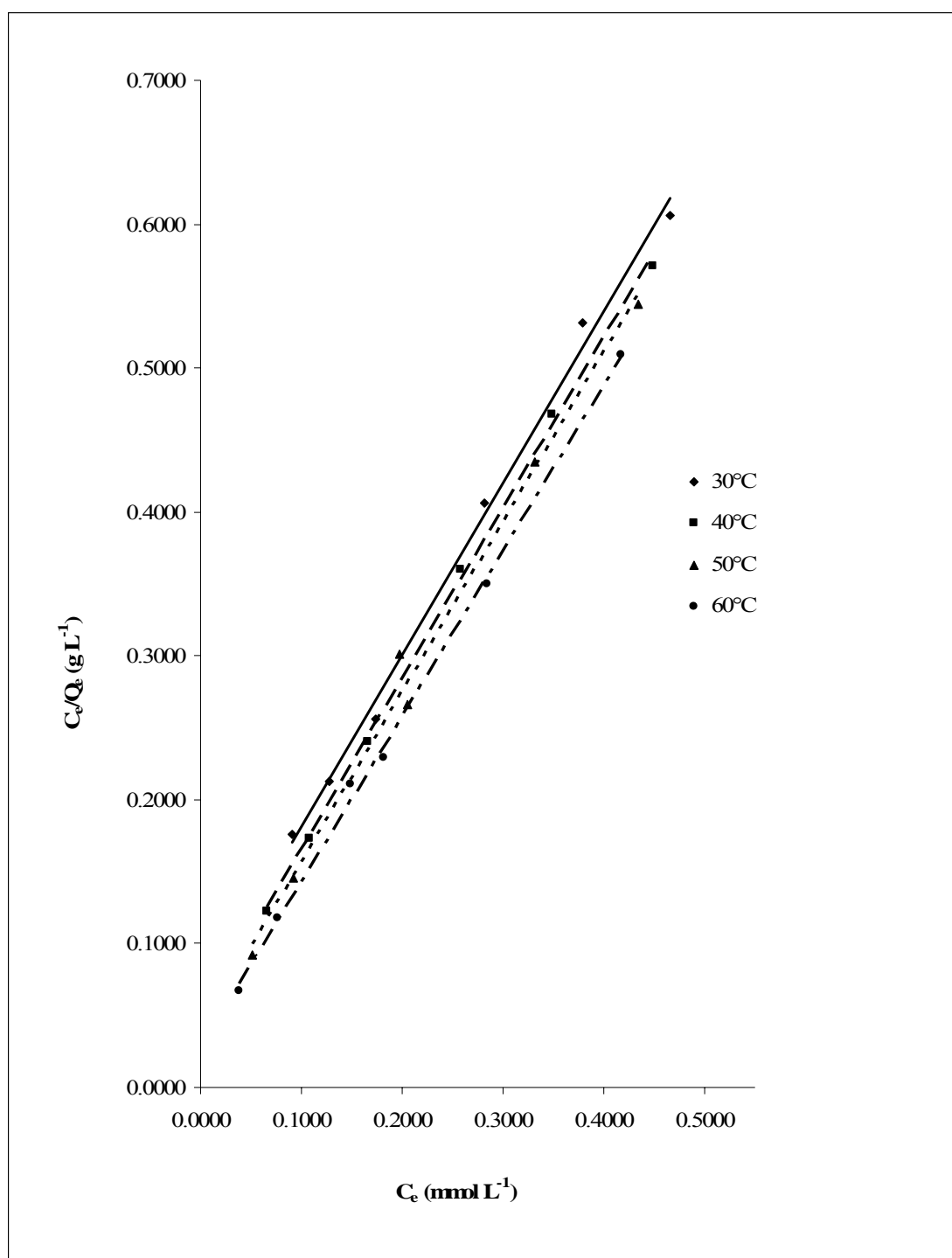
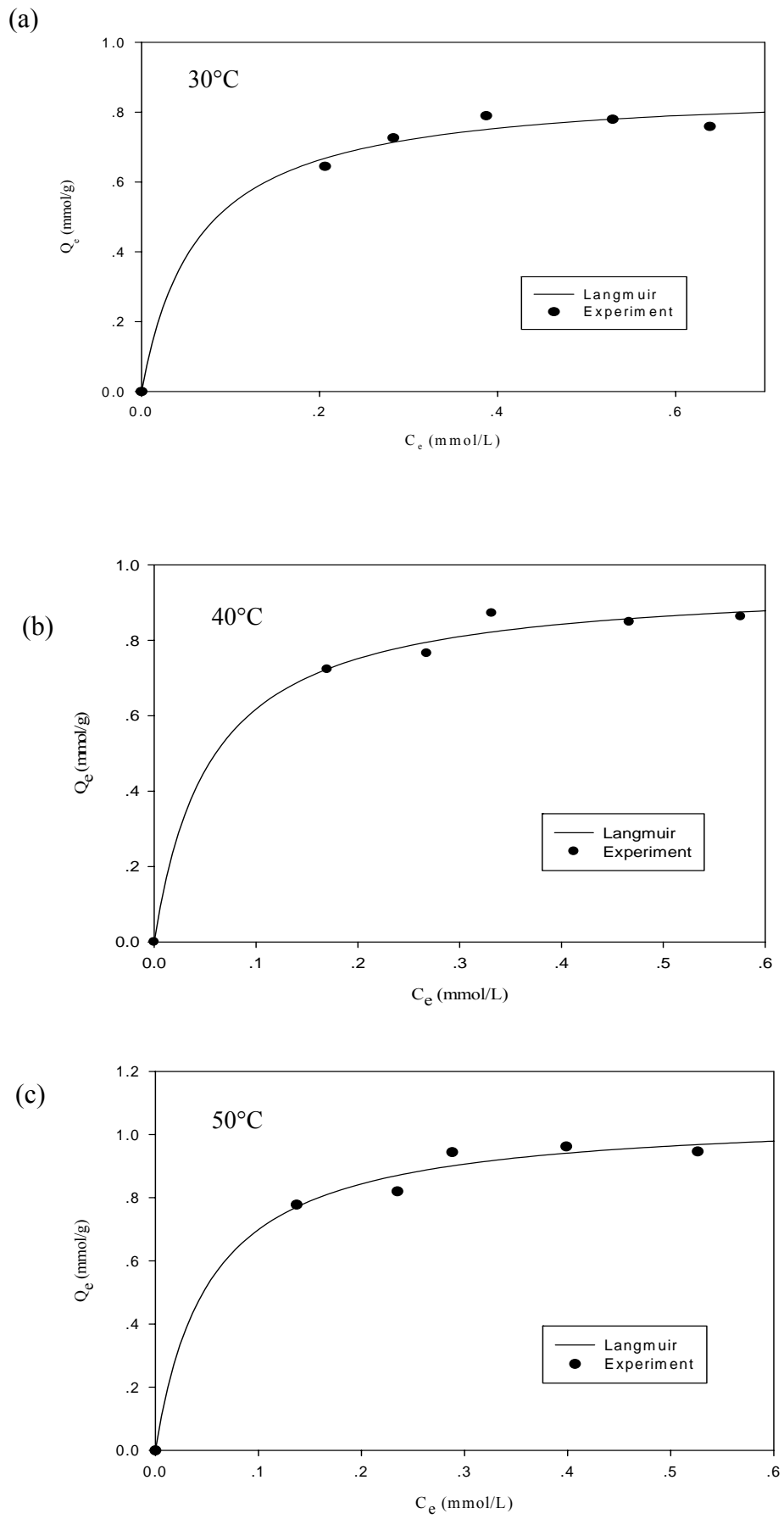


Figure 16 Langmuir adsorption isotherm of Crystal Violet on BAC (0.05 g) at 30 °C, 40 °C, 50 °C and 60 °C, dye concentrations 250-500 mg L^{-1} and pH = 5.

Table 5 Parameter values of the Langmuir equations for linear form fitted to the experimental of adsorption Crystal Violet on CAC and BAC at different temperatures.

AC Temp (°C)	CAC			BAC		
	Q_m (mmol g ⁻¹)	b (L mmol ⁻¹)	R^2	Q_m (mmol g ⁻¹)	b (L mmol ⁻¹)	R^2
30	0.86	17.97	0.9929	0.83	19.13	0.9956
40	0.95	18.79	0.9963	0.84	25.41	0.9988
50	1.06	19.81	0.9954	0.85	29.84	0.9919
60	1.30	19.97	0.9932	0.87	42.07	0.9981

The weight of CAC was 0.03 g and the weight of BAC was 0.05 g. Those adsorption data were also fitted with the non-linear form of Langmuir equation by plotting the adsorbed amount of dye, Q_e (mmol g⁻¹) against the equilibrium concentration of dye, C_e (mmol L⁻¹) as shown in Figure 16 and Figure 17.



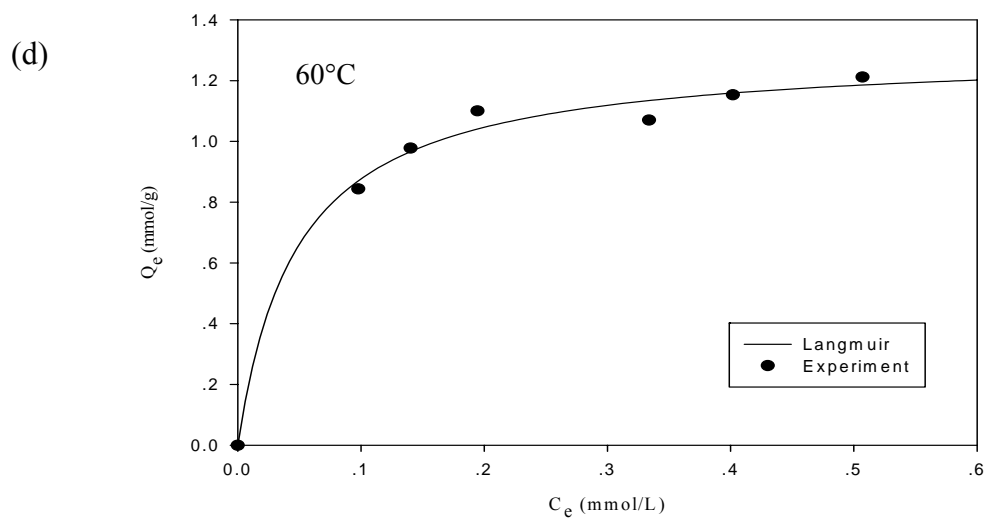
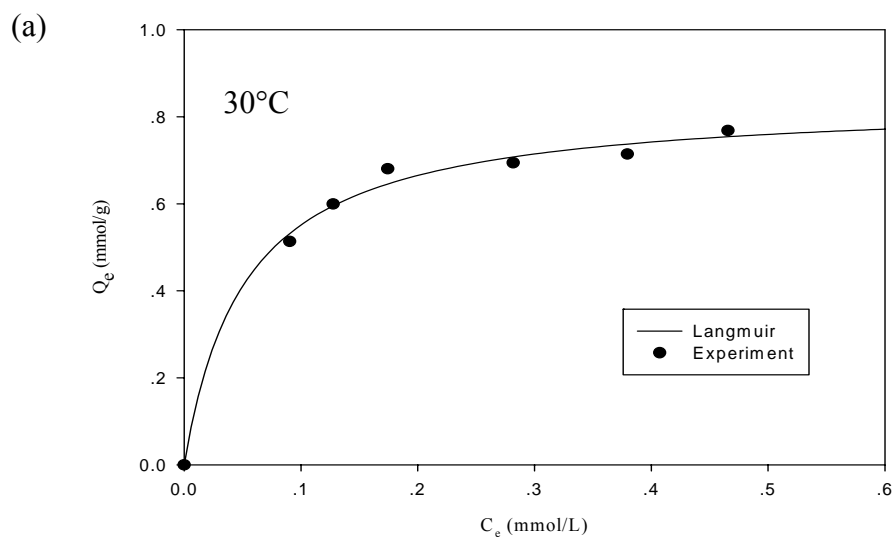


Figure 17 Langmuir adsorption isotherm for non-linear form of Crystal Violet on CAC (0.03 g) at different temperatures (a) 30 °C (b) 40 °C (c) 50 °C and (d) 60 °C, dye concentrations 250 – 500 mg L⁻¹ and pH =5.



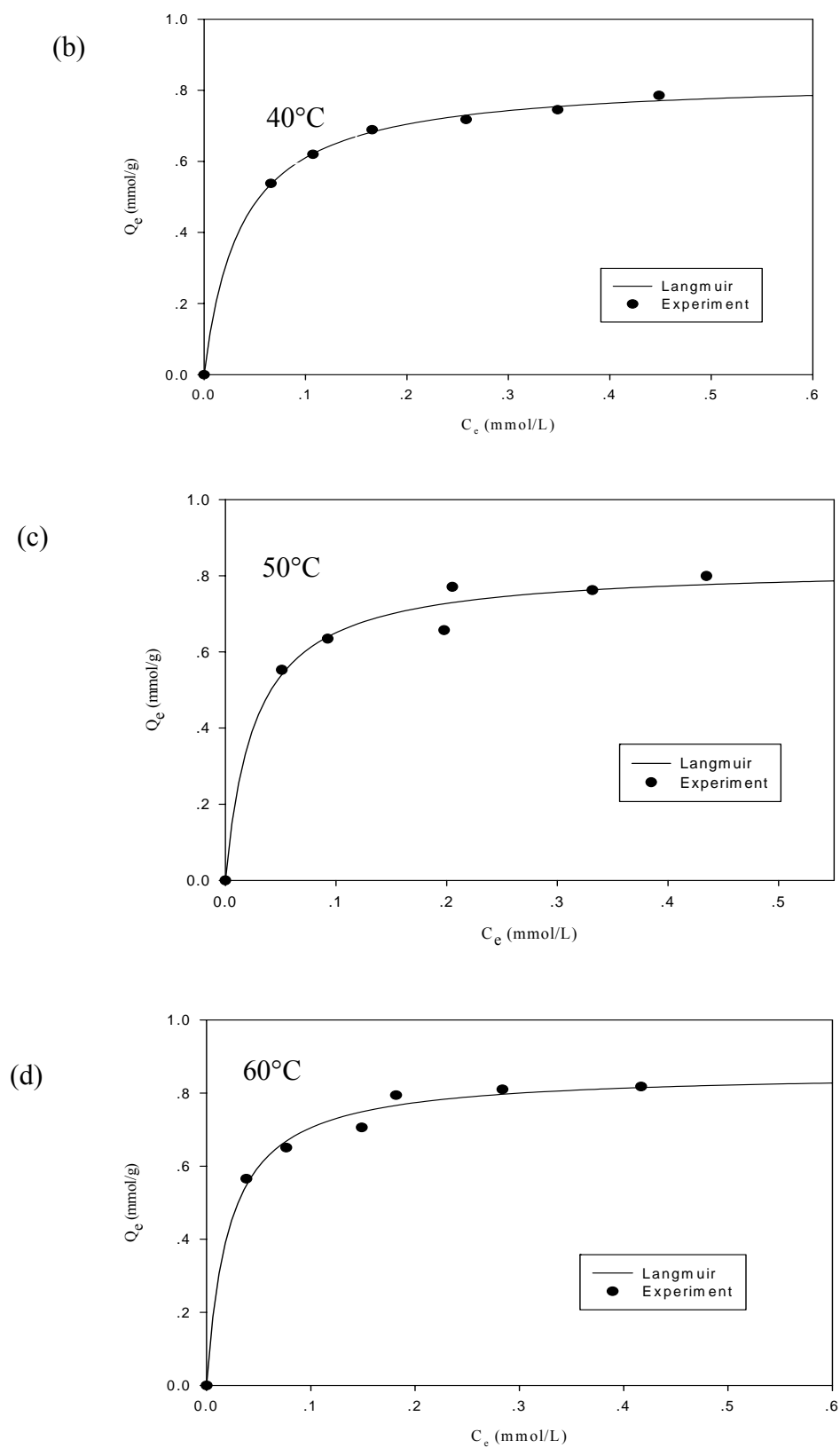


Figure 18 Langmuir adsorption isotherm for non-linear form of Crystal Violet on BAC (0.05 g) at (a) 30 °C, (b) 40 °C, (C) 50 °C and (d) 60 °C, dye concentrations 250 – 500 mg L⁻¹ and pH = 5.

The values of Q_m , b and R^2 calculated from the non-linear form of Langmuir equation are tabulated in Table 6.

Table 6 Parameter values of the Langmuir equation for non-linear form fitted to the experimental adsorption of Crystal Violet (250 – 500 mg L⁻¹) on CAC (0.03 g) and BAC (0.05 g) at different temperatures.

AC Temp (°C)	CAC			BAC		
	Q_m (mmol g ⁻¹)	b (L/mmol)	R^2	Q_m (mmol g ⁻¹)	b (L mmol ⁻¹)	R^2
30	0.87	15.75	0.9930	0.82	19.16	0.9940
40	0.96	18.08	0.9941	0.83	27.32	0.9988
50	1.06	19.12	0.9927	0.84	37.31	0.9844
60	1.30	20.79	0.9912	0.86	46.30	0.9932

Figures 15 – 18 show that adsorption capacities of CAC for Crystal Violet are greater than BAC at pH = 5 and 30 °C, 40 °C, 50 °C, and 60 °C. We can imagine that in the case of the high ionic radius of Crystal Violet, the result may be explained in terms of pore accessibility (Kadirvalu, et al., 2000). Since BAC has micropore more than CAC, some micropore entrances may be blocked by hydrolyzed dyes species which are larger than the dye ions. Accordingly, surface groups located in micropores are no longer accessible and some surface sites are not used for adsorption. In the case of CAC which contain more mesopores, accessibility to micro- and mesopores is not blocked by hydrolyzed species and almost surface sites can be used for adsorption of Crystal Violet. In addition, acidity of surface becomes another factor to define adsorption capacities (Ferro-Garcy, et al., 1998). CAC which has lower pH_{pzc} values should have more adsorption capacities than BAC. Therefore, it is unequivocal to

support the CAC higher adsorption Crystal Violet than on BAC because CAC has the higher mesopore and lower pH_{pzc} value.

To confirm the favorability of the adsorption process, the dimensionless separation factor (R_L) was presented in Table 7 for CAC and Table 8 for BAC and calculated by the following equation: (Arivoli, et al., 2007).

$$R_L = \frac{1}{1 + bC_0} \quad (12)$$

Where R_L is dimensionless separation factor, b is an equilibrium constant related to the heat of adsorption and C_0 is the initial dye concentration.

The R_L values were found between 0 and 1 confirms the ongoing adsorption process is much more favorable (Arivoli, et al., 2007).

Table 7 Dimensionless separation factor (R_L) of Crystal Violet adsorption on CAC at different temperature.

R_L C_0 (mg L ⁻¹)	Temperature (°C)			
	30	40	50	60
250	0.0797	0.0612	0.0526	0.0379
300	0.0671	0.0513	0.0441	0.0317
350	0.0576	0.0440	0.0377	0.0271
400	0.0508	0.0388	0.0332	0.0238
450	0.0456	0.0347	0.0297	0.0213
500	0.0406	0.0309	0.0264	0.0189

Table 8 Dimensionless separation factor (R_L) of Crystal Violet adsorption on BAC at different temperatures.

R_L C_0 (mg L ⁻¹)	Temperature(°C)			
	30	40	50	60
250	0.0844	0.0810	0.0772	0.0766
300	0.0711	0.0682	0.0649	0.0644
350	0.0611	0.0586	0.0558	0.0554
400	0.0540	0.0517	0.0492	0.0488
450	0.0484	0.0464	0.0441	0.0438
500	0.0431	0.0413	0.0393	0.0390

From knowledge of Freundlich equation, it is expected to employ this equation for considering behavior of adsorption isotherm. According to the Freundlich equation the adsorbed amounts of dye at equilibrium ($\log Q_e$) were plotted against the equilibrium concentrations of dye ($\log C_e$) at various temperatures as shown in Figure 19 for CAC and Figure 20 for BAC. For each temperature the graph was fitted to a straight line.

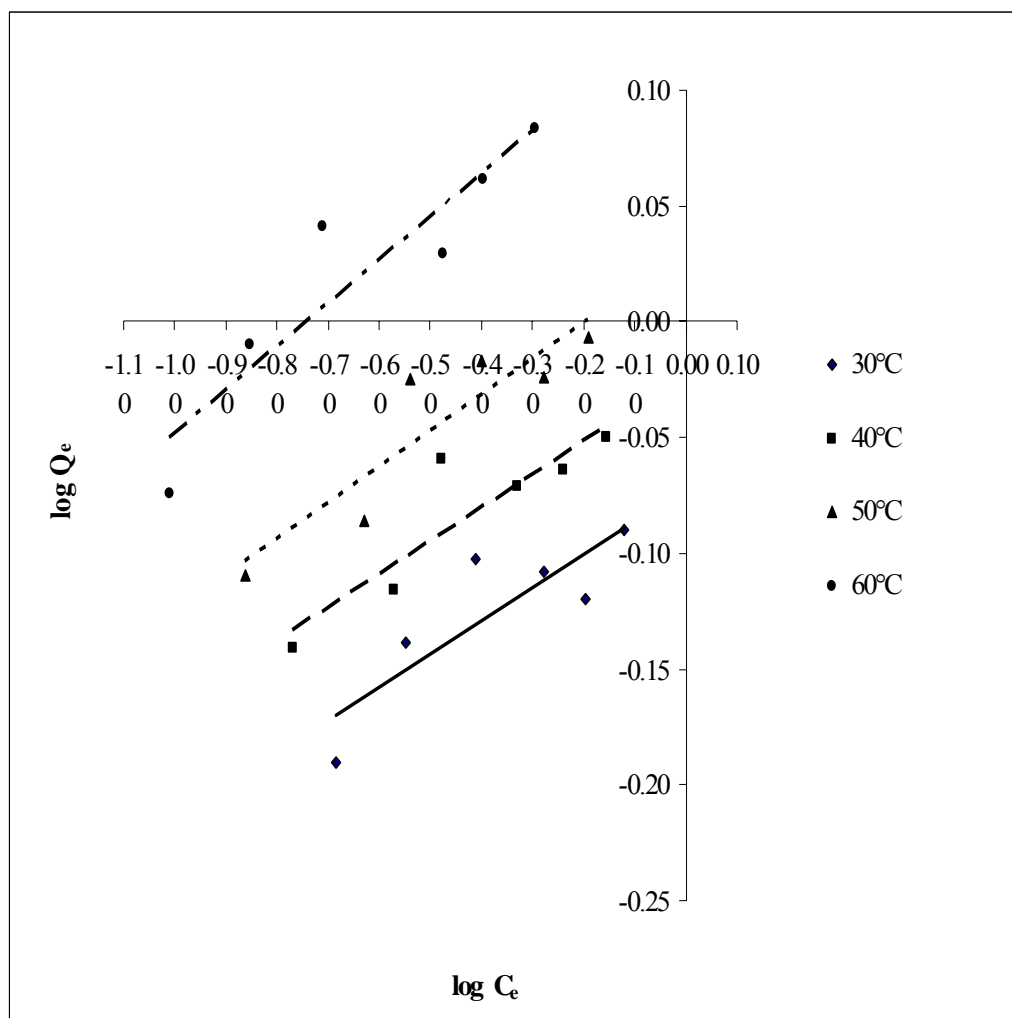


Figure 19 Freundlich adsorption isotherms for linear form of Crystal Violet on CAC (0.03 g) at different temperatures (a) 30 °C (b) 40 °C (c) 50 °C and (d) 60 °C, dye concentrations 250 – 500 mg L⁻¹ and pH = 5.

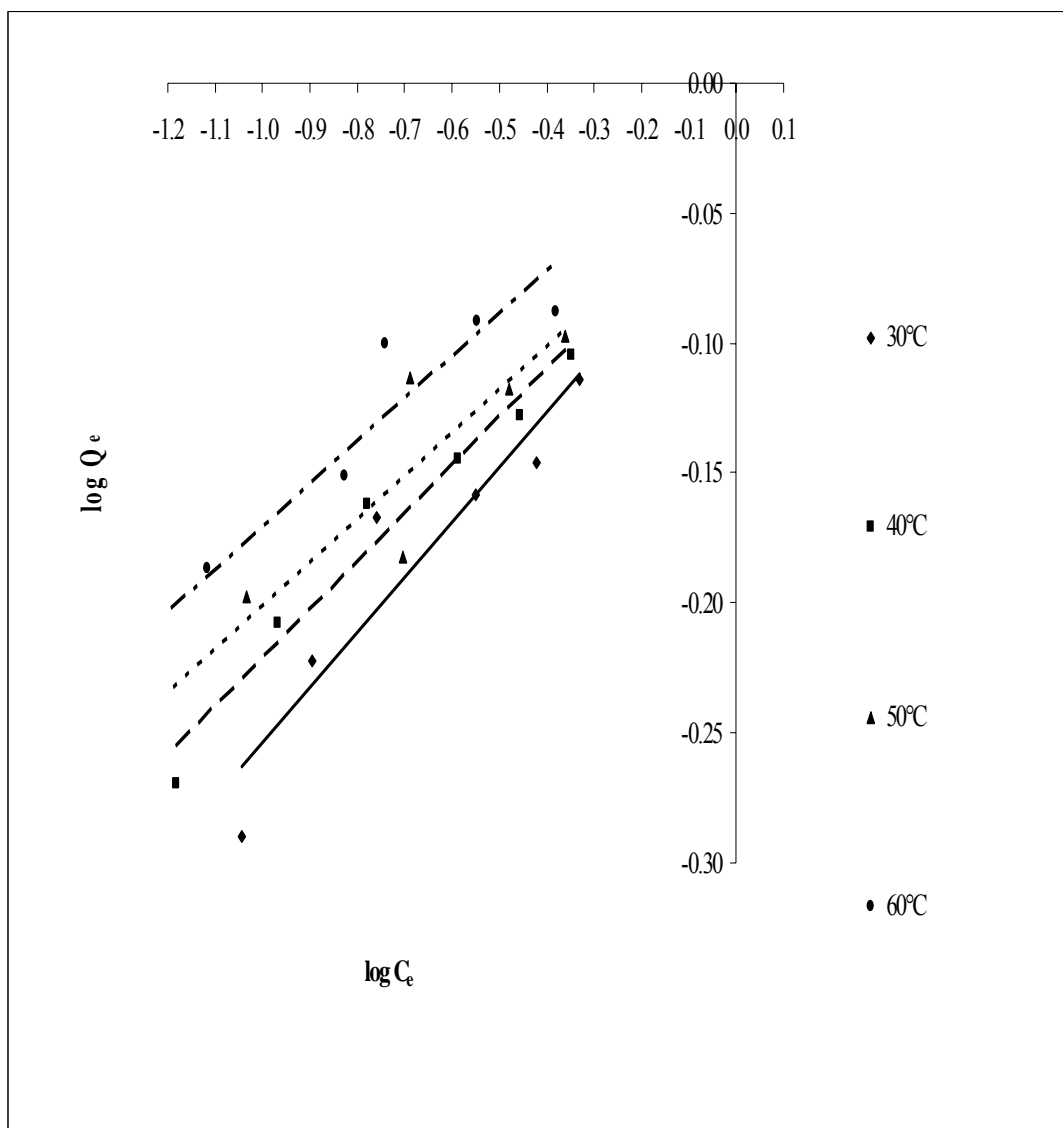


Figure 20 Freundlich adsorption isotherms for linear form of Crystal Violet on BAC (0.05 g) at different temperatures (a) 30 °C (b) 40 °C (c) 50 °C and (d) 60 °C, dye concentrations 250 – 500 mg L⁻¹ and pH = 5.

Adsorption isotherms

The adsorption data of Crystal Violet on CAC and BAC are fitted with Langmuir isotherm both in linear and non-linear forms as shown in Figure 15 – 16 and Figure 17 – 18, respectively, and the adsorption data of Crystal Violet on CAC and BAC are fitted with Freundlich isotherm in linear form as shown in Figure 19 and 20, respectively. In Figures 19 and 20 indicated the correlation coefficient (R^2) for Freundlich equation is not approaches 1. Thus, another alternative use the Langmuir equation to explain adsorption isotherm.

Adsorption characteristics between the CAC and BAC with Crystal Violet can be described by adsorption isotherms. In this work, the Langmuir isotherm has been used for studying the adsorption data. These isotherms relate the amounts of Crystal Violet per unit weight of adsorbents (Q_e , mmol g⁻¹) to the equilibrium concentration of Crystal Violet (C_e , mmol L⁻¹). The Langmuir parameter is obtained by using nonlinear regression by fitting the data directly to the equation (1), since algebraic transformation to linear forms (equation (2)) can negatively influence the estimated constants. The values of parameter of Langmuir equation for CAC and BAC are summarized in Table 5 and Table 6, respectively. Also, to compare the reliability of these adsorption isotherms, the correlation coefficient (R^2) for each adsorption isotherm has been calculated and shown together with Langmuir parameter. The correlation coefficient (R^2) is a good criteria and means that the difference between experimental data and theoretical values is small when the values of the coefficient approaches 1 (Bembnowska, et al., 2003). The values of R^2 form linear fitting are greater than the values form non-linear fitting so linear fitting is better than non-linear fitting.

It appears that the adsorption isotherm results of both activated carbons, CAC and BAC can CAC be well described by the Langmuir equation but BAC gave a slightly better fit than based on the values of the correlation coefficient (R^2) for the different isotherm plots. Because of this, it is apparent that most of adsorption behavior of Crystal Violet on CAC and BAC will be monolayer adsorption.

3.2.5 Thermodynamic considerations

From the previous study, some general conclusions can be deduced regarding the energetic changes occurring during the process. Therefore, the b parameter from Langmuir equation can be related to the enthalpy or heat of adsorption (ΔH_{ads}) as follows (Adamson and Gast, 1997)

$$b = b' e^{H_{ads}/RT} \quad (3)$$

Where b is equilibrium constant related to the heat of adsorption, R is the universal gas constant ($8.314 \text{ J K}^{-1}\text{mol}^{-1}$), T is the temperature in Kelvin and b' is pre-exponential factor constant. The heat of the adsorption (H_{ads}) process at monolayer coverage can be investigated from equation (3) if the isotherm of adsorption can be fitted with Langmuir model adequately. The heat of adsorption (H_{ads}) can be determined from slope of the observed linearity from the plot of $\ln b$ versus $1/T$ that leads to heat process involved in adsorption at monolayer coverage.

The correlation coefficient (R^2) for each heat of adsorption has been calculated with equation (3). However, the correlation coefficient (R^2) is not approaches 1. Thus, another alternative use the Clausius-Clapeyron equation (10) to explain heat of adsorption. Adsorption data obtained at different temperatures are used to estimate the isosteric heat of the process. The heat of adsorption was calculated by applying the Clausius-Clapeyron equation to the adsorption isotherm as follows (Alberty and Silbey, 1992 and Sirichote, et al., 2002)

$$\ln C_e = \frac{H_{ads}}{RT} + c \quad (10)$$

Where C_e is the equilibrium concentrations (mmol L^{-1}), H_{ads} is the isosteric heat of adsorption (kJ mol^{-1}), R is the universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), and c is the integration constant. Plot of $\ln C_e$ versus $1/T$ should give a straight line of slope $-(\Delta H_{ads}/R)$. The Clausius-Clapeyron plots of $\ln C_e$ versus $1/T$ of Crystal Violet on CAC and BAC are show in Figures 21 and 22, respectively. The values of R^2 from Clausius-Clapeyron equation are greater than the values from equation (3) fitting and approaches 1 so Clausius-Clapeyron equation is better than equation (3).

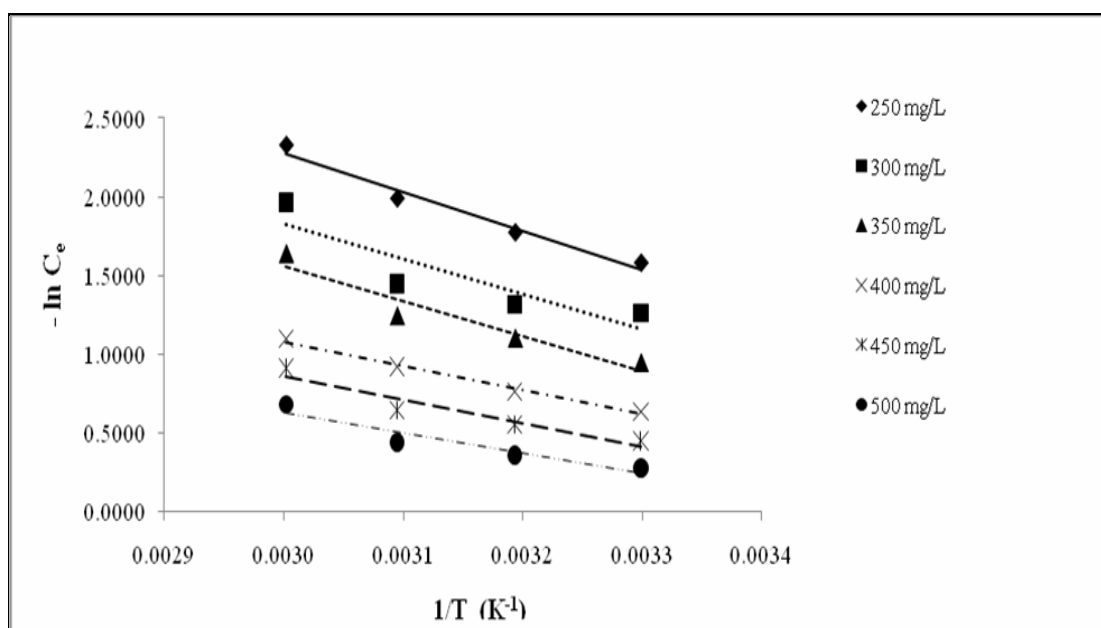


Figure 21 Clausius-Clapeyron plots for adsorption of Crystal Violet on CAC at 30 °C, 40 °C, 50 °C and 60 °C, dye concentrations 250 – 500 mg L⁻¹ and pH = 5.

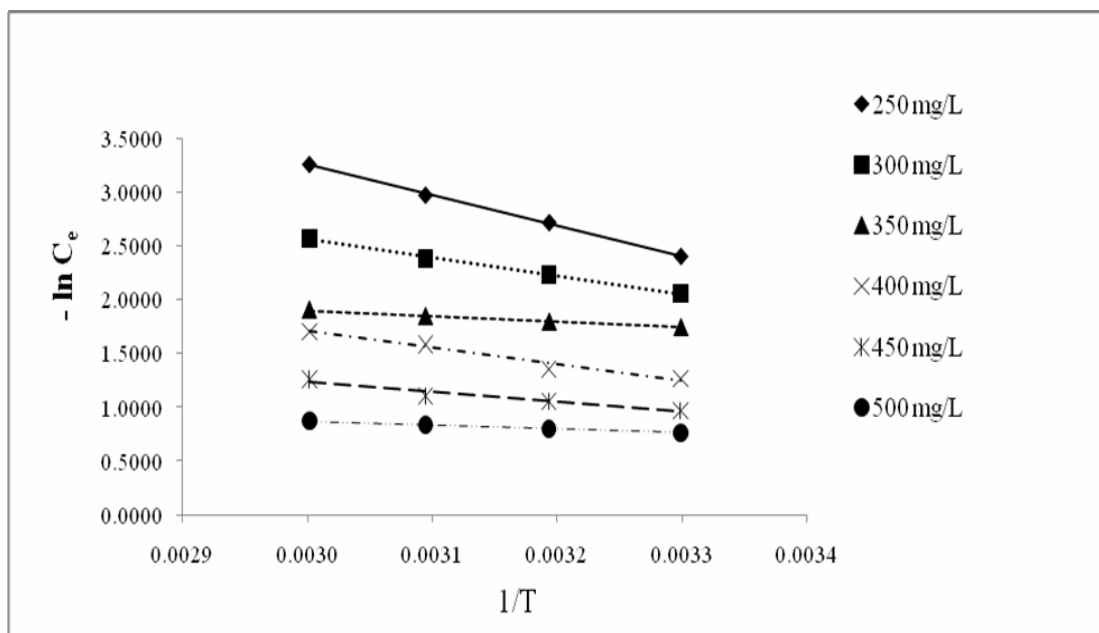


Figure 22 Clausius-Clapeyron plots for adsorption of Crystal Violet on BAC at 30 °C, 40 °C, 50 °C and 60 °C dye concentrations 250 – 500 mg L⁻¹ and pH = 5.

Table 9 The heat of adsorption (H_{ads}) of Crystal Violet adsorption on CAC and BAC at 30 °C, 40 °C, 50 °C and 60 °C dye concentrations 250 – 500 mg L⁻¹ and pH = 5.

AC C ₀ (mg L ⁻¹)	CAC		BAC	
	H _{ads} (kJ mol ⁻¹)	R ²	H _{ads} (kJ mol ⁻¹)	R ²
250	20.51	0.9732	23.76	0.9990
300	18.51	0.7903	14.12	0.9960
350	18.40	0.9192	4.40	0.9959
400	12.90	0.9895	12.94	0.9678
450	12.33	0.9121	7.70	0.9402
500	10.77	0.9057	3.06	0.9945

The positive values of the heat of adsorption (H_{ads}) from Table 9 show the endothermic nature of adsorption and H_{ads} is between 0 – 40 kJ mol⁻¹ indicating the possibility of physical adsorption (Bond, 1987). Moreover, while increasing the temperature of the system, the extent of dye adsorption increases, this rules out the possibility of chemisorption (Arivoli, et al., 2002).

CHAPTER 4

CONCLUSION

The commercial activated carbon (CAC) and activated carbon obtained from bagasse (BAC) were characterized for some physical properties and tested for their efficiencies in adsorption of Crystal Violet.

From SEM micrographs both CAC 140 – 170 and BAC 140 – 170 have porous texture which are full of holes with diameters ranging around 10 – 20 μm and 5 - 10 μm , respectively. These holes are defined as macropore of the activated carbon (>50 nm). Both micropore and mesopore are not resolved by our scanning microscopy. Thus, this research has used BJH model for determining pore size distribution. Result from BJH pore size distribution show CAC remarkably has more incremental pore volume of mesopore and macropore than BAC.

BET surface area of CAC and BAC are 1,308.83 and 786.24 $\text{m}^2 \text{g}^{-1}$, respectively which indicate that both activated carbons possess a well developed porous structure. Percentages of micropore fractions of BAC (73%) are more than the CAC (35%). Noticeably, CAC has more BET surface area than BAC but CAC show less micropore fraction. Therefore, the physical characteristics of raw materials seem to be important factor for porous nature of activated carbon.

FT-IR spectrum of CAC is very similar to spectrum of BAC. The strong band appears at about 3,400 cm^{-1} is mainly assigned to O-H stretching vibrations. The band observed at about 2,900 cm^{-1} which is ascribed to symmetric and asymmetric C-H stretching vibrations in aliphatic CH, CH₂ and CH₃ groups are detected. The band at about 1,600 cm^{-1} is C=C stretching vibration in aromatic ring. Many bands because of hydrogen, oxygen, and nitrogen functional groups are observed in the range 1,400 - 400 cm^{-1} which is not mentioned herein except the strong band at about 1,020 cm^{-1} can be attributed to C-O stretching vibrations.

Point of zero charge (pH_{pzc}) measurements of CAC and BAC are 3.5 and 4.5, respectively. So the surface of CAC and BAC are negative at $\text{pH} > \text{pH}_{\text{pzc}}$ (3.5) for CAC and $\text{pH} > \text{pH}_{\text{pzc}}$ (4.5) for BAC. When pH of solution increased with increasing

amount of adsorbed because the increase of solution pH values, the electrical repulsion force become weaker and the Crystal Violet may be transported to the surfaced of the activated carbons.

The percentage of adsorption increased with increasing weight of both activated carbons. Effect of weight of activated carbon is attributed to the increase of surface area and availability of more adsorption sites. The percent adsorption decreased with increasing initial dye concentration. The adsorptions equilibrium of CAC and BAC required 8 hours and 12 hours, respectively, for all concentrations. The percentage of adsorption increased with increasing the temperature. It confirms the endothermic nature of the process involved in the system. The maximum percentages of adsorption dye solution 250 mg L^{-1} are 84% and 94% for CAC 0.03 g and BAC 0.05 g, at 60°C and pH 5.

The experimental data are correlated reasonably well by the Langmuir adsorption isotherm in linear and non-linear forms. The values of correlation coefficients (R^2) from the linear fitting approach to one more than the values from non-linear fitting for all temperatures. Therefore, the maximum adsorption (Q_m) obtained from linear fitting are in the report. At 30, 40, 50 and 60°C the maximum adsorption (Q_m) for Crystal Violet on CAC 0.86, 0.95, 1.06 and 1.30 mmol g^{-1} , respectively. And for adsorption of Crystal Violet on BAC the maximum adsorption (Q_m) are 0.83, 0.84, 0.85 and 0.87 mmol g^{-1} , respectively. The R_L values are found to in the range between 0 and 1 which confirms that the ongoing adsorption process is much more favorable.

In thermodynamic consideration (effect of temperature), the Clausius-clapeyron equation was used to calculate the isosteric heat of adsorption of Crystal Violet because the values of correlation coefficients (R^2) from the Clausius-clapeyron equation fitting approach one better than the values from equation (3) for all temperatures. The values of heat adsorption (H_{ads}) of Crystal Violet 250, 300, 350, 400, 450, 500 mg L^{-1} on CAC are 20.51, 18.51, 18.40, 12.90, 12.33 and $10.77 \text{ kJ mol}^{-1}$, respectively. And the heat adsorptions (H_{ads}) of Crystal Violet on BAC are 23.76, 14.12, 4.40, 12.94, 7.70 and 3.06 kJ mol^{-1} , respectively. These H_{ads} is between 0 –

40 kJ mol⁻¹ confirm the adsorption processes to be endothermic and controlling the physical adsorption.

The efficiency of adsorption of Crystal Violet on BAC is about 80-90%. Therefore, the agricultural waste like BAC can replace the commercial activated carbon for removal of dyes from waste water.

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APPENDIX

Table A1 Data of adsorption isotherm of Crystal Violet on CAC (0.03 g), pH = 5

30 °C		40 °C	
C_e (mmol L ⁻¹)	Q_e (mmol g ⁻¹)	C_e (mmol L ⁻¹)	Q_e (mmol g ⁻¹)
0.2062	0.6448	0.1701	0.7228
0.2828	0.7262	0.2679	0.7653
0.3873	0.7895	0.3316	0.8716
0.5293	0.7796	0.4666	0.8486
0.6384	0.7589	0.5761	0.8627
0.7588	0.8133	0.6994	0.8911

50 °C		60 °C	
C_e (mmol L ⁻¹)	Q_e (mmol g ⁻¹)	C_e (mmol L ⁻¹)	Q_e (mmol g ⁻¹)
0.1371	0.7777	0.0978	0.8433
0.2349	0.8202	0.1403	0.9779
0.2881	0.9442	0.1945	1.1001
0.3986	0.9619	0.3338	1.0700
0.5261	0.9460	0.4018	1.1533
0.6431	0.9850	0.5070	1.2117

Table A2 Data of adsorption isotherm of Crystal Violet on BAC (0.05 g), pH = 5

30 °C		40 °C	
C_e (mmol L ⁻¹)	Q_e (mmol g ⁻¹)	C_e (mmol L ⁻¹)	Q_e (mmol g ⁻¹)
0.0903	0.5134	0.0659	0.5378
0.1276	0.5995	0.1074	0.6197
0.1743	0.6803	0.1658	0.6888
0.2817	0.6941	0.2583	0.7175
0.3795	0.7143	0.3486	0.7451
0.4655	0.7685	0.4486	0.7855

50 °C		60 °C	
C_e (mmol L ⁻¹)	Q_e (mmol g ⁻¹)	C_e (mmol L ⁻¹)	Q_e (mmol g ⁻¹)
0.0510	0.5527	0.0383	0.5655
0.0925	0.6346	0.0765	0.6505
0.1977	0.6569	0.1488	0.7058
0.2051	0.7706	0.1818	0.7940
0.3316	0.7621	0.2838	0.8099
0.4347	0.7993	0.4167	0.8174

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