REMOVAL OF TEXTILE DYES FROM AQUEOUS SOLUTIONS USING *LUFFA CYLINDRICA* OF KENYA ORIGIN: KINETIC AND EQUILIBRIUM SORPTION STUDIES

BY

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DECLARATION

This work is my original work and has not been submitted for examination for a degree in any other University

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Abstract

Luffa cylindrica, a lignocellulosic material that grows in tropical climates as found in Kenya, was bought from Gikomba, Kangemi, Kawangware markets and kiosks within parklands areas of Nairobi. A total of 287 pieces of *luffa cylindrica* was procured and found to be sufficient for this work. Both batch and continuous mode of operation were employed in this study. All the procured pieces were mixed and subjected to the same treatment.

In the batch mode the effects of contact time, initial dye concentration, adsorbate weight, solution media ionic strength, pH and treatment of *luffa cylindrica* with both nitric acid and hydrogen peroxide (as possible regeneration agents) were investigated. Luffa-derived activated carbon was prepared and investigated.

Twenty minutes contact time was found to be adequate producing up to 95.1% adsorption. The % adsorption of methylene blue dye onto the *luffa cylindrica* was found to increase with increase in the ratio of weight of luffa to initial dye concentration. Ionic strength of the solution did not have any effect on the % adsorption signifying a possible non-ionic type of interaction between the adsorbate and the adsorbent. A highly acidic condition (i.e. pH below 3.0) was found to be unfavourable for adsorption and higher % adsorptions only occurred in the initial mixture pH 3.9 – 11 range. The near-buffering effect of *luffa cylindrica* produced a final

solution pH that indicated % adsorption was optimal between pH 4.3-5.6 range. Nitric acid instantaneously regenerated the spent luffa without any deleterious effect while the hydrogen peroxide-regenerated spent luffa had a slightly reduced adsorption capacity (from 96.4% to 94.9%) and took a minimum of 8hours to regenerate under sonication.

Adsorption Isotherm studies showed that the uptake of methylene blue dye by *luffa cylindrica* occurred by monolayer sorption while Freundlich adsorption isotherm yielded values for adsorption intensity, n, greater than 1, indicating favourable adsorption.

The continuous flow mode of operation showed the practical utility of *luffa cylindrica* in the removal of methylene blue dye from aqueous solution. Breakthrough studies indicated that breakthrough point was attained with less dye solution volume when a higher concentration dye solution was used in a fixed weight of *luffa cylindrica* and takes more dye solution for increased weight of *luffa cylindrica*. For instance, with a 1.695 a.u. methylene blue dye solution, 10g of luffa material involved use of 34,000ml of the dye solution to reach the breakthrough point. Alternatively for 1.595 a.u. methylene blue dye solution, a total volume of 130,000ml of the dye solution was required with 40g luffa to reach the breakthrough point signifying a 3.8% increase in solution volume.

Luffa cylindrica was applied to a real textile dye effluent (direct red dye) with quite good results. 4.5g of *luffa cylindrica* removed 58.2% of the dye

while 6g removed 77.9%, confirming that *luffa cylindrica*, in its natural form, has the potential to be used in stripping textile dye off effluents before discharge into water bodies.

Luffa-derived activated carbon resulted in 77.5% weight loss and therefore it was found unnecessary to produce activated carbon from *luffa cylindrica* considering its already proven effectiveness in the removal of methylene blue dye in its raw form.

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CHAPTER ONE

1.0 Introduction

Water is one of the essentials for all forms of life (Vanloon and Duffy, 2002). All living things need it in order to grow and prosper. It is also an important part of the atmosphere in that its physical and chemical properties are a major factor in controlling climate (Vanloon and Dufy, 2002). The hydrosphere occupies 73% of the earth's surface. About one third of the world's population does not have access to safe drinking water despite there being so much water on earth, (Jerome, 1986). Of the total water supply on earth, only about 3% is fresh, most of which is stored as ice at the poles or so deep under the earth that it is too expensive to get (Krantz and Kifferstein, 2001)

The rapid population explosions and per capita water usage, averaging 1,374m^3 in North America to 181m^3 in Africa in the past century demands efficient allocation of water resources among competing uses such as cooking, washing, irrigation, carrying waste, and cooling machines, among other uses. These water demands pose an increasing challenge for many societies, often resulting in conflicts. Some estimates show that almost all the economically accessible water in the world will be required to meet the needs of agriculture,

household and industry by 2025 when the world population is projected to reach 8 billion (Hunter *et al*, 1998).

These competing areas of water usage especially urban domestics, agriculture and industry release pollutants that degrade the water quality. Some of the pollutants released into water bodies may be lethal even in small quantities. An estimated one half of the people living in the developing countries suffer from diseases and infections related directly to water or indirectly to disease-causing/carrying organisms and/or substances that breed in water or released in water due to anthropogenic activities. Water shortage and pollution cause untold misery due to widespread public health problems, limited agriculture and economic development beside harm to the ecosystem (Hunter *et al,* 1998)

According to the World Commission on water for the 21st century, industrial, agricultural and municipal wastes foul both surface and ground water in many places. More than half of the world's major rivers are so depleted and polluted that they endanger human health and poison surrounding ecosystems (IPS, 1959). Heavy metals, organics or biological wastes constitute some of the pollutants that are released into water bodies. Some of these are released into the environment from uncontrolled emissions by industrial activities; unsafe disposal of industrial wastes, paint and gasoline wastes and

spills, sewage disposal, food wastes, and agricultural wastes among others.

Almost every sector of any economy requires dyes and colours in one form or the other: motor industry, roads, food industry, cosmetic, building, textile industry and others.

For world economies to meet the needs of the population to clad, they establish textile industries. Textile industry is charged with the responsibility of providing attire to the general population. In order to meet this important service, the industry strives to provide attire that is not only protective but also attractive to the eye. Thus dyes are used to colour the textiles and make them attractive to the user. Inevitably, textile industries release wastewater, which contains dyes among other pollutants.

Besides being made generally from organic compounds such as naphthalene reacted with an alkali or an acid along with an intermediate and a solvent to form dye mixtures (some of which may be highly toxic and persistent), some dyes also require metal additives including heavy metals as mordants. Therefore, textile industry effluents are inevitably harmful due to the toxicity of the chemicals from which the dyes are made.

Most dyes are too refractory to undergo degradation in the required time and also interfere with the transparency of water to visible light. Substantial dyes display a poor affinity for oxidation and pass into wastewater in large amounts. They are removed with difficulty due to their high level of solubility.

Among the various pollutants that may be contained in industrial wastewaters, colour is considered to be a big nuisance from the aesthetic point of view and is at times termed a 'visible pollutant'. Most industries use colouring matter to colour their products. Unspent colouring materials are usually discharged, with or without treatment into the aquatic environment. Dyes, being some of the most important recalcitrant materials, persist for long distances in flowing water. They retard photosynthetic activity, inhibit the growth of aquatic biota by blocking out sunlight and they may utilise dissolved oxygen and thus decrease the recreational value of streams.

Colour in wastewater is a characteristic which is easily detected. Presence of even minute amount of colouring substance make water unsuitable for drinking or other recreational purposes due to its undesirable appearance. Some dyes are stable and do not suffer biodegradation and those containing heavy metals are toxic. Consequently, it is important to remove these pollutants from the wastewaters before discharge.

Dye wastewaters discharged from textile and dyestuff industries, or any other source have to be treated due to their impact on water bodies and the growing public concern over their toxicity, in particular, carcinogenicity. Dyes usually have synthetic origins and complex aromatic molecular structures (Banat *et al,* 1996). The many different and complicated molecular structures make dye wastewaters difficult to be treated by conventional biological and physico-chemical processes. Therefore, innovative and affordable treatment technologies need to be developed.

Removal of colour from dye-bearing wastewaters is one of the major environmental challenges because of the costs and difficulty in treating such wastewaters by conventional treatment methods as most of the dyes are stable to light and oxidizing agents (Banat *et al,* 1996).

There is no general method for the removal of colour from dye wastewater. Methods of primary clarification, including sedimentation and flotation are not effective for the removal of colour without simultaneous chemical treatment. Processes such as membrane separation, coagulation and ion exchange are some of the methods used for the removal of colour from dye wastewaters but the cost of these processes is the main drawback of the techniques (Mishra and Tripathy, 1993).

Photocatalytic oxidation and ozone treatment are the other alternative technologies commonly employed. However, these treatment methods are effective and economical only in the case where the solute concentrations are relatively high. Activated carbon is the most effective alternative for the removal of lower concentration of dye ions. However, activated carbon adsorption is limited due to its high cost and the costs involved in its regeneration. Therefore, although activated carbon is the most commonly and conventionally used adsorbent with very high efficiency, its price is a draw-back and therefore the need to discover other cheaper alternatives remain paramount (McKay and Al-Duri, 1990).

The use of biomaterials for the removal of colour from aqueous solution provides a potential alternative to the conventional treatment techniques. Bio-sorption, which exploits the ability of plant biomass to sequester solute particles from aqueous solution by physicochemical mechanisms, is the selective uptake of dye ions (solute) by microbial cells (Gupta *et al,* 2003). Recent investigations by several researchers have proved that algae, whether dead or alive are some of the effective bio-sorbents for treating wastewaters (Hashim and Chu, 2003; Ho *et al,* 2002; Kaewsarn, 2002).

Adsorption has become one of the most effective methods of decolourisation of textile wastewater (McKay, 1980; Yeh *et al,* 1993;

McKay and Al-Duri, 1990). Other materials such as activated clay, wood and different types of cellulose-based materials have also been recently investigated, (Kumar *et al,* 2004) However, one important point to be considered when choosing an adsorbent is the possibility of easy regeneration, (Yeh *et al,* 1993; Nassar and Geundi, 1990; Yeh and Thomas, 1995a).

In the present investigation, the ability of *Luffa Cylindrica,* (a plant that grows in diverse climatic conditions of most parts of Kenya) to adsorb a basic dye of methylene blue and other dyes from aqueous solution, is reported. Methylene blue was selected as a model dye compound. Investigations were done with fresh *luffa cylindrica* as well as regenerated-spent *luffa cylindrica*.

1.1 Justification

The demand for water to meet the various needs is increasing to the point where there have been instances of conflict reported. Agriculture, municipal and industrial wastes foul the water to the extent of endangering human health. Anthropogenic activities use water as the sink for waste and textile industry is no exemption. The textile industry is charged with the responsibility of providing attire to clad and therefore the textiles must not only cover and protect but must also be attractive to the eye. Considering the important role of

the textile industry, it is prudent to ensure it does not foul the water bodies so that the effluents released from the industries do not interfere with the aesthetics of the waters, aquatic life and can be used to meet some of the many other needs for water. Abundant clean water will contribute to happy, healthy and harmonious communities.

1.2 Statement of the Problem

Technology to remove textile dyes has been developed and adopted in developed countries. The technology can also work in developing countries but the costs of such technology is prohibitive, thus the need to develop indigenous technology that is affordable, efficient and acceptable. Since the material (*luffa cylindrica*) is grown locally and preliminary work shows it may have some potential, there is need to investigate its properties and its potential for use in the textile effluent purification particularly for the removal of textile dyes before the effluent is discharged into water bodies.

1.3.0 Objective of the study

The overall objective of the work was to establish the efficacy of *luffa cylindrica* in its natural form as an affordable and locally available material to treat waste water containing textile dyes.

1.3.1 Specific objectives

The specific objectives of the work were to:

a) Determine effect of contact time, initial dye concentration, weight of *luffa cylindrica,* ionic strength, and pH on % adsorption of methylene blue dye (as a representative textile dye) in a batch mode of operation,

b) Determine the effect of treating *luffa cylindrica* with nitric acid and Hydrogen Peroxide and their effect as agents for regeneration of spent *luffa cylindrica*,

c) Determine the breakthrough curves of methylene blue dye on *luffa cylindrica* in a continuous flow method and apply the *luffa cylindrica* to real textile dye industrial effluent,

d) Fit the experimental results obtained in the batch mode to Langmuir and Freundlich adsorption isotherm models for the purpose of understanding the adsorption mechanism and the degree of adsorption.

CHAPTER TWO

2.0 Literature Review

2.1 Dyes

Dyes are large and important groups of industrial chemicals for which world production in 1978 was estimated at 640,000 tons (Kumar *et al,* 2004). Most of this quantity was used in the textile industry. Dyes in use include many different compounds whose environmental behaviour is largely unknown (Kumar, *et al,* 2004). Most dyes and pigments are considered either inert or non-toxic, although some are not totally innocuous (Kumar *et al,* 2004). Interest in the environmental behaviour of dyes is prompted primarily by concern over their possible toxicity and carcinogenicity, heightened by the fact that many dyes formerly were made of known carcinogens such as benzidine, which may be reformed as a result of metabolism (Clarke and Anliker, 1980; Baughman and Perenich, 1988). Disperse dyes have been shown to have high partition coefficients and solubility, suggesting significant potential for bioconcentration (Anliker, *et al,* 1981).

Most dyestuffs are designed to be resistant to environmental conditions like light, effects of pH and microbial attack (Pagga and Taeger, 1994). Some dyes are considered toxic to the aquatic biota

and carcinogenic to humans and some chemical groups present in the dye molecule may form carcinogenic degradation products (Chung and Cerniglia 1992; Shenai 1995). Therefore, removal of dye from process or waste effluents becomes environmentally important.

2.2 Methods of Colour Removal from Wastewaters

The most commonly used method for the removal of colour from dye stuffs are chemical precipitation and biological oxidation (Mall and Upadhyay, 1998; Donmez, *et al,* 1999; and Fernadez, 1995). Photo-catalytic oxidation and ozone treatment are the other alternative technologies commonly employed. However, as cited earlier, these treatment methods are effective and economical only in the case where the solute concentrations are relatively high. A potential alternative to the conventional treatment techniques is the use of biomaterials for the removal of colour from its aqueous solution. Bio-sorption is the selective uptake of dye ions (solute) by microbial cells. It exploits the ability of plant biomass to sequester solute particles from aqueous solution by physicochemical mechanisms (Gupta, *et al,* 2003)

In most situations, the use of a combination of different methods of treatment is necessary in order to remove all the contaminants present in a particular wastewater. Combined methods, such as activated sludge-coagulation, activated sludge-adsorption and

coagulation-chemical oxidation, are being used by many industries (Lin and Chen, 1997). Textile dyes are slowly degraded and some authors have reported that colour removal is due to adsorption on micro-organisms (Pagga and Brown, 1986; Grau, 1991).

Biological processes are commonly cited for the treatment of coloured effluents alone (Bell and Buckley, 2003; Fu, *et al,* 2001), or in combination with sorption processes (Walker and Weatherley, 1999). Some other processes such as photochemical (Arslan and Balcioglu, 2001; Genç, 2004) and catalytic degradation processes also exist. These oxidation processes may cause pollution hazards since in some cases the products generated during the oxidation are more hazardous to the environment than the original contaminants.

Membrane processes using nano-filtration techniques have received great attention (Chabot *et al,* 1999; Diaper *et al,* 1996; Koyuncu, *et al,* 2004). However, processes such as coagulation and flocculation are shown to be simpler and more cost-effective (Choi, *et al,* 2001; Chu, 2001; Kacha, *et al,* 2003; Kim, *et al*, 2004; Metes, *et al,* 2000; Zemaitaitiene, *et al,* 2003). The use of some conventional materials for coagulation and flocculation is frequently discussed due to changes in environmental regulations (Divakaran and Pillai, 2001; Ozacar and Sengil, 2003). For example, the use of inorganic salts (frequently used as coagulants) such as aluminium chloride or sulphate is now

controversial due to the possible impact of aluminium on Alzheimer disease. Polyacrylamide is the basis of many flocculants and its discharge in the environment is now considered hazardous due to the possible release of monomers that could enter the food chain, with potential negative impact on health (carcinogenic effect).

For these reasons, recent research has focused on the use of bio-coagulants and bio-flocculants (Chen, *et al,* 2003; Strand, *et al*, 2003; Tripathy, *et al,* 2001). Among these natural products, chitosan, a polymer of glucosamine and acetylglucosamine units, has received a great deal of attention over the past 20 years for many applications in wastewater treatment, including sorption of metal ions (Guibal, 2004), dyes (Gibbs, *et al,* 2003; McCarrick, *et al,* 2003), besides coagulation and flocculation (Ashmore and Hearn, 2000; Bratskaya, *et al,* 2002; Divakaran and Pillai, 2002; Huang, *et al,* 2000, Roussy, *et al,* 2004, Strand, *et al*, 2002).

The economical decolourization of effluents by removal of dyes remains an important problem, although recently a number of successful systems using adsorption techniques have been developed. Activated carbon has been successfully used as an adsorbent for removal of dyes from wastewater. The performance of an activated carbon treatment process depends on the type of carbon and the characteristics of the wastewater in addition to the operating

conditions. Activated carbon has been found to be an effective alternate for the removal of even low concentration of dyes in solution. Due to the high cost and the cost involved in regenerating it, activated carbon adsorption is limited in usage. Granular activated carbon (Mishra and Tripathy, 1993) is suitable for the removal of colour and other organic compounds in effluents, and it is efficient when used in adsorption columns. However, granular char is an expensive material and regeneration results in a 10 to 15% loss of adsorbent (McKay, *et al,* 1980).

Mixtures of fly-ash and coal in different proportions have shown a high adsorption capacity for cationic dyes (DeJohn and Hutchins, 1976). By increasing the amount of coal in the mixture, the adsorption capacity is increased because of the high surface area available for adsorption.

Previous studies have shown that high-ash char can be produced by pyrolysis at temperatures in the range of 600 to 800°C and the proportion of transitional pores increases for the solid prepared at 600°C (Moreira, *et al,* 1998).

Adsorption is the process which is most frequently employed for the treatment of coloured effluents, using for example activated carbon (McKay, 1983; Walker and Weatherley, 1999; Wu, *et al,* 2001a; Yang

and Al-Duri, 2001), resins (Karcher, *et al*, 2002), agricultural wastes (Annadurai, *et al,* 2002; Morais, *et al*, 2000; Robinson, *et al,* 2002), micro-organisms (Fu and Viraraghavan, 2003) and biopolymers (Chiou and Li, 2002; McCarrick, *et al,* 2003; Wu, *et al,* 2001b). However, these processes usually comprise a simple transfer of pollutant from a dispersed phase to a concentrated phase. The use of expensive materials and the necessity to control the discharge of these loaded materials sometimes makes the process non-cost effective.

2.3 Adsorption

Adsorption is the process through which a substance, originally present in one phase, is removed from that phase by accumulation at the interface between that phase and a separate (solid) phase. In principle, adsorption can occur at any solid-fluid interface. Examples include:

- gas-solid interface (as in the adsorption of a Volatile Organic Compounds on activated carbon);
- liquid-solid interface (as in the adsorption of an organic pollutant on activated carbon).

Adsorbate or solute is the material being adsorbed while adsorbent is the solid material being used as the adsorbing phase. The driving

force for adsorption is the reduction in interfacial (surface) tension between the fluid and the solid adsorbent as a result of the adsorption of the adsorbate on the surface of the solid. The surface or interfacial tension is the change in free energy resulting when the area between two phases is increased.

Absorption is the process through which a substance, originally present in one phase, is removed from that phase by dissolution in another (typically a liquid), as opposed to the accumulation at the interface as in the case of adsorption.

Several reasons provide a motivation for the use of adsorption processes in wastewater treatment: the main reasons being that many industrial wastewaters contain substances that:

- are difficult to remove via conventional secondary treatment
- are toxic or hazardous
- are volatile and should not be transferred to the atmosphere
- have the potential for creating noxious vapours or odours, or for imparting colour to the wastewater and
- are present in very small concentrations that make their removal via other methods difficult or too expensive

2.3.1 Adsorption as a Physical Process

In any adsorption process, the material being adsorbed (e.g., a pollutant) is simply but effectively removed from one phase (e.g., a wastewater) and transferred to another phase. This means that adsorption is a physical separation process in which the adsorbed material is not chemically altered. Since the chemical characteristics of the adsorbed material are not changed the use of adsorption in wastewater treatment is associated with the removal of hazardous material(s) from the wastewater and its transfer to the adsorbent. This implies that the adsorbent now contains the hazardous material. Therefore, appropriate actions must then be taken to treat the spent adsorbent at the end of the adsorption cycle. The adsorbent can be:

- regenerated (i.e., the hazardous material may be removed via stripping)
- disposed of (together with the pollutants it contains) in a landfill
- destroyed (together with the pollutants it contains) in an incinerator

Adsorption is typically used in wastewater treatment to remove toxic or recalcitrant organic pollutants and to a lesser extent, inorganic contaminants from the wastewater. Adsorption finds applications in tertiary wastewater treatment as a polishing step before final

discharge. It is also commonly used in the treatment of industrial wastewaters containing organic compounds not easily biodegraded during secondary (biological) treatment or are too toxic to be safely handled by any other method.

Common Adsorbents include:-

1 Activated carbon - a char-like material with high surface area.

2 Silica gel - hard, granular, porous material made by precipitation from sodium silicate solutions treated with an acid.

3 Activated alumina - aluminium oxide activated at high temperature and used primarily for moisture adsorption.

4 Aluminosilicates (molecular sieves) – porous synthetic zeolites used primarily in separation processes.

2.3.2 Activated Carbon as an Adsorbent

Activated carbon is by far the most common adsorbent used in wastewater treatment. During adsorption, the pollutant is removed by accumulation at the interface between the activated carbon (absorbent) and the wastewater (liquid phase). The adsorbing capacity of activated carbon is always associated with very high surface area per unit volume. The high surface area per unit volume

characteristic of activated carbon is obtained through a two-step process used in carbon manufacturing:

- Pyrolysis of raw material (typically a high carbon source such as coal, wood, nut shells) to drive off (distil) the lighter fraction producing a charred, highly carbonaceous solid residue;
- Activation of the charred residue by oxidation with air or steam to form a network of pores and passages with high surface area.

2.4 Adsorption Equilibrium

Upon contacting an amount of an adsorbent with a wastewater containing an adsorbable substance, adsorption takes place. Adsorption will continue until equilibrium is established between the substance in solution and the same substance in the adsorbed state. At equilibrium, a relationship exists between the concentration of the species in solution and the "concentration" of the same species in the adsorbed state (i.e., the mount of species adsorbed per unit mass of adsorbent).

2.4.1 Langmuir and Freundlich Equations

Two important physicochemical aspects for the evaluation of the adsorption process as a unit operation are (i) the equilibria and (ii) kinetics process. Equilibrium studies give the capacity of the adsorbent (Ho, 1995). The equilibrium relationships between

adsorbent and adsorbate are described by adsorption isotherms, the ratio between the quantity adsorbed and that remaining in solution at a fixed temperature at equilibrium. The two most used types of adsorption isotherms are: Langmuir adsorption isotherms and Freundlich adsorption isotherms.

Irving Langmuir, an American chemist who was awarded the Nobel Prize for chemistry in 1932 for "his discoveries and researches in the realm of surface chemistry", developed a relationship between the amount of gas adsorbed on a surface and the pressure of that gas. Such equations are now referred to as Langmuir adsorption isotherms; theoretical adsorption isotherms in the ideal case. The Langmuir adsorption isotherm is often used for adsorption of a solute from a liquid solution. The Langmuir adsorption isotherm is perhaps the best known of all isotherms describing adsorption and is often expressed as:

$$q_e = \frac{q_{max} b C_{eq}}{1 + b C_{eq}} \quad \text{..... Equation 1}$$

Where:

q_e is the adsorption density at the equilibrium solute concentration C_{eq} (mg of adsorbate per gram of adsorbent or the sorption capacity at equilibrium); C_{eq} is the concentration of adsorbate in solution (mgL^{-1})

at equilibrium; q_{max} is the maximum adsorption capacity corresponding to complete monolayer coverage (milligram of solute adsorbed per gram of adsorbent) or maximum amount of sorbent at equilibrium; and b is the Langmuir constant related to energy of adsorption or the affinity constant and is also a temperature dependent constant. Equation 1 above can be rearranged to the following linear form:

$$\frac{C_{eq}}{q_e} = \frac{1}{q_{max} b} + \frac{C_{eq}}{q_{max}} \quad \text{..... Equation 2}$$

The linear form can be used for linearization of experimental data by plotting $\frac{C_{eq}}{q_e}$ against C_{eq}. The Langmuir constants q_{max} and b can be evaluated from the slope (gradient) and intercept of linear equation where the gradient is $\frac{1}{q_{max}}$ and the y-intercept is $\frac{1}{q_{max} b}$.

Herbert Max Finley Freundlich, a German physical chemist, presented an empirical adsorption isotherm for non-ideal systems in 1906. The Freundlich isotherm is the earliest known relationship describing the adsorption equation and is often expressed as: (Ho *et al*, 2001)

$Q_e = K_f C_e^{1/n}$ .....Equation 3

where:

Q_e is the adsorption density (milligram of adsorbate per gram of adsorbent); C_e is the equilibrium concentration of adsorbate in solution (mgL^{-1}); K_f and n are the empirical constants dependent on several environmental factors and n is greater than one. This equation is conveniently used in the linear form shown below:

$\ln(Q_e) = \ln(K_{f)} + \frac{1}{n}\ln(C_e)$ ..... Equation 4

Here, a plot of $\ln(Q_e)$ against $\ln(C_e)$) yielding a straight line indicates conformity with the Freundlich isotherm of adsorption. The constants $\frac{1}{n}$ and $\ln(K_f)$ can be determined from the slope and the intercept respectively.

The Langmuir model assumes that the uptake of the adsorbate molecules occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed molecules. However, the Freundlich model assumes that the uptake of adsorbate molecules occur on a heterogeneous surface by monolayer adsorption isotherm.

2.5 *Luffa Cylindrica*

Luffa is the genus name of a group of gourds also known as vegetable sponges, dishcloth gourds, running okra, strainer vine, Chinese okra, California okra, and loofah. Two species commonly grown in many

parts of the world are the angled luffa called *Luffa acutangula*, and the smooth-fruited version called *Luffa cylindrica* (*Stephens, 2003*). *Luffa cylindrica* is a warm season, cold sensitive genus originating from India. It grows throughout the tropics. Luffa should be grown during the warm season (*Stephens, 2003*).

2.5.1 Description of *Luffa Cylindrica*

Luffa cylindrica has value as a food item, but is seldom eaten in other parts of the world other than Asia. It has vigorous, climbing, annual vines with several lobed cucumber-like leaves as seen in plate 1. Most gardeners grow it for its fibrous interior as shown in plate 2, which is useful as a rough cloth or sponge for cleaning and scouring. When crushed, the leaves give off a rank odour. Both male and female flowers occur on the same plant with a much greater number of male flowers. The rather large male flowers are bright yellow and occur in clusters. The female flowers are solitary and have the tiny slender ovary attached. Angled luffa flowers appear later in the day than the smooth type and stay open through the night.

Bees pollinate the flowers. Leaves are covered with short stiff hairs. Smooth luffa fruits are shaped like cucumbers but are larger, 30-60cm in length and 10-12.5cm in thickness. The exterior is green, sometimes mottled, and smooth with longitudinal lines. Fruits of the

angled luffa are characterized by sharp, elevated ridges running the length of the pods. The interiors of both are cucumber-like when immature, but quickly develop a Gourd (Stephens, 2003).

Plate 1: *Luffa cylindrica* plant

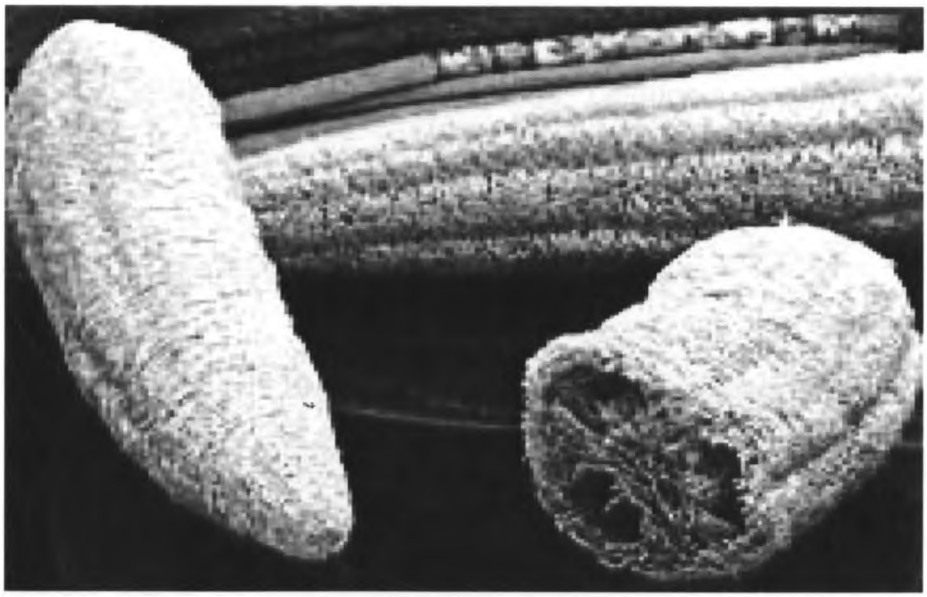

Plate 2: Mature dried fruit of luffa

This vegetable is a climbing, somewhat hairy or nearly smooth vine, reaching a length of 10 meters or more. The stems are 4-angled. The leaves are rounded-ovate to kidney-shaped, 10 to 20 centimetres across, shallowly 5 or 7 –angled or lobed, denticulate scabrous, pointed-tipped, and deeply heart shaped at the base. The male flowers occur singly in the axils of the leaves on long-peduncled racemes, and are crowded at the near apex of the peduncle. The calyx is green and the lobes are ovate-lanceolate, being about 1 centimetre long. The corolla is rotate, yellow, and 5 to 7 centimetres in diameter. The female flowers are solitary and peduncled. The fruit is oblong, cylindrical, green 12 to 30 centimetres long, and smooth. The seeds are black, about 1 centimetre long, very narrowly winged, and smooth or very sparingly tubercled.

Luffa is a spongy fibre which contains cellulose, xylan, mannan, galactan, and lignin. The seeds contain fixed oil about 46%.

2.5.2 Uses of *Luffa Cylindrica*

Small (less than 15cm long) young luffa gourds are used as a vegetable either prepared like squash or eaten raw like cucumbers. Some varieties, especially smooth type, are sweeter than others. Bitter types should not be eaten as some poisonous properties have been reported (Stephens, 2003). However, best sponges come from mature-green

fruits (plate 1), although dry fruits may be used (plate 2). The fruits should be soaked for several days and then peeled. Once cleaned, the sponges should be bleached and then dried in the sun. Sponges have been used for cleaning, filtering, and bathing among other uses (Stephens, 2003).

CHAPTER THREE

3.0 Materials and Methods

3.1 Materials and Reagents

The *luffa cylindrica* used in this research work was sourced from Gikomba, Kangemi and Kawangware markets of Nairobi together with various kiosks in Parklands area of Nairobi. All the 287 pieces of *luffa cylindrica* obtained were mixed together. The amount (3-4Kg) sourced was estimated to be enough for the envisaged set of experiments.

The 287 pieces of *luffa cylindrica* obtained were dried in an oven at a temperature of 80°C for eighteen hours. Higher temperature was found to char the material and was therefore avoided. The dried luffa was then ground using a grinder to finer pieces that were non homogeneous and of undetermined sizes. The ground luffa was then placed in a bucket and washed twice with cold distilled water followed with hot distilled water and then finally soaked for 24 hours in distilled water. The following day it was washed four times with distilled water, twice with hot distilled water until the water remained clear. In all, the material was washed eight times until all the elutriate water remained clear. All the material was washed together to ensure uniformity in the treatment.

The washed luffa was all dried in an oven for a period of 48 hours at 60°C with occasional turning after every two hours. Drying at 100°C and turning the material every five minutes quickened the process but risked the material being charred.

All the reagents used in this research were analytical grade. The methylene blue dye solution used was a stock solution of 0.01M concentration which was diluted to various concentrations required using the expression $C_1V_1=C_2V_2$; where:-

C_1= Initial concentration

V_1= Initial volume

C_2= Final desired concentration

V_2= Final desired volume

The hydrochloric acid (HCl) used was 12M concentrated acid which was diluted as required. Hydrogen peroxide was 30% v/v used without any dilution.

Potassium chloride pellets used were analytical grade of 74.55% purity. Appropriate weight was weighed and dissolved in distilled water to make a 0.1M stock solution from which other desired dilutions were made.

3.2 Apparatus

The apparatus used in this work included the following:

1) Mettler balance with an accuracy of 0.0001g and maximum capacity of 160g - used to weigh the samples.

2) SP8-1S Turner, UV-VIS spectrophotometer of a wavelength range of 330-900nm equipped with 10mm path length sample cell - used to determine the absorbance of the test solution.

3) An Accumet Silver-Silver Combination electrode (model 15, Fisher Scientific) - used for pH measurements.

4) Maximix Type 65800 Thermolyne Orbital Shaker – used for agitating the solution mixtures consistently over the period of equilibration time

5) A sonicator bath Model 8891, Cole Parmer - used in the regeneration of spent *luffa cylindrica* using hydrogen peroxide as the solvent.

6) Erlenmeyer flasks

7) Conical flasks

8) Volumetric flasks

9) Pipettes

3.3 Experimental Section

3.3.1 Determination of Wavelength of Maximum Absorbance (λ_{max}) for Methylene Blue Dye

A $2.5x10^{-5}$M solution of methylene blue dye was prepared from the 0.01M stock solution. A sample of the dye solution was placed in a cuvette and placed in the UV- Vis Spectrophotometer that had been set to the absorbance mode.

Starting from the lower wavelength of the Spectrophotometer (330nm), the wavelength was adjusted at 10nm unit intervals and the wavelength together with the corresponding absorbance was recorded over the entire wavelength range of the spectrophotometer. Within the range where absorbance showed maxima, finer adjustments of the wavelength setting were done to obtain the exact wavelength at which the absorbance was at the maximum. The spectrophotometer was then set to this wavelength value for all the absorbance measurements thereafter (Appendix 1).

3.3.2 Determination of the Effect of Contact (Equilibrium) Time on Adsorption

1.0g of *luffa cylindrica* was weighed and placed into a conical flask. 50ml of $2.5x10^{-5}$M methylene blue dye was used to soak the 1g *luffa cylindrica* with constant agitation. Aliquot samples of the solution were

removed at every five minute time intervals and their corresponding absorbance measurements taken (before the aliquot was returned to the solution mixture) and tabulated as shown in Appendix 2.

3.3.3 Determination of the Effect of Initial Dye Concentration on Dye Adsorption by *Luffa Cylindrica*

Seven dilutions of $2.50x10^{-6}M$, $5.00x10^{-6}M$, $1.00x10^{-5}M$, $1.50x10^{-5}M$, $1.75x10^{-5}M$, $2.00x10^{-5}M$ and $2.50x10^{-5}M$ solutions of Methylene blue were prepared from the 0.01M stock solution. From each of these dilutions, three 50ml portions were placed in separate conical flasks. To one of the three 50ml portions taken from each of the solutions, 0.5g *luffa cylindrica* was soaked. To the second and third 50ml-portions of each solution, 1.0g and 2.0g respectively, of *luffa cylindrica* were soaked. Each of the soakings was placed on a mechanical shaker and dye samples withdrawn from each at 10, 20, 40 and 60 minutes intervals using a syringe and placed in a cuvette and absorbance reading taken. The solution from the cuvette (after absorbance measurements) was returned to the original solution mixture. The results from these series of experiments are tabulated and given as Appendices 3A, 3B, 3C & 3D.

3.3.4 Effect of Weight of *Luffa Cylindrica* on Adsorption.

From the 0.01M methylene blue stock solution, $2.5x10^{-5}$M, $1.75x10^{-5}$M and $1.25x10^{-5}$M dilutions were made and absorbance readings taken on each as reference. From each of the three dilutions, five 50ml portions were taken and placed in five separate conical flasks, then, to one of the five aliquots from each of the three dilutions, 0.5g, of *luffa cylindrica* was soaked and placed on a mechanical shaker for 20 minutes after which a sample was drawn with syringe and the absorbance reading taken. This procedure was repeated with 1.0g, 2.5g, 5.0g, and 7.5g of the luffa adsorbent. The results are tabulated and given as Appendix 4.

3.3.5 Effect of Treatment of *Luffa Cylindrica* with Nitric Acid

A portion of fresh *luffa Cylindrica* was treated with 1.0M Nitric acid and then washed several times with distilled water until the eluate had no effect on a blue litmus paper. The resultant luffa was then dried in the oven over a period of 48 hours at 60°C with occasional turning every two hours. The acid-treated *luffa cylindrica* was then subjected to adsorption experiments using methylene blue alongside an equal weight of fresh untreated luffa but using the same concentration of the dye solution for the adsorption results to be compared. This was done with three different dilutions of $2.5x10^{-5}$M, $1.75x10^{-5}$M, and $1.25x10^{-5}$M methylene blue dye solutions.

3.3.6 Effect of Treatment of *Luffa Cylindrica* with Hydrogen Peroxide

Some 30g *Luffa cylindrica* estimated to exceed the amount required for the next set of experiments was washed twice with 30% (v/v) hydrogen peroxide and then placed in a sonicator for eight hours with fresh hydrogen peroxide. This was followed with several washes using distilled water before drying in the oven at 60°C for 48 hours. Three portions of 2.0g each of the luffa thus treated were weighed out and separately placed in conical flasks alongside equal weights of fresh luffa. Three dilutions of methylene blue solution were used where each pair of fresh luffa untreated and H_2O_2-treated luffa were subjected to the same dye solution of known concentration. Absorbance readings were then taken at regular time intervals for comparison of the results.

3.3.7 Regeneration of the Spent *Luffa Cylindrica*.

The spent *luffa cylindrica* was regenerated by two methods:

a) Using hydrogen peroxide

The spent *luffa cylindrica* was washed with 30% (v/v) hydrogen peroxide twice and then placed in a sonicator for eight hours with fresh hydrogen peroxide. After the eight hours, the *luffa cylindrica* was rinsed several times with distilled water after which it was dried overnight in

an oven at 60°C. A portion of the fresh *luffa cylindrica* was subjected to the same treatment for comparison.

b) Using nitric acid

Spent *luffa cylindrica* was washed with 1.0M nitric acid and then washed several times with distilled water while testing the eluate with a blue litmus paper. A portion of fresh *luffa cylindrica* was subjected to the same treatment for comparison of the experimental results.

The four portions of *luffa cylindrica* used comprised of the following:

1 regenerated spent *luffa cylindrica* using hydrogen peroxide,

2 fresh *luffa cylindrica* treated with hydrogen peroxide,

3 regenerated spent *luffa cylindrica* using nitric acid, and

4 fresh luffa nitric acid-treated, were subjected to the same dye adsorption treatment as follows:

From each of the four *luffa cylindrica* samples subjected to the varying treatments described above, three-2.0g portions were weighed and placed in separate conical flasks. For comparison purposes, three-2.0g portions of fresh *luffa cylindrica* were also weighed alongside the treated *luffa cylindrica* samples. To one of each of the four sets of the differently obtained *luffa cylindrica* weighings, 50ml of 2.5×10^{-5}M dye solution was added and shaken on a mechanical shaker for 20 minutes. A dye sample

from the luffa-dye mixture was then withdrawn with a syringe and placed in a cuvette of the UV-Vis spectrophotometer and its absorbance measured. The same procedure was repeated using the other two dilutions of methylene blue dye solutions, which comprised of $1.75x10^{-5}$M and $1.25x10^{-5}$M methylene blue dye solutions made from the 0.01M stock dye solution which were used with the other sets of *luffa cylindrica* weighings.

3.3.8 Effect of Ionic Strength.

Ten portions of 2.0g luffa were weighed accurately and each placed in separate conical flasks and appropriately labelled. A 0.1M KCl solution was prepared by weighing 2.5002g of KCl pellets of 74.55% purity and dissolving in distilled water in a 250ml volumetric flask and topping it with distilled water up to the mark. From 0.01M methylene blue stock solution, two dilutions of $5.0x10^{-5}$M and $2.5x10^{-5}$M were prepared. From each of the two dilutions:-

a) Five portions of 25ml each were measured and placed in separate 50ml volumetric flasks labelled with numbers 1 to 5.

b) To the portion labelled 1, 1ml of 0.1M KCl was added and the distilled water added to the mark. To the portion labelled 2, 2ml of the 0.1MKCl solution was added and then distilled water was added to the mark. The same process was repeated for the other portions marked 3, 4 and 5 where, 3, 4 and 5ml of 0.1M KCl was

added and topped to the mark with distilled water to produce solutions of constant $2.5x10^{-5}$M methylene blue concentration from the $5.0x10^{-5}$M. Similarly, methylene blue solution of $1.25x10^{-5}$M concentration was prepared from an initial $2.5x10^{-5}$M methylene blue dye solution but containing different amounts of KCl and thus possessing different ionic strengths.

c) The absorbance of each of these solutions containing different amounts of 0.1M KCl was taken and recorded as reference.

Five of the ten portions of 2.0g each of the *luffa cylindrica* previously weighed were labelled 1-2.5, 2-2.5, 3-2.5, 4-2.5 and 5-2.5 and the luffa in each of them soaked for 20 minutes in 50ml of $2.5x10^{-5}$M dye solutions containing different amounts (1,2,3,4 and 5ml) of KCl corresponding to the labelling. The other five were similarly labelled and the luffa in them soaked for 20 minutes in 50ml of $1.25x10^{-5}$M dye solutions containing the different amounts of KCl. After 20 minutes, aliquot amounts were drawn with a syringe and their corresponding absorbances measured. The readings obtained were tabulated as in Appendix 5.

3.3.9 Effect of pH on Adsorption.

Hydrochloric acid of 0.01M concentration was prepared from a stock HCl (12M) by appropriate dilution and 0.01M KOH was also prepared by dissolving 0.1403g KOH pellets in 250ml distilled water in a volumetric flask and filling to the mark.

Methylene blue dye solution of $2.5x10^{-5}$M concentration and containing 5, 4, 3, 2, 1, 0.5 and 0.1ml 0.01M HCl and 0.5, 1, 2, 3, 4 and 5 ml 0.01M KOH were separately prepared in portions of 50ml.

The absorbance and the pH of each of these solutions were taken as reference. Then 2.0g portions of *luffa cylindrica* were separately soaked in each of these solutions for 20 minutes with continuous shaking on a mechanical orbital shaker and the pH together with absorbances measured thereafter.

In order to obtain solution mixtures of varying pHs, different portions of the dye solution were prepared to contain 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 ml of either HCl or KOH of 0.01, 0.1 and 0.2M stock concentrations. These pH adjustments were made while ensuring the concentration of the dye in each solution mixture did not change in each case. The absorbance and pH of the solutions were taken before soaking the luffa and after soaking *luffa cylindrica* for 20 minutes. The readings obtained were tabulated (See appendix 6).

3.3.10 Preparation of Activated Carbon from *Luffa Cylindrica*

Eight ceramic crucibles were cleaned and dried and then distinctly labelled and weighed. The weight of each was recorded. The crucibles were then filled with *luffa cylindrica* and weighed again so that the weight of the *luffa cylindrica* was obtained by difference.

The crucible with the weighed luffa was placed in the furnace and the furnace switched on. The temperature knob of the furnace was set to 600°C and the crucible with content was steadily heated in a stream of nitrogen to a temperature of 600°C, when a jet of steam was opened. The system was maintained at 600°C for 30 minutes for activation. The steam was produced using a pressure cooker.

The furnace was then left to cool slowly before opening. It is important to note that faster cooling would amount to quenching the system which would result in breakage of the furnace linings and the heater elements.

Once the ceramic crucible with the activated carbon had cooled to room temperature, it was removed and weighed again to give the weight of the activated carbon obtainable from the original luffa in the crucible.

3.3.10.1 Effect of Activation on Weight of Activated Carbon

Before activation, the weight of the luffa in each crucible was obtained. After activation the weight of the activated carbon obtained was

determined. The results obtained were used to calculate the percentage weight loss due to activation of the luffa.

The activated carbon was weighed accurately and then treated with concentrated hydrochloric acid to remove any ash. After the treatment with conc. HCl (12M), the activated carbon was washed several times with distilled water until the elutriate solution had no effect on blue litmus paper. The washed activated carbon was dried and weighed again to determine the amount of ash contained in the activated carbon.

3.4 Luffa-Derived Activated Carbon Experiments

3.4.1 Determination of Optimum Contact Time with Luffa-Derived Activated Carbon

The luffa-derived activated carbon which had been treated with HCl and washed several times with distilled water was used. 0.5g of the activated carbon was soaked in 50ml of 2.5×10^{-5}M dye solution (whose absorbance had been determined) and placed on an orbital shaker. Aliquot samples of the dye solution were then withdrawn from the dye-activated carbon mixtures using a syringe at predetermined time intervals and the absorbance determined before returning the aliquot to the solution mixture to continue with the adsorption process. Measurement of the absorbance readings were carried out until the absorbance readings stabilised. The absorbance readings were recorded

against time and used to determine the optimum time of equilibration (Appendix 7).

3.4.2 Effect of Dye Concentration on Adsorption on the Luffa-Derived Activated Carbon

Seven-0.5g portions of activated carbon were accurately weighed and each placed into separate 50ml Erlenmeyer flasks. 50ml portions of each of the seven methylene blue dye solutions of varying concentrations were measured and separately placed in each of the 0.5g luffa-derived activated carbon-containing flasks. The luffa-derived activated carbon-methylene blue solution mixtures were continuously agitated in an orbital shaker over a period of 24 hours. During this period, aliquot amounts were withdrawn using a syringe at predetermined time intervals and their corresponding absorbances measured (before returning solution to their respective flasks). The above process was repeated with 1.0g and 2.0g portions of the luffa-derived activated carbon and the results were tabulated as shown in Appendix 8.

3.5 Determination of the Adsorption Breakthrough of Luffa for Methylene Blue

Breakthrough experiments were performed using the following initial bed and feed conditions:

Column length = 29 cm

Column Capacity = 100ml

Flow Rate = 10ml/sec

A glass column of 29 cm length was used to contain the various weights of *luffa cylindrica*, as a fixed-bed adsorber. The column of *luffa cylindrica* was prepared by a dry packing technique where after weighing the weights desired (e.g. 10g); it was inserted bit-by-bit and squeezed to pack with a glass rod. Then, the bed was rinsed with distilled water and left overnight to ensure a closely packed arrangement of adsorbent without voids or channels as much as was practicable. The dye solution was fed at a known flow rate through the bed of luffa using a fountain pump. Samples of the effluent were collected periodically and analyzed for the remaining dye concentration (C) using a spectrophotometer. The desired breakthrough concentration (C_b) was determined at 10% of the influent dye concentration, which was $0.1C/C_o$ or $0.1x2.5x10^{-5}$ = $2.5x10^{-6}$M (the initial dye concentration C_o was $2.5x10^{-5}$M). The flow through the test column was continued until the dye concentration of column effluent approached 0.95 C/C_o, or until the concentration of the effluent was equal to or very close to that of the influent, which indicated the exhaustion point (C_x), also defined as the column effluent dye concentration at exhaustion point. This was calculated to

be $2.375x10^{-5}M$. The set up for the experiment is shown in plate 3a and 3b below. The result was analysed by plotting a graph of C/C_o against the volume passed through the bed to obtain the breakthrough curve.

(a) (b)

Plate 3a and 3b: Photograph of the inprocess adsorption breakthrough experiments for *luffa cylindrica* on methylene blue dye

3.6 Testing with Real Samples

For real life application, direct dye red was used. Although *luffa cylindrica* was found to work with other dyes (from the physical appearance of the luffa-treated dye solutions) the chemical used to improve the solubility and for fixing the dyes was found to interfere with the absorbance reading except the direct red dye which does not require any chemicals for fixing. Absorbance readings of the direct red dye solution were taken before and after using the luffa on the dye and the plotted results superimposed on each other for ease of comparison.

CHAPTER FOUR

4.0 Results and Discussion

4. 1 Determination of the Working Wavelength (λ_{Max}) for the Methylene Blue Dye

Figure 1 below is a plot of absorbance against wavelength for methylene blue dye solution. From Figure 1, it is evident that the wavelength at which there is maximum absorption is 658 nm. This wavelength (λ_{max}) was used for the rest of the experiments and the UV-Vis spectrophotometer was set to that value.

4.2 Determination of the Optimum Contact (Equilibration) Time

As part of the optimization process, it was important to establish the optimum (or minimum) time required for maximum adsorption to occur. Figure 2 below shows the effect of contact time on the % adsorption.

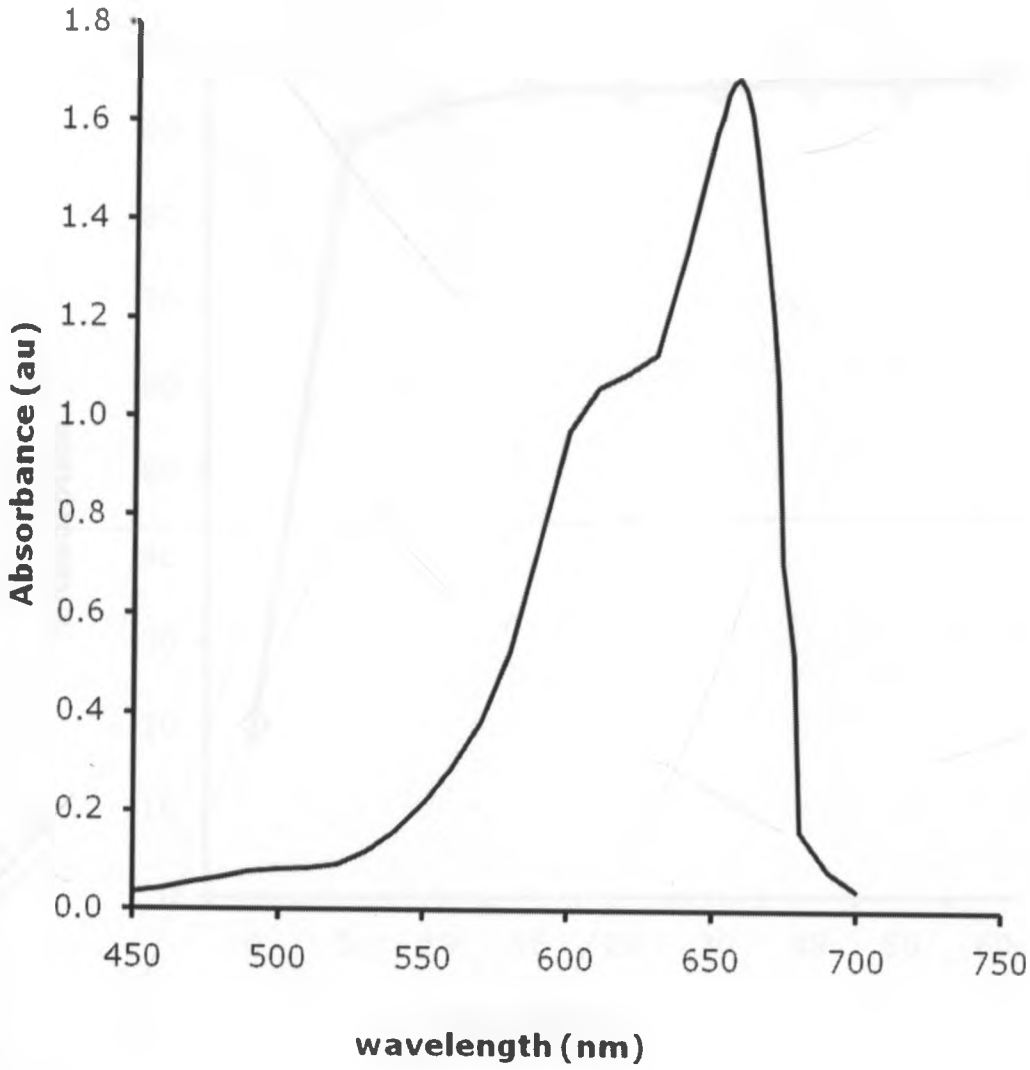

Figure 1: UV-Vis absorption spectrum of methylene blue solution

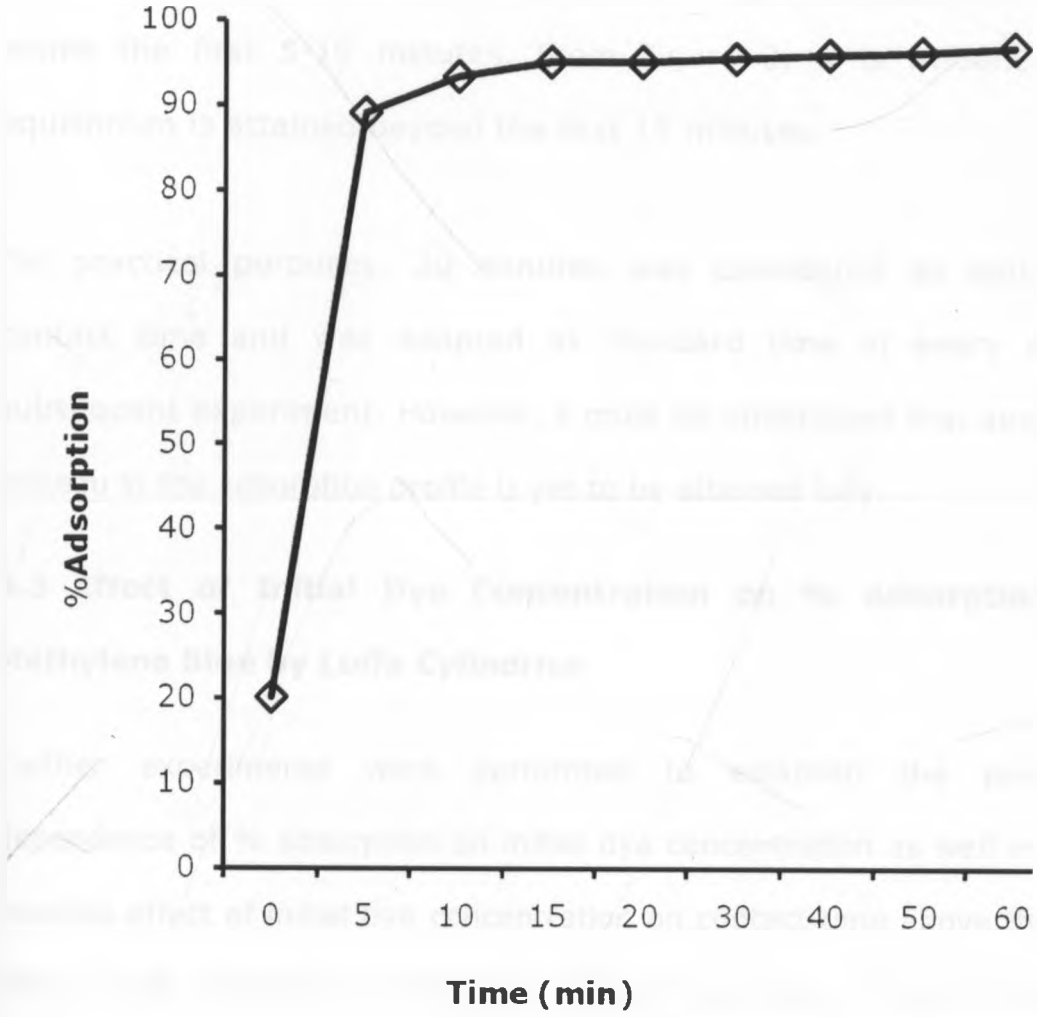

Figure 2: Effect of contact time between 1 .0g *luffa cylindrica* and methylene blue dye solution of $2.5x10^{-5}$M concentration on % dye adsorption

It was observed that initially the amount of dye adsorbed increases rapidly from about 20% to 90% within the first five minutes or so. Beyond this time, there is a gradual increase in % adsorption as the system approaches equilibrium. Generally, it is evident that the

initial rapid adsorption process removed a large fraction of the dye within the first 5-10 minutes. From Figure 2, it is evident that equilibrium is attained beyond the first 15 minutes.

For practical purposes, 20 minutes was considered as optimum contact time and was adopted as standard time in every other subsequent experiment. However, it must be understood that absolute plateau in the adsorption profile is yet to be attained fully.

4.3 Effect of Initial Dye Concentration on % Adsorption of Methylene Blue by *Luffa Cylindrica*

Further experiments were performed to establish the possible dependence of % adsorption on initial dye concentration as well as the possible effect of initial dye concentration on contact time above the 15 minute time obtained as optimal in the previous study. Figure 3 shows the effect of initial concentration of methylene blue dye solution on % adsorption by different weights of *luffa cylindrica* during the first 10 minutes contact time.

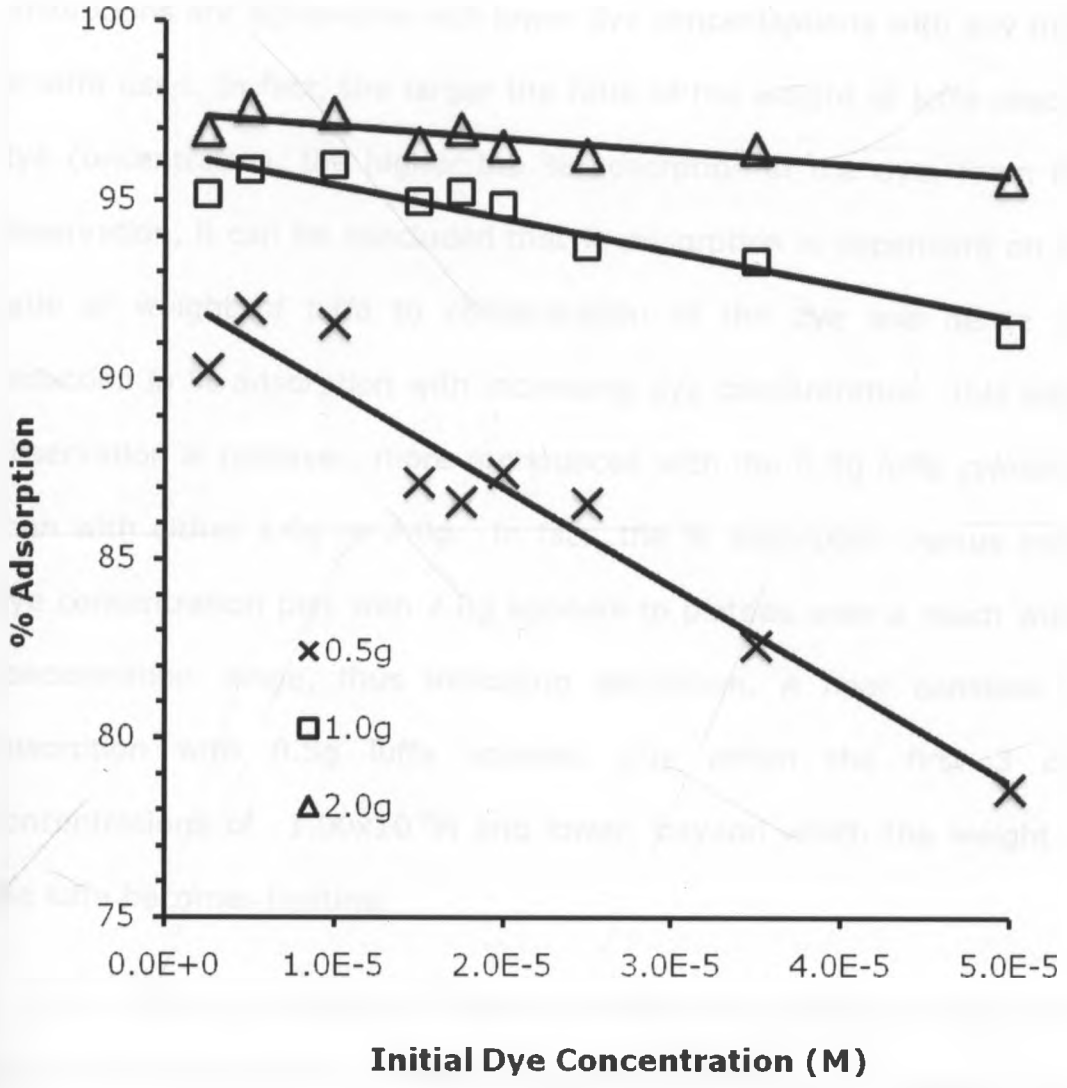

Figure 3: Effect of initial concentration of dye on % adsorption during the first 10 minutes of contact time using different weights of adsorbent (i.e. 0.5, 1.0, 2.0g)

From Figure 3, a general decrease in the percentage adsorption with increased initial dye concentration is observed. It is also clear that % adsorption is also dependent on the weight of adsorbent used. The adsorption profile with 2.0g was found to be highest and least with the smaller weight of 0.5g. It is also evident from Figure 3 that higher %

adsorptions are achievable with lower dye concentrations with any mass of luffa used. In fact, the larger the ratio of the weight of luffa used to dye concentration, the higher the % adsorption of the dye. From this observation, it can be concluded that % adsorption is dependent on the ratio of weight of luffa to concentration of the dye and hence the reduction in % adsorption with increasing dye concentration. This latter observation is however, more pronounced with the 0.5g *luffa cylindrica* than with either 1.0g or 2.0g. In fact, the % adsorption versus initial dye concentration plot with 2.0g appears to plateau over a much wider concentration range, thus indicating saturation. A near constant % adsorption with 0.5g luffa appears only within the first 3 dye concentrations of $1.00x10^{-5}M$ and lower, beyond which the weight of the luffa becomes limiting.

A similar trend is reflected in Figure 4 where a 20 minute contact time was used instead of the 10 minutes applicable in Figure 3. However, it is evident that with 20 minutes as the contact time, the % adsorption with 2.0g luffa changes only very slightly. In Figure 4 the trend of decrease in the percentage adsorption with increase in initial dye concentration is much less pronounced than is the case with Figure 3. With this, it can be concluded that not only the ratio of weight of adsorbent to the initial dye concentration is important, but also the contact time.

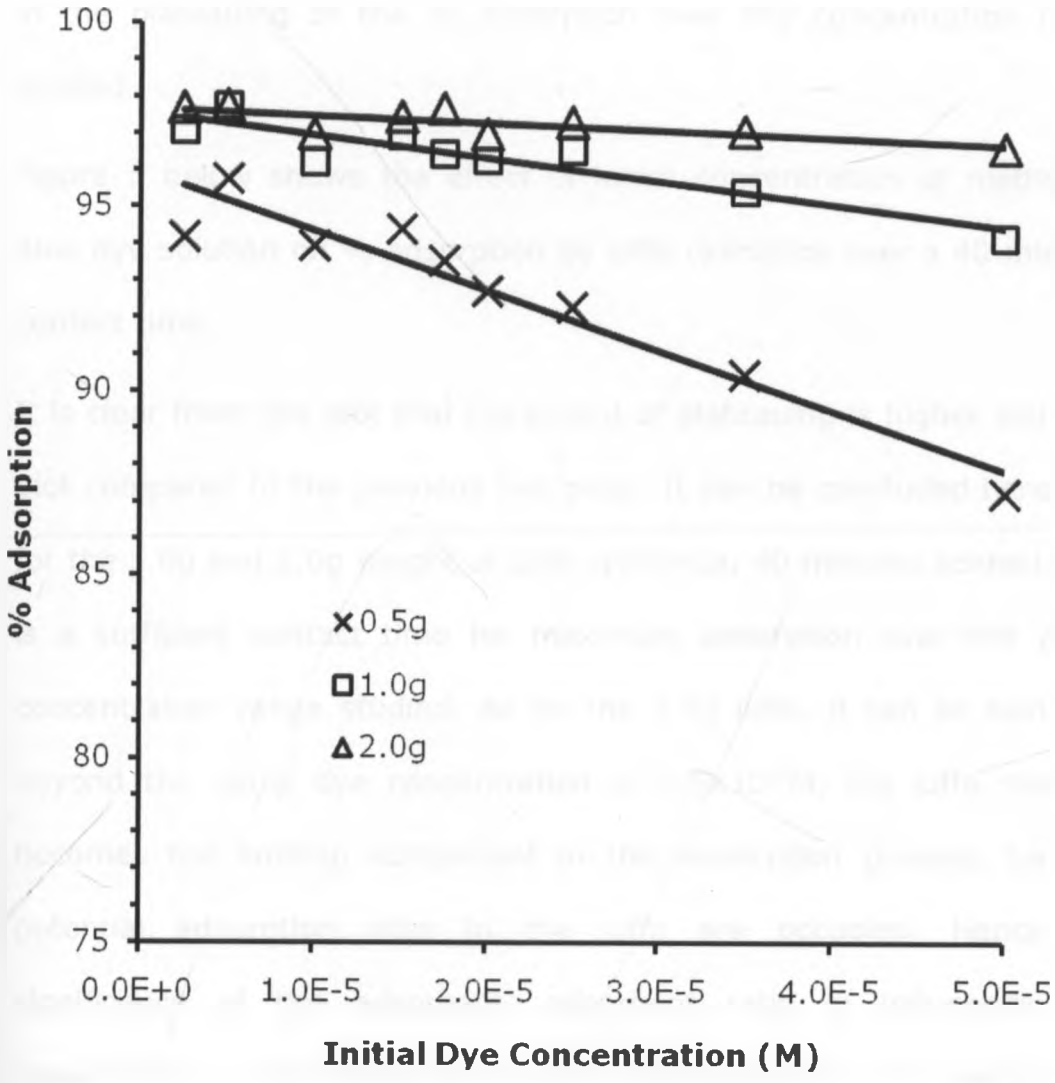

Figure 4: Effect of initial concentration on % adsorption during the first 20 minutes of contact time

It is also clear that 20 minutes contact time may not yet be a very optimal time for maximum adsorption by either the 1.0g or 2.0g luffa over the whole concentration range chosen. In fact, results obtained for higher contact time (see Figures 5 and 6) indicate progressive increase

in the plateauing of the % adsorption over the concentration range studied.

Figure 5 below shows the effect of initial concentration of methylene blue dye solution on % adsorption by *luffa cylindrica* over a 40 minutes contact time.

It is clear from this plot that the extent of plateauing is higher with this plot compared to the previous two plots. It can be concluded here that for the 1.0g and 2.0g weight of *luffa cylindrica*, 40 minutes contact time is a sufficient contact time for maximum adsorption over the whole concentration range studied. As for the 0.5g luffa, it can be said that beyond the initial dye concentration of $2.5X10^{-5}M$, the luffa material becomes the limiting component in this adsorption process, i.e., all potential adsorption sites in the luffa are occupied. Hence the significance of the adsorbate: adsorbent ratio in influencing the adsorption process Results of Figure 5 further confirms the adequacy of 40 minutes as optimum contact time for maximum adsorption over the whole concentration range studied.

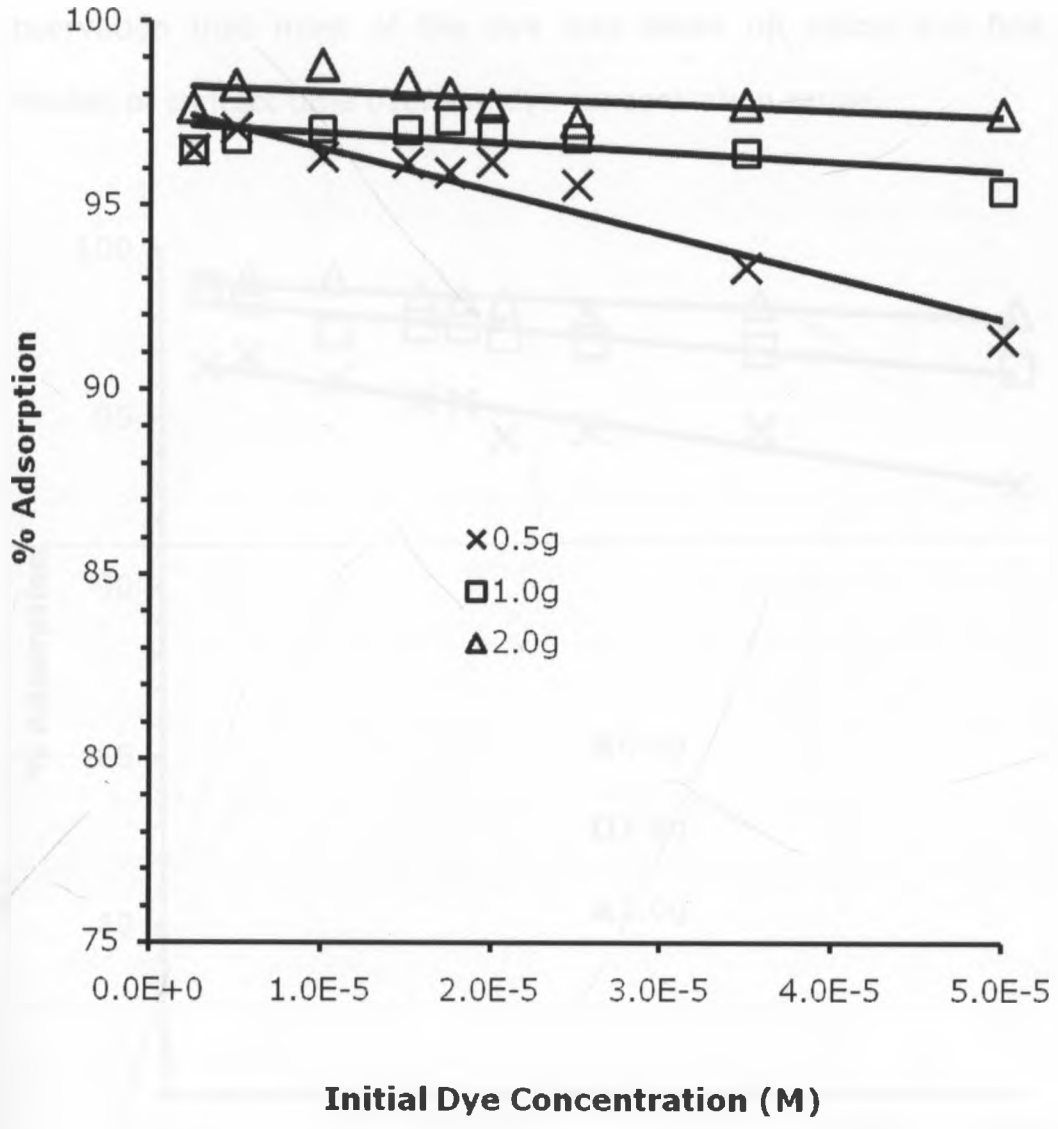

Figure 5: Effect of initial concentration on % adsorption during the first 40 minutes of contact time

Figure 6 shows the effect of initial concentration of methylene blue dye solution on % adsorption by *luffa cylindrica* during the first 60 minutes contact time. The contact time of 60 minutes does not seem to make a significant difference in % adsorption and hence confirming our earlier

observation that most of the dye was taken up within the first 40 minutes of contact time over the dye concentration range.

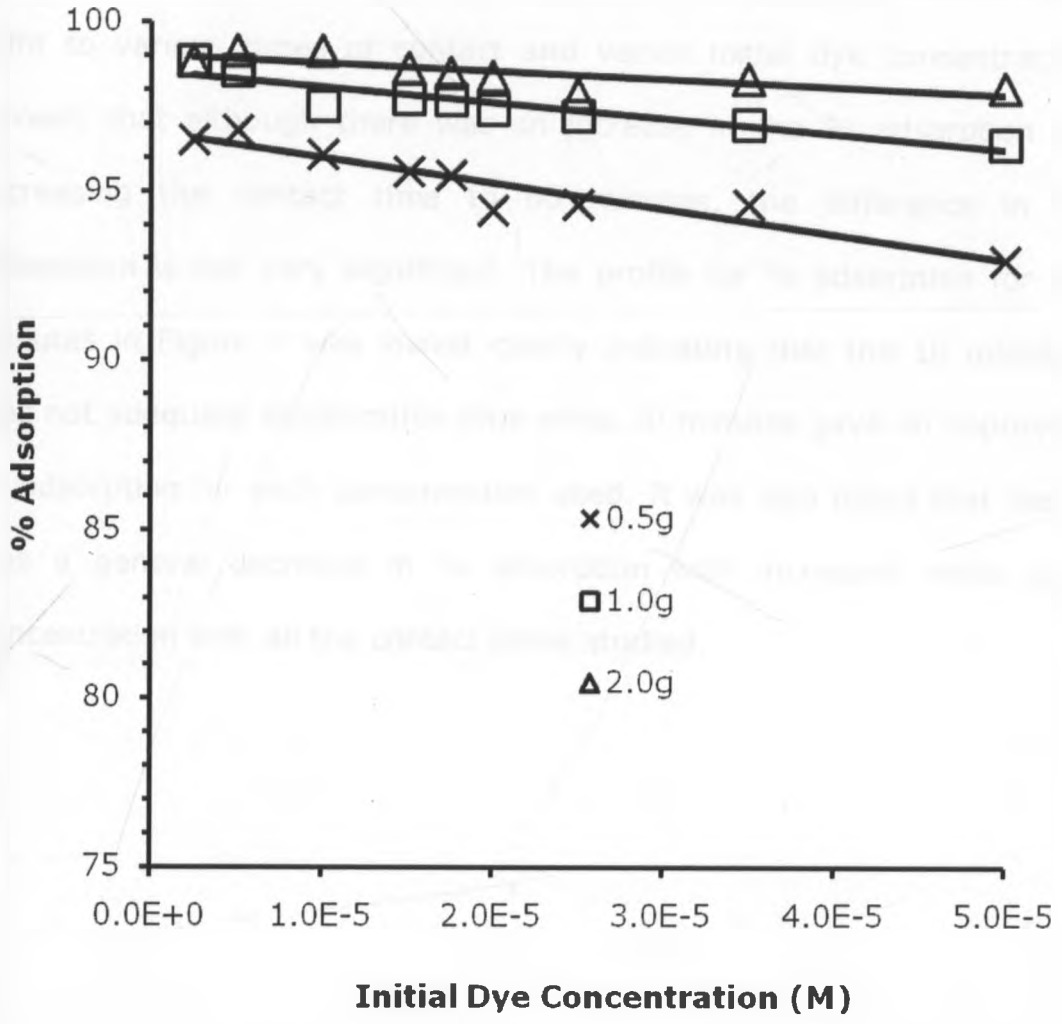

Figure 6: Effect of initial dye concentration on % adsorption during the first 60 minutes of contact time

In all the four different times of contact studied, it is observed that higher % adsorptions are possible with lower concentration of the dye.

This confirms the observation that % adsorption is dependent on the ratio of the weight of luffa to concentration of the dye solution.

As a further confirmation of the effect of contact time, exposure of 0.5g luffa to various times of contact and varied initial dye concentration reveals that although there was an increase in the % adsorption by increasing the contact time to 60 minutes, the difference in % adsorption is not very significant. The profile for % adsorption for 10 minutes in Figure 7 was lowest clearly indicating that the 10 minutes was not adequate equilibration time while 20 minutes gave an improved % adsorption for each concentration used. It was also noted that there was a general decrease in % adsorption with increased initial dye concentration with all the contact times studied.

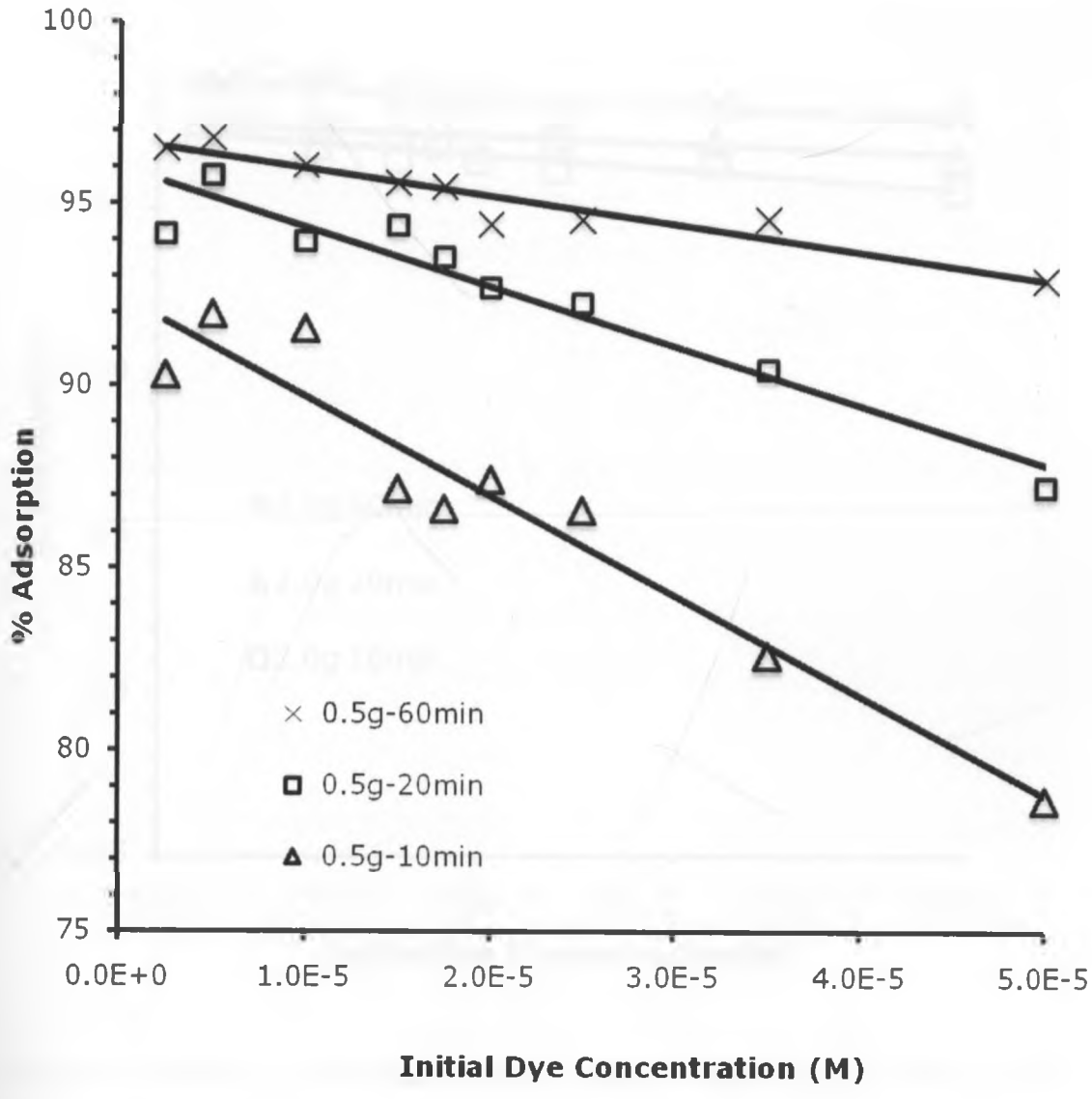

Figure 7: Effect of initial dye concentration and contact time on % adsorption using 0.5g luffa

The effect of initial dye concentration and contact time on % adsorption using 2.0g luffa as depicted in Figure 8 shows that 60 minute contact time gave the highest % adsorption and 10 minutes contact time the lowest: An observation similar to those reported with the lower weights.

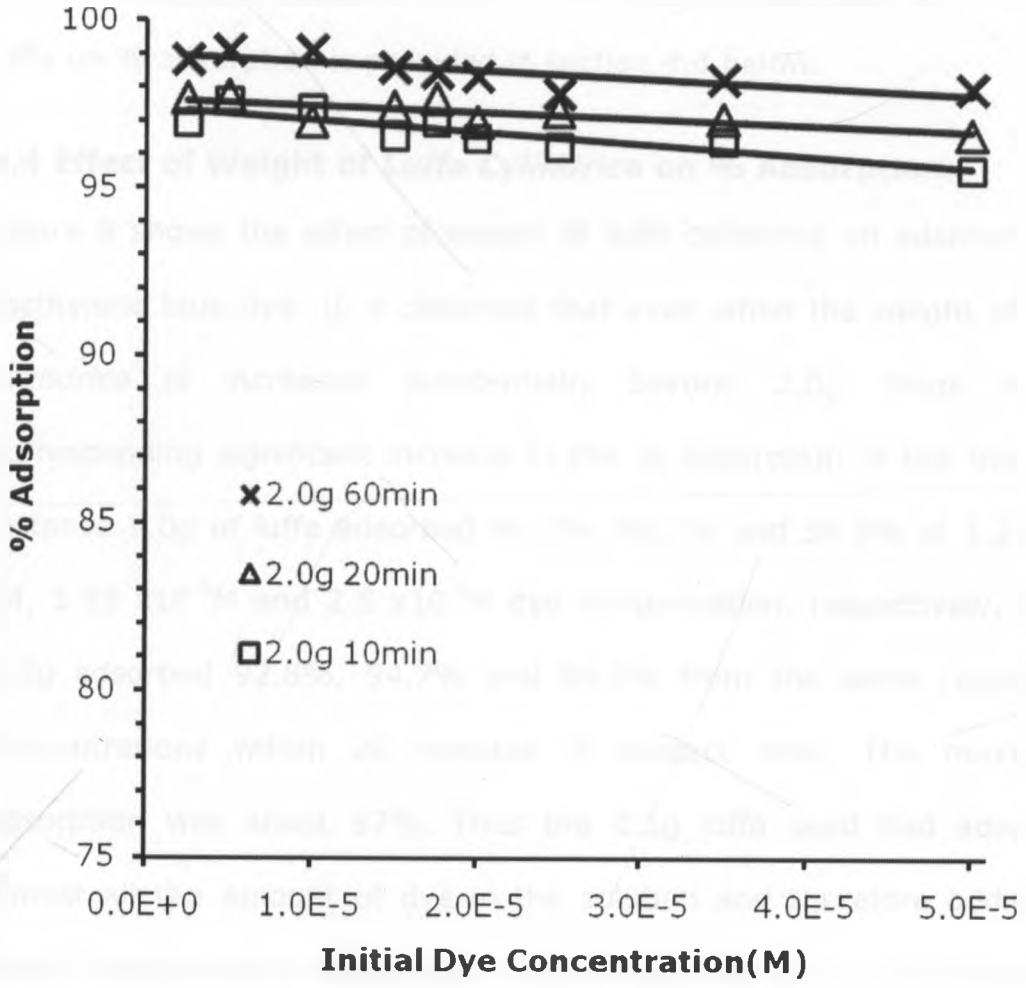

Figure 8: Effect of initial dye concentration and contact time on % adsorption using 2.0g luffa

However, the difference is not very large indicating that any additional time of contact would not provide any further advantage in so far as adsorption is concerned. It is also now clearly evident that 0.5g luffa is the limiting "reagent" since with a higher weight of luffa such as 2.0g, near plateau adsorption profiles are evident as depicted in Figure 8 for

all concentrations studied. Further evidence on the effect of weight of luffa on % adsorption is provided in section 4.4 below.

4.4 Effect of Weight of *Luffa Cylindrica* on % Adsorption.

Figure 9 shows the effect of weight of *luffa cylindrica* on adsorption of methylene blue dye. It is observed that even when the weight of *luffa cylindrica* is increased substantially beyond 2.0g, there is no corresponding significant increase in the % adsorption of the dye. For instance 5.0g of luffa adsorbed 96.2%, 96.2% and 96.9% of $1.25x10^{-5}$M, $1.72 x10^{-5}$M and $2.5 x10^{-5}$M dye concentration, respectively, while 0.5g adsorbed 92.8%, 94.7% and 94.6% from the same respective concentrations within 20 minutes of contact time. The maximum adsorption was about 97%. Thus the 0.5g luffa used had adsorbed almost all the amount of dye in the solution and therefore additional weight had almost no appreciable effect on the amount of dye adsorbed.

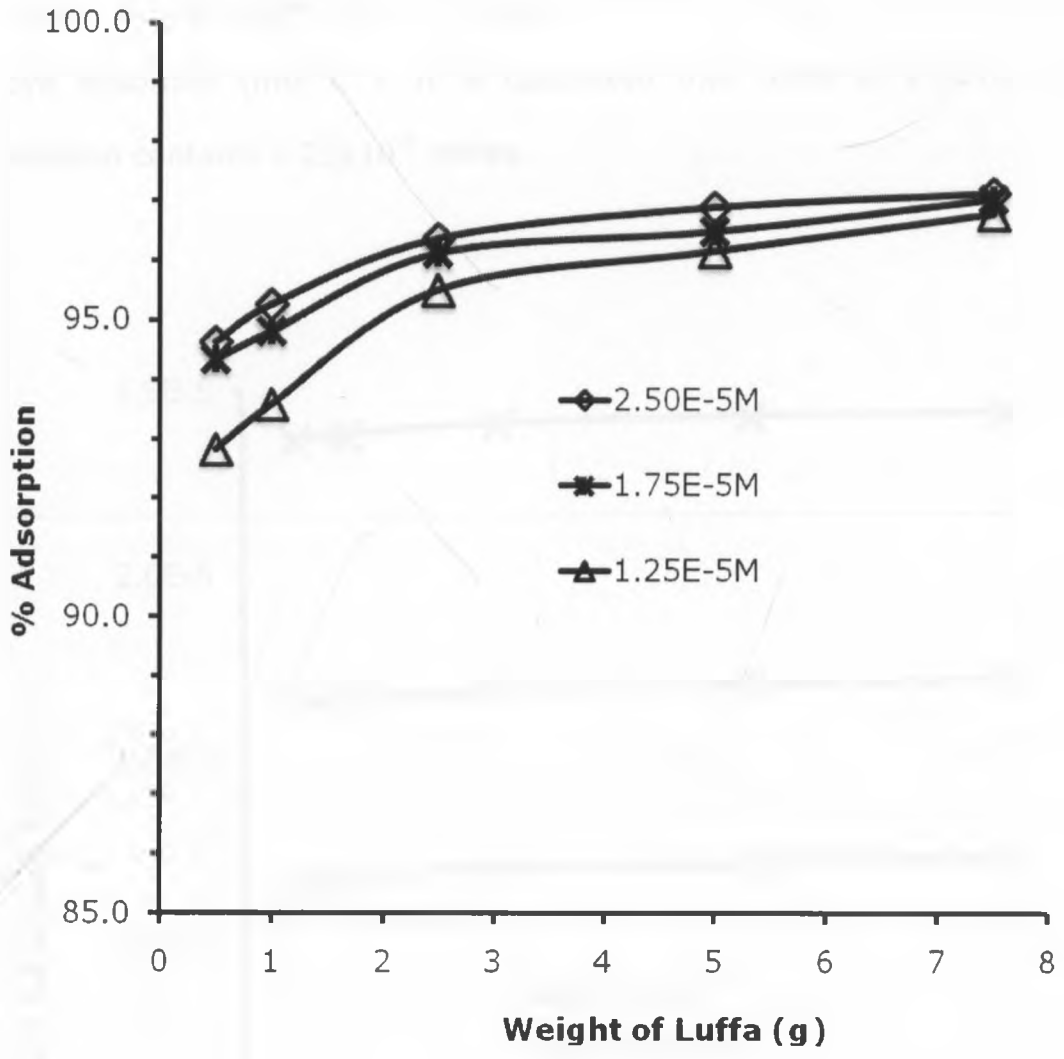

Figure 9: Effect of weight of *luffa cylindrica* on % adsorption for different initial dye concentration of $1.25x10^{-5}M$, $1.75x10^{-5}M$ and $2.5x10^{-5}M$

In order to determine the maximum adsorption capacities of the different weights of luffa for the three different dye concentrations, a plot of amount adsorbed (mol L^{-1}) verses weight of luffa was made.

Figure 10 shows the effect of weight of *luffa cylindrica* on the amount of dye adsorbed (mol L^{-1}). It is calculated that 50ml of $2.5x10^{-5}$M dye solution contains $1.25x10^{-6}$ moles.

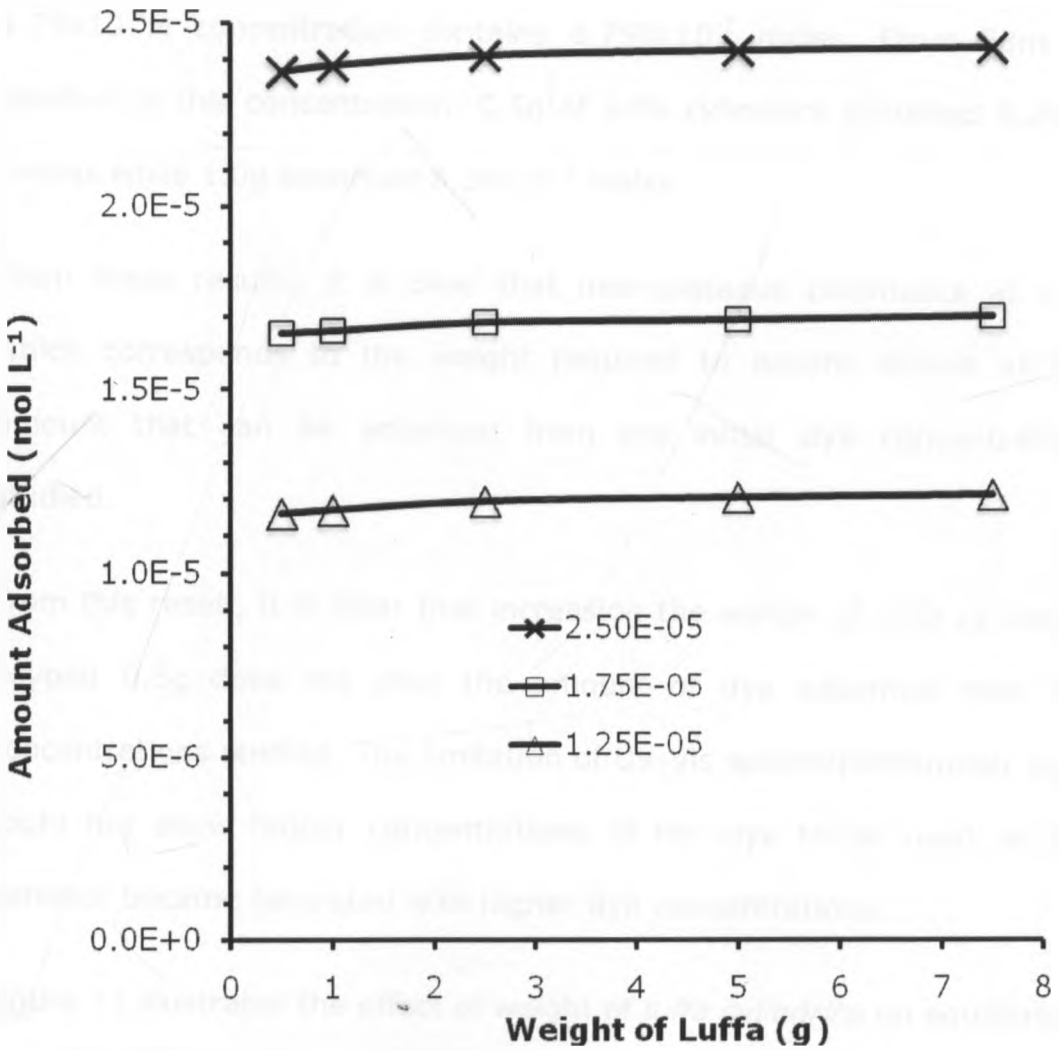

Figure 10: Effect of weight of *luffa cylindrica* on amount of dye adsorbed (Mol L^{-1})

From Figure10, it is observed that 0.5g of *luffa cylindrica* adsorbed $1.18x10^{-6}$ moles out of the initial possible $1.25x10^{-6}$moles and also 1.0g *luffa cylindrica* adsorbed $1.18x10^{-6}$moles from 50ml dye solution of the same concentration.

Similar calculations also indicate that a volume of 50ml dye solution of $1.75x10^{-5}$M concentration contains $8.750x10^{-7}$ moles. From 50ml dye solution of this concentration, 0.5g of *luffa cylindrica* adsorbed $8.29x10^{-7}$moles while 1.0g adsorbed $8.30x10^{-7}$ moles.

From these results, it is clear that near-plateaus commence at 1.0g which corresponds to the weight required to adsorb almost all the amount that can be adsorbed from the initial dye concentrations studied.

From this result, it is clear that increasing the weight of *luffa cylindrica* beyond 0.5g does not alter the amount of dye adsorbed from the concentrations studied. The limitation of UV-Vis spectrophotometer used could not allow higher concentrations of the dye to be used as the detector became saturated with higher dye concentrations.

Figure 11 illustrates the effect of weight of *luffa cylindrica* on equilibrium dye concentration (mol L^{-1}). The equilibrium amount of dye in the solution was found to be almost constant for all the weights used beyond 0.5g. It can be concluded that the weight of 0.5g of luffa used adsorbed almost all the dye available in the solution and therefore any

additional weight did not make any significant difference on the equilibrium concentration

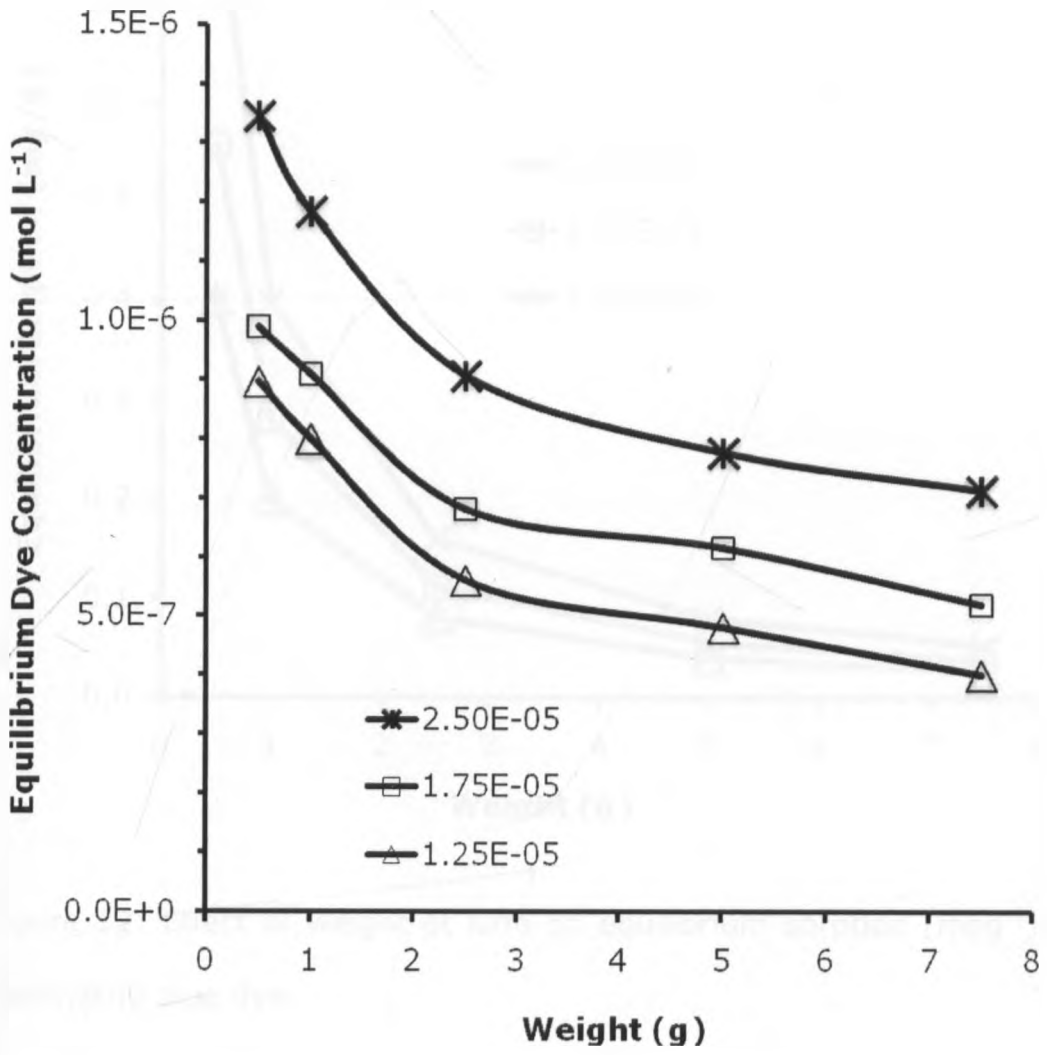

Figure 11: Effect of weight of *luffa cylindrica* on equilibrium dye concentration (mol L^{-1}).

Figure 12 shows a plot of the equilibrium sorption (expressed in mgg^{-1}) for three dye concentrations used verses adsorbent weights.

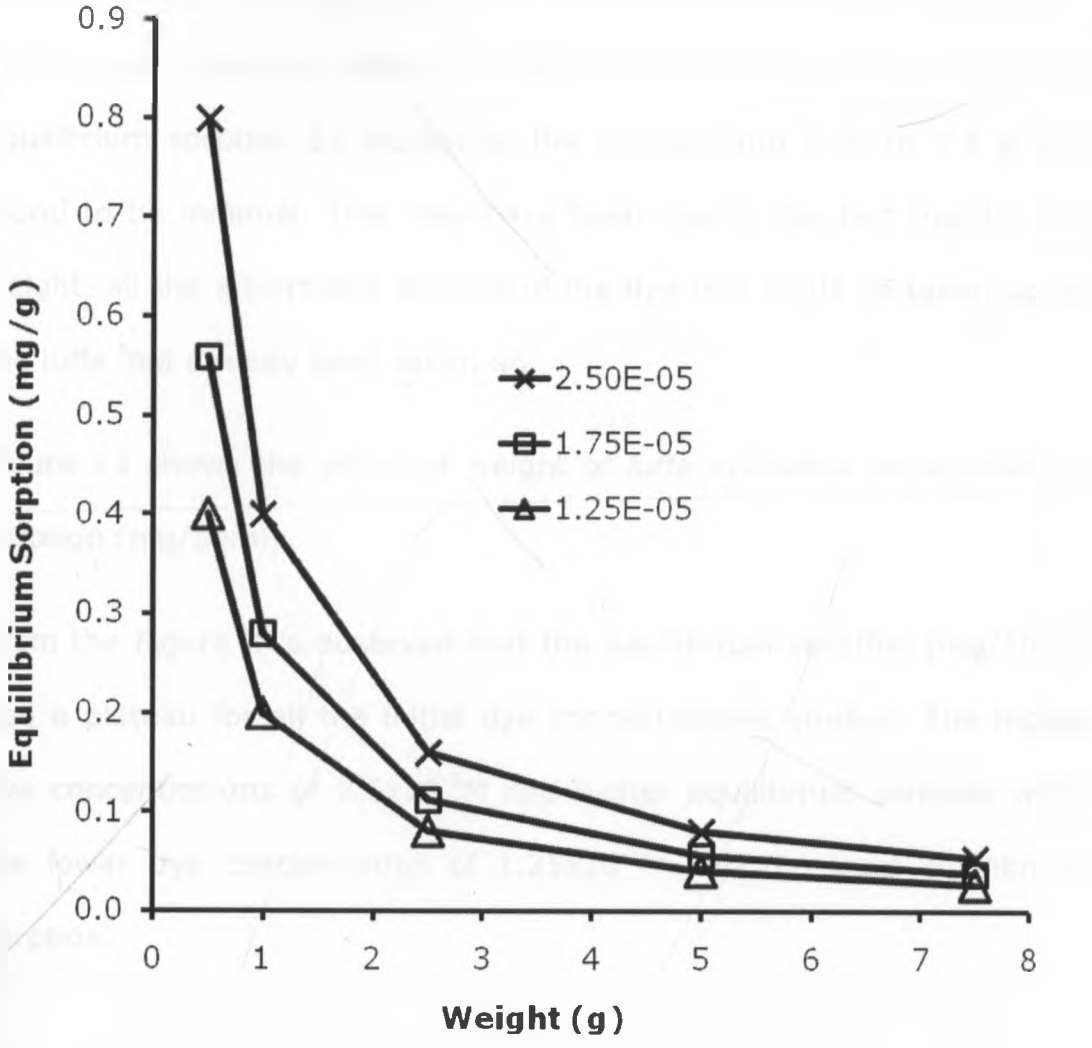

Figure 12: Effect of weight of luffa on equilibrium sorption (mgg^{-1}) for methylene blue dye.

The equilibrium sorption is larger with higher initial dye concentration and decreases as initial dye concentration reduces. This trend was observed for all the adsorbent weights studied. For a particular weight, the equilibrium sorption reduced with decreasing initial dye concentration.

For a particular concentration, the equilibrium sorption was observed to reduce with increasing weight of luffa used although the reduction in the equilibrium sorption by increasing the weight from 5.0g to 7.5 g was found to be minimal. This may have been due to the fact that by this weight, all the adsorbable amount of the dye that could be taken up by the luffa had already been taken up.

Figure 13 shows the effect of weight of *luffa cylindrica* on equilibrium sorption (mg/50ml).

From the Figure it is observed that the equilibrium sorption (mg/50ml) had a plateau for all the initial dye concentrations studied. The higher dye concentrations of $2.5x10^{-5}M$ had higher equilibrium sorption while the lower dye concentration of $1.25x10^{-5}M$ had the least equilibrium sorption.

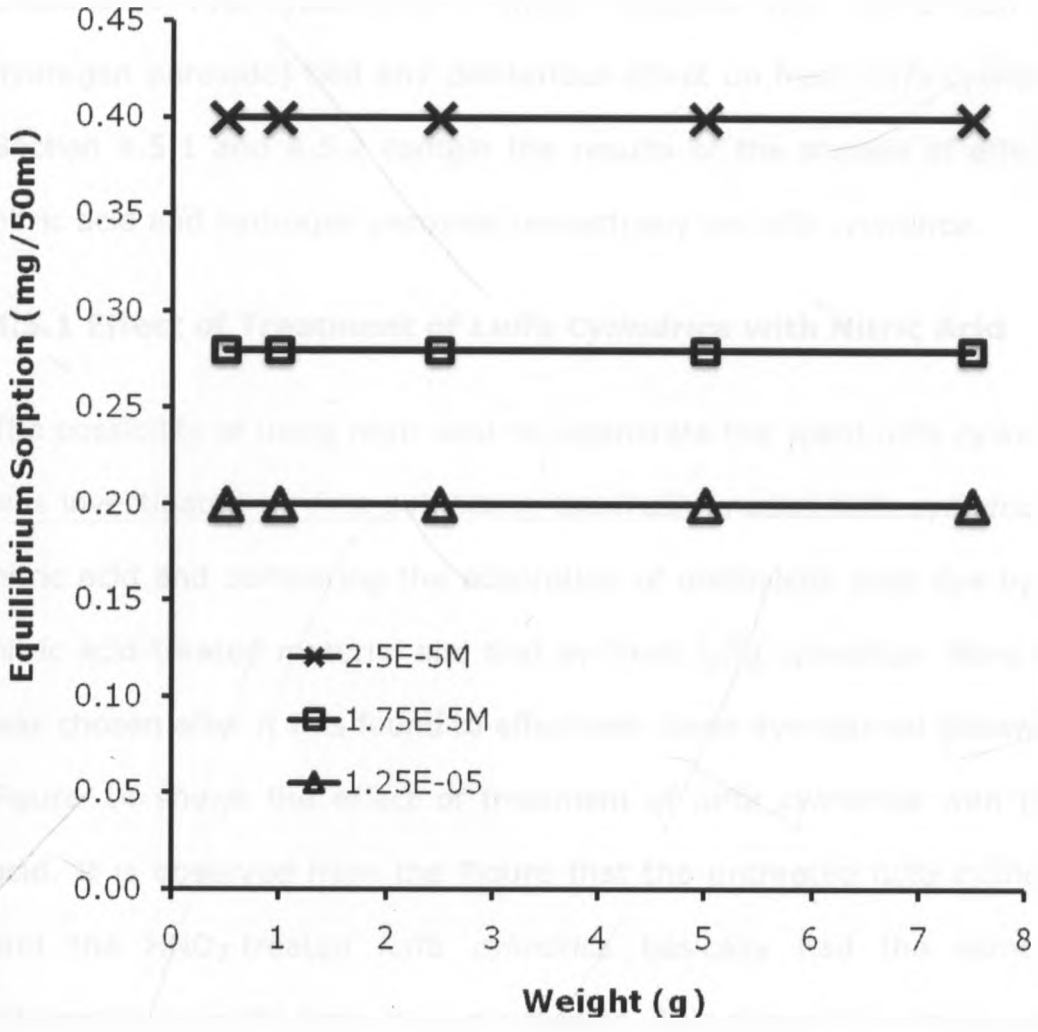

Figure 13: Effect of weight of *luffa cylindrica* on equilibrium sorption (mg/50ml).

4.5 Regeneration of Spent Luffa Studies

Hydrogen peroxide and nitric acid were considered for use as possible spent-*luffa cylindrica* regeneration agents. However before testing their efficacy in the regeneration exercise, experiments were conducted to establish the effects of these agents on fresh *luffa cylindrica*. It was

prudent to first determine if these reagents (i.e. nitric acid and hydrogen peroxide) had any deleterious effect on fresh *luffa cylindrica*. Section 4.5.1 and 4.5.2 contain the results of the studies of effect of nitric acid and hydrogen peroxide respectively on *luffa cylindrica*.

4.5.1 Effect of Treatment of *Luffa Cylindrica* with Nitric Acid

The possibility of using nitric acid to regenerate the spent *luffa cylindrica* was investigated by first subjecting the fresh unused *luffa cylindrica* to nitric acid and comparing the adsorption of methylene blue dye by the nitric acid-treated material and that by fresh *luffa cylindrica*. Nitric acid was chosen after it was found to effectively clean dye stained glassware. Figure 14 shows the effect of treatment of *luffa cylindrica* with nitric acid. It is observed from the Figure that the untreated *luffa cylindrica* and the HNO_3-treated *luffa cylindrica* basically had the same % adsorption over the time intervals studied. This shows that treatment of *luffa cylindrica* with nitric acid had no adverse or other effect on its ability to adsorb methylene blue dye from solution.

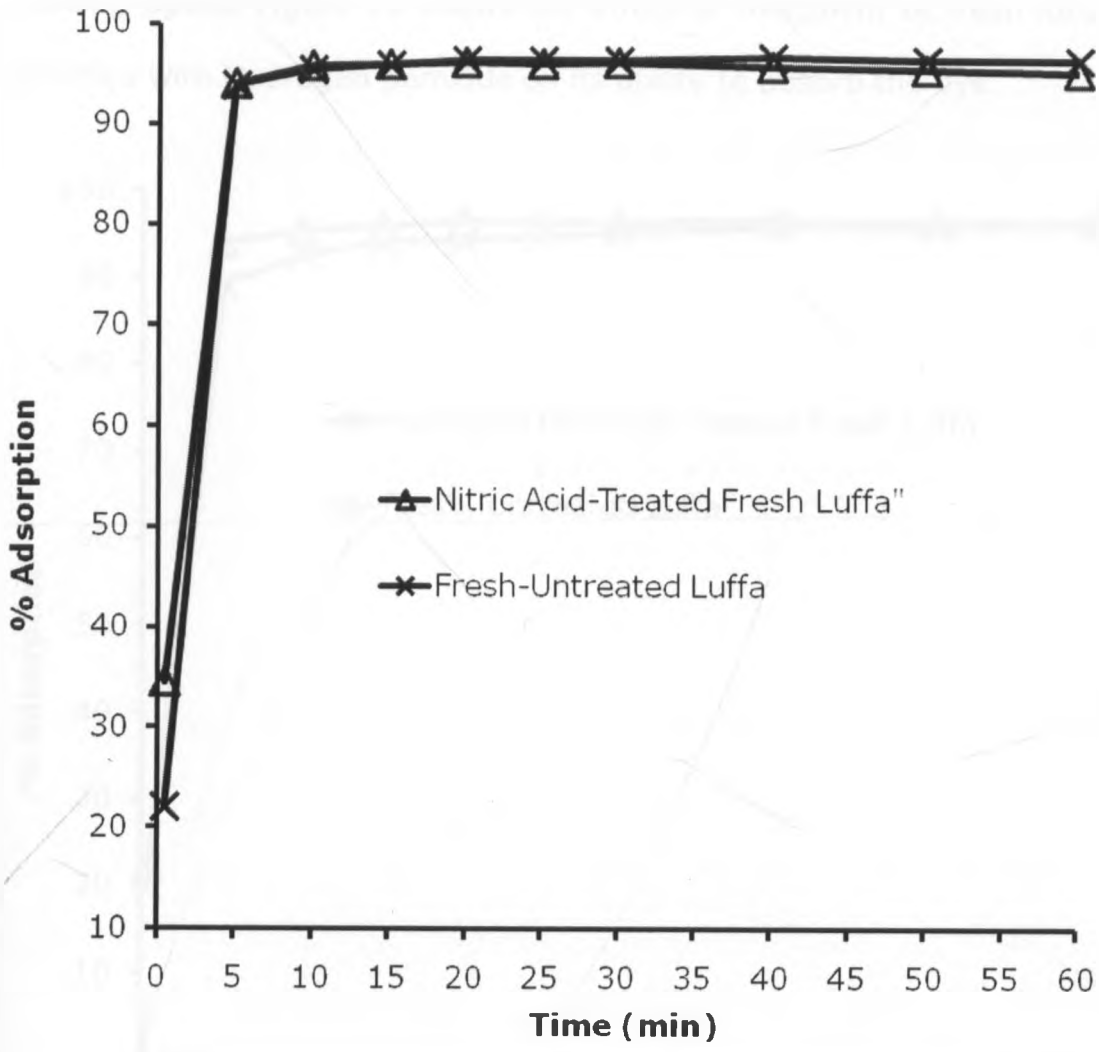

Figure 14: Effect of treatment of *luffa cylindrica* with nitric acid

4.5.2 Effect of Treatment of *Luffa Cylindrica* with Hydrogen Peroxide

Hydrogen peroxide was also investigated as a possible agent for the regeneration of spent *luffa cylindrica* due to the fact that it is a strong

oxidising agent. Figure 15 shows the effect of treatment of fresh *luffa cylindrica* with Hydrogen peroxide on its ability to adsorb the dye.

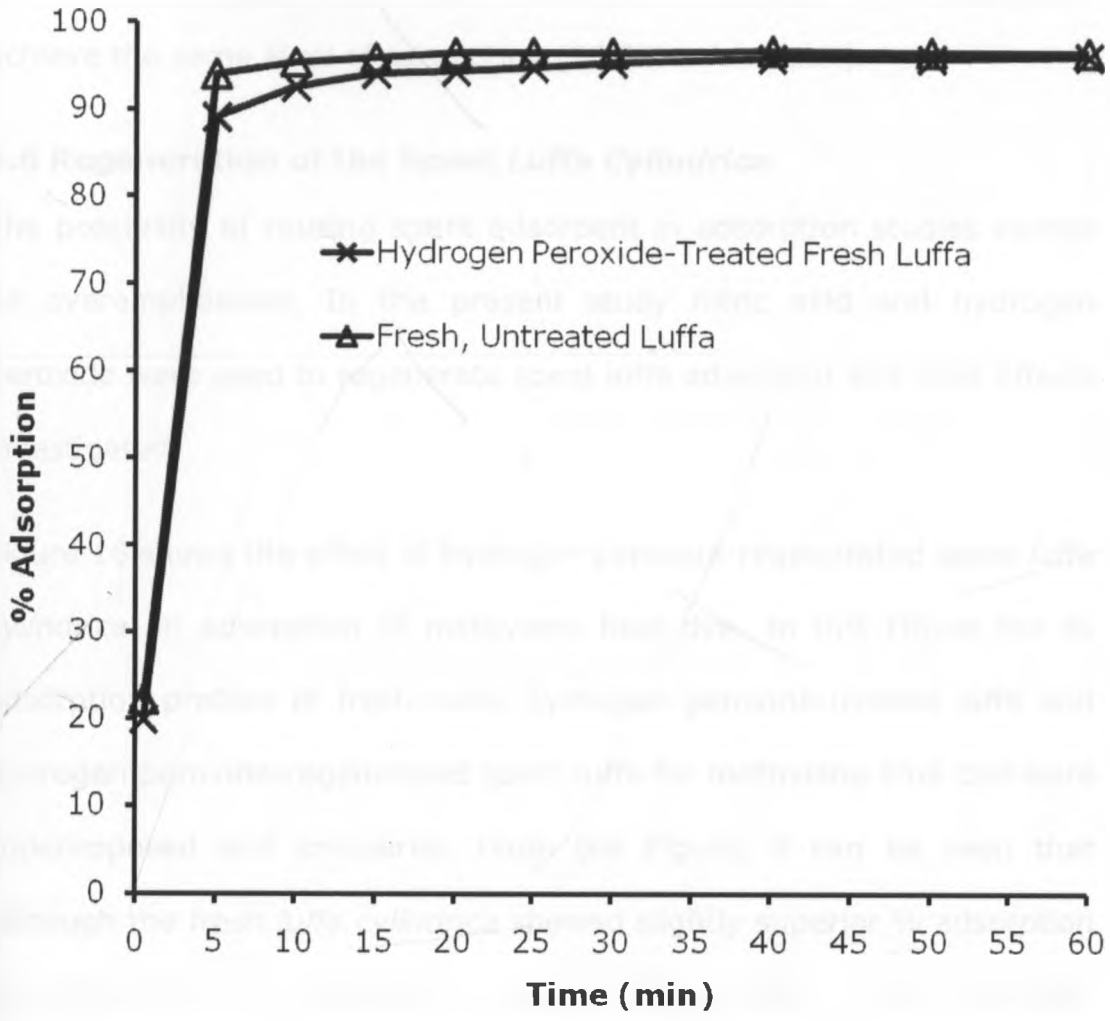

Figure 15: Effect of treatment of *luffa cylindrica* with hydrogen peroxide

It is observed from Figure 15 that although the H_2O_2-treated *luffa cylindrica* showed a slightly lower ability to adsorb the dye, the difference can be considered as negligible, in the order of 96.5% against 94.4% for fresh luffa compared to the hydrogen peroxide-treated luffa,

respectively, after 20 minutes of equilibration time. It is also significant to note that whereas the fresh luffa took only 15 minutes to attain 96.0% adsorption, it took the H_2O_2-treated luffa about 60 minutes to achieve the same level of adsorption (96.2% adsorption).

4.6 Regeneration of the Spent *Luffa Cylindrica*

The possibility of reusing spent adsorbent in adsorption studies cannot be overemphasised. In the present study nitric acid and hydrogen peroxide were used to regenerate spent luffa adsorbent and their effects investigated

Figure 16 shows the effect of hydrogen peroxide-regenerated spent *luffa cylindrica* on adsorption of methylene blue dye. In this Figure the % adsorption profiles of fresh luffa, hydrogen peroxide-treated luffa and hydrogen peroxide-regenerated spent luffa for methylene blue dye were superimposed and compared. From the Figure, it can be seen that although the fresh *luffa cylindrica* showed slightly superior % adsorption over the first 15 minutes of contact time, there is no significant difference in % adsorption thereafter. This indicates that regeneration of spent luffa using hydrogen peroxide has no deleterious effect on the adsorption properties of $H_2\Theta_2$-regenerated luffa.

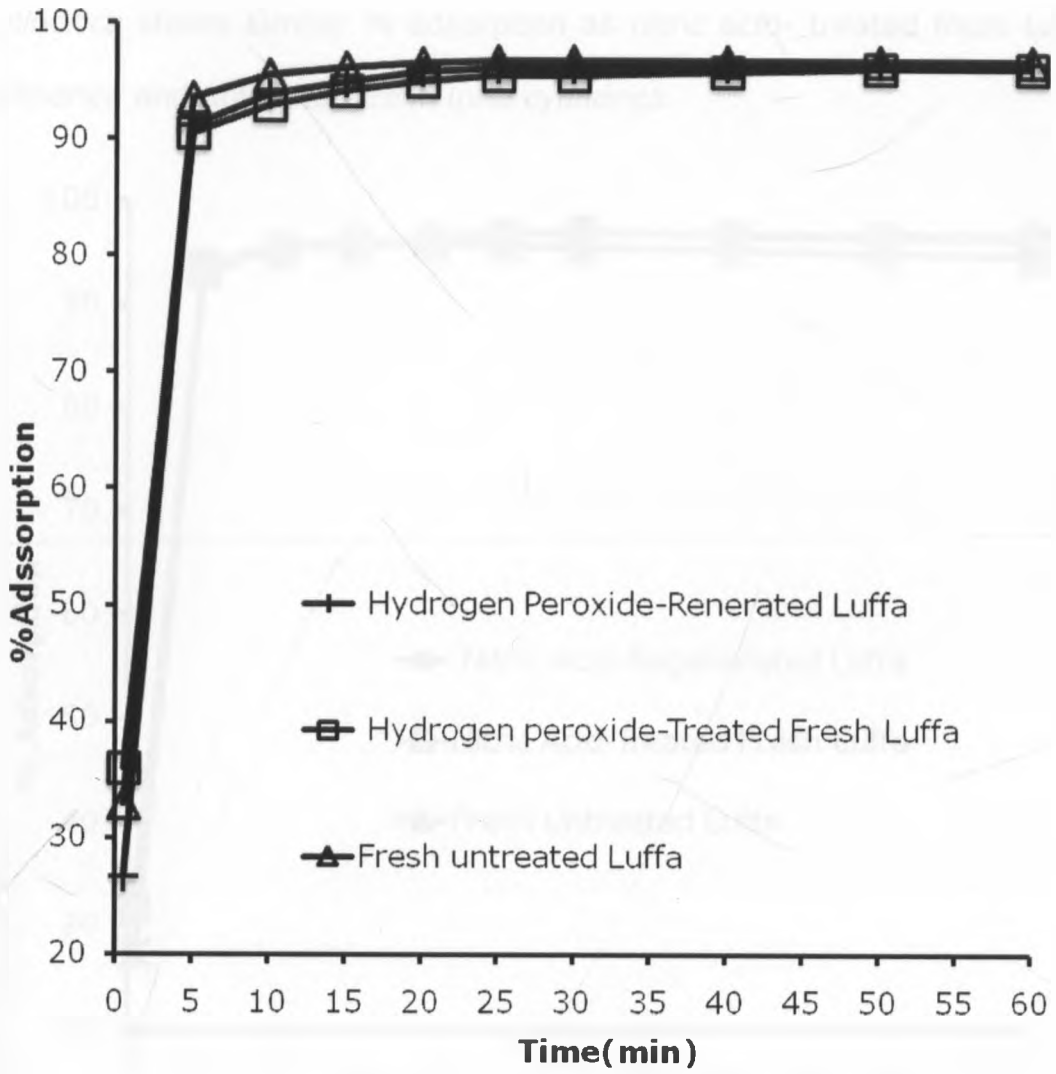

Figure 16: Effect of regeneration of spent *luffa cylindrica* with hydrogen peroxide.

Similarly, nitric acid was found not to have any negative effect on % adsorption of the dye by nitric acid-regenerated spent luffa.

Figure 17 compares the % adsorption of methylene blue dye by nitric acid regenerated spent luffa, nitric acid-treated fresh luffa and fresh *luffa cylindrica*. It is clear from the Figure that the regenerated *luffa*

cylindrica shows similar % adsorption as nitric acid- treated fresh *luffa cylindrica* and untreated fresh *luffa cylindrica*.

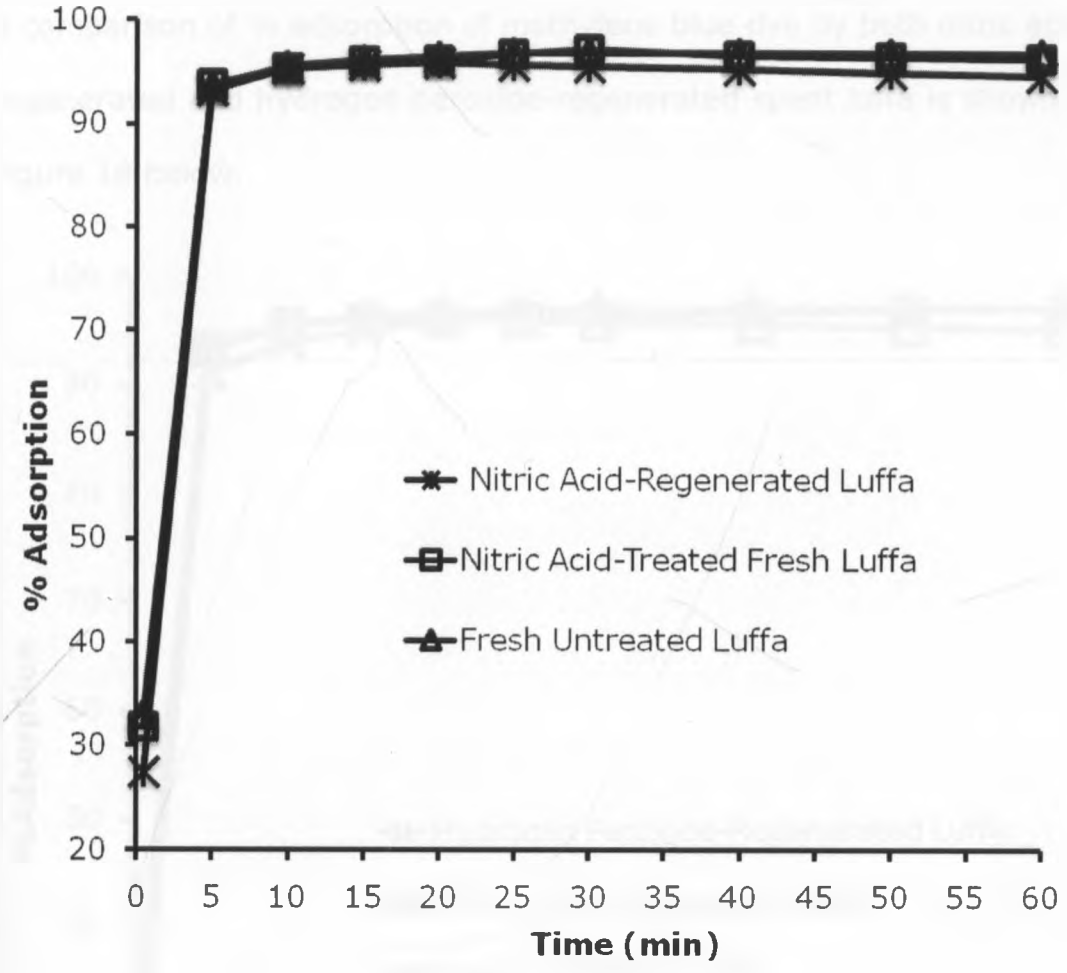

Figure 17: Superimposed % adsorption profiles of nitric acid-regenerated luffa, nitric acid-treated fresh luffa and untreated fresh luffa on methylene blue dye

Thus, it can be concluded that the acid does not affect the ability of the luffa to adsorb the dye but it only aids in the spent luffa's regeneration.

4.6.1 Comparison of Nitric Acid and Hydrogen Peroxide as Regeneration Agents

A comparison of % adsorption of methylene blue dye by both nitric acid-regenerated and hydrogen peroxide-regenerated spent luffa is shown in Figure 18 below.

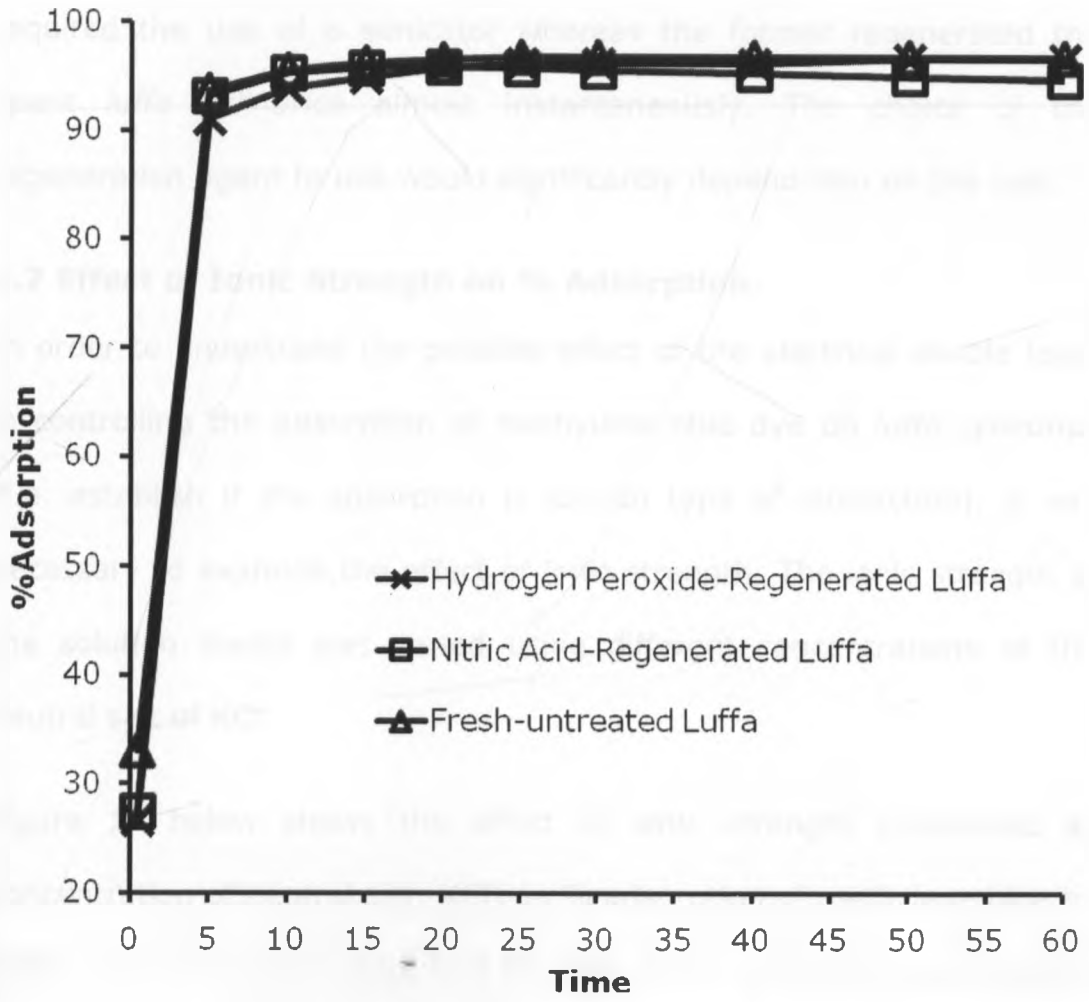

Figure 18: comparison of the effect of hydrogen peroxide and nitric acid on regeneration of spent *luffa cylindrica*

It is clear from the superimposed % adsorption plots that the two regeneration agents produced quite similar effects across the whole contact time. Therefore, both the acid and the peroxide can be used to effectively regenerate spent *luffa cylindrica*. It is however important to note that nitric acid would be a better choice over hydrogen peroxide as the latter took a much longer time to regenerate an equal mass and it required the use of a sonicator whereas the former regenerated the spent *luffa cylindrica* almost instantaneously. The choice of the regeneration agent to use would significantly depend also on the cost.

4.7 Effect of Ionic Strength on % Adsorption.

In order to understand the possible effect of the electrical double layer in controlling the adsorption of methylene blue dye on *luffa cylindrica* (i.e. establish if the adsorption is ion-ion type of interaction), it was necessary to examine the effect of ionic strength. The ionic strength of the solution media was varied using different concentrations of the neutral salt of KCl.

Figure 19 below shows the effect of ionic strength (measured as concentration of neutral salt, KCl) on % adsorption of methylene blue by *luffa cylindrica*. It is evident that for each of the two dye concentrations used, there was no discernible effect on the % adsorption caused by increase in the ionic strength of the solution mixture. Thus the % adsorption was found to be independent of ionic strength of the dye solution. This is indicative of the non-ionic nature of the interaction

between the adsorbate and adsorbent in this luffa – methylene blue adsorption system under these near neutral pH conditions employed.

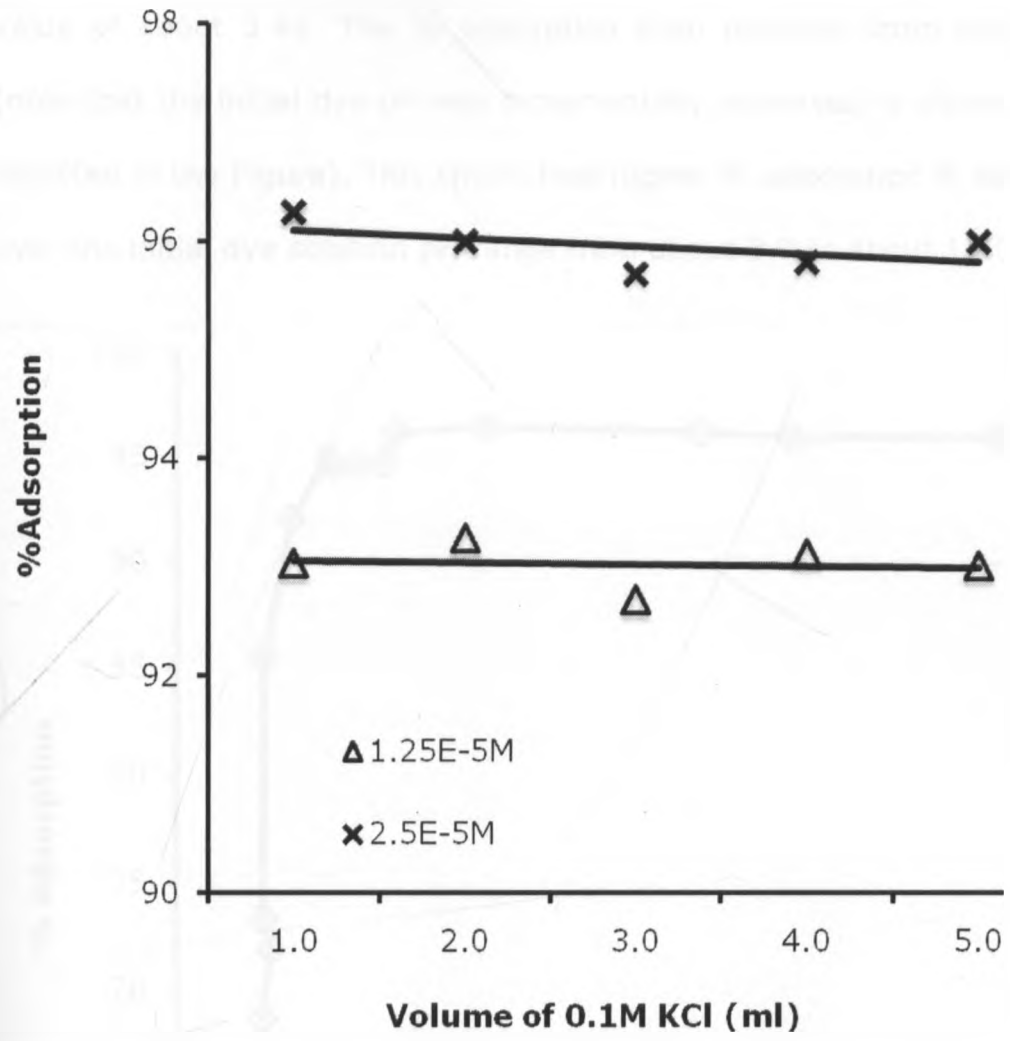

Figure 19: The effect of ionic strength (expressed as concentration of KCl) on % adsorption of methylene blue dye.

4.8 Effect of pH on Adsorption.

In order to illustrate whether there is a relationship between the % adsorption and the pH of the methylene blue dye solution, a plot of %

adsorption verses initial dye pH is provided in Figure 20. From the Figure, it is clearly evident that the % adsorption increases sharply from below 70% at an initial pH of 2.81 to about 95% at initial solution pH value of about 3.41. The % adsorption then plateaus from there on, (note that the initial dye pH was incrementally increased to above 10 as depicted in the Figure). This shows that higher % adsorption is obtained over the initial dye solution pH range from about 3.9 to about 11.0.

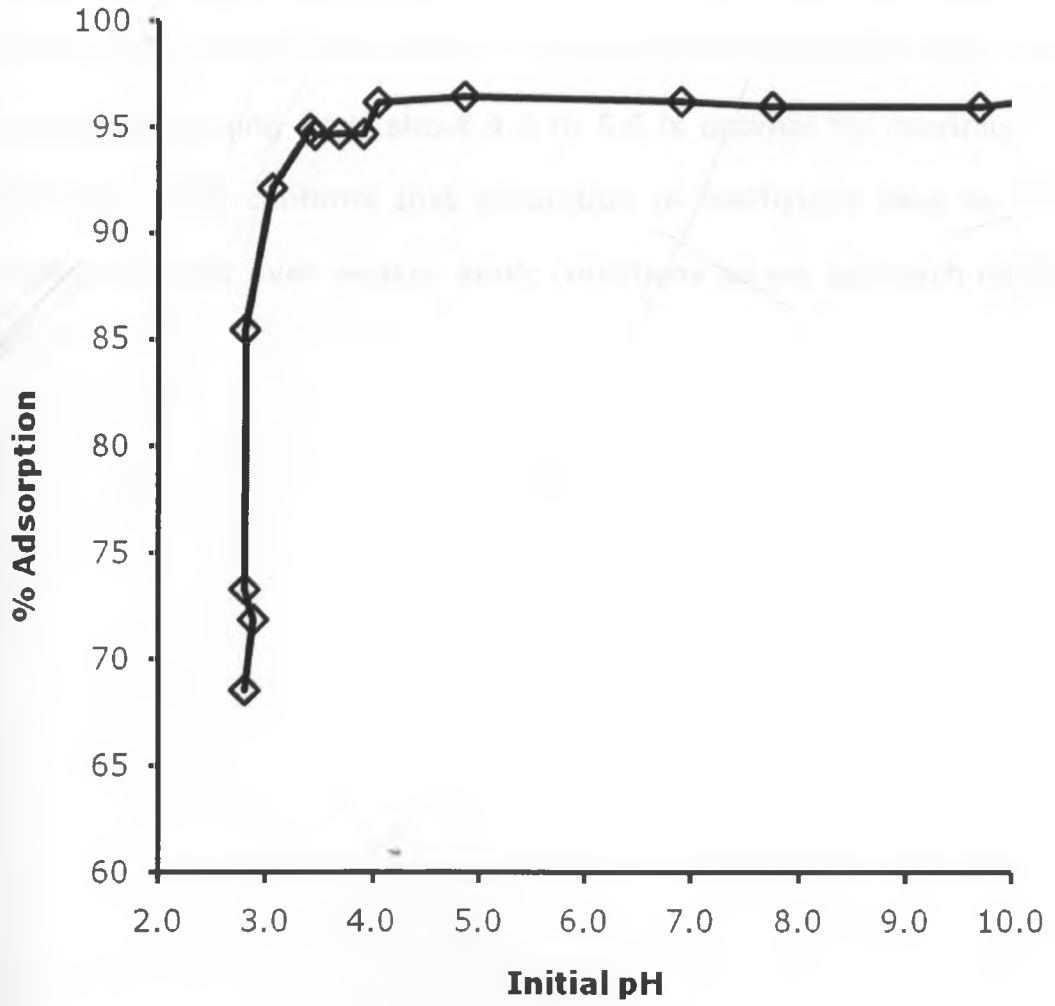

Figure 20: Effect of initial dye solution pH on % adsorption.

It is clear that highly acidic conditions are not favourable for the adsorption of methylene blue dye by *luffa cylindrica*.

As part of the understanding of the possible mechanism of adsorption between the dye and *luffa cylindrica*, the resultant pH of the dye-luffa solution mixture was measured and compared with the initial pH of the dye solution alone.

The corresponding plot of % adsorption versus final or resultant solution mixture pH is shown in Figure 21. From this plot it is evident that a final solution pH ranging from about 4.3 to 5.6 is optimal for maximum % adsorption. This confirms that adsorption of methylene blue by *luffa cylindrica* is best over weaker acidic conditions as we approach neutral pHs.

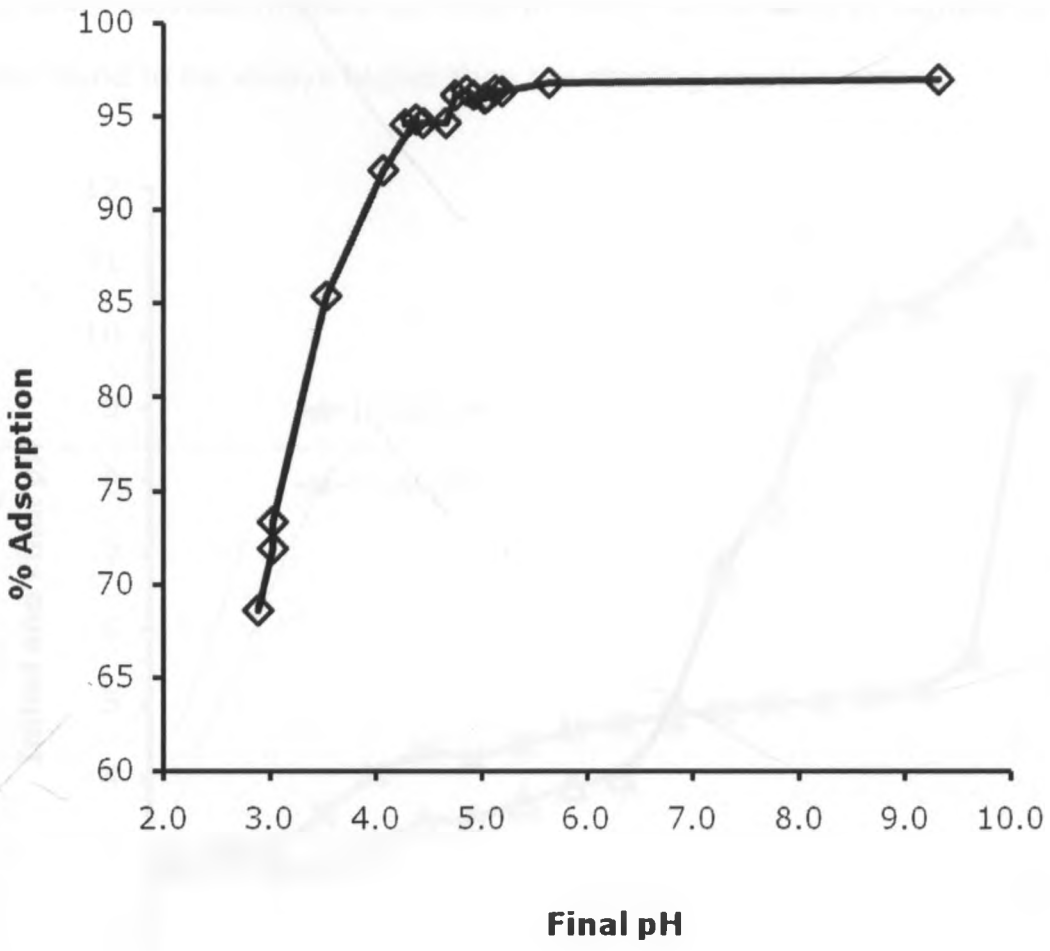

Figure 21: % Adsorption versus final dye solution-luffa mixture pH

A superimposed plot of initial pH of methylene blue dye solution and the pH of the resultant dye-*luffa cylindrica* solution mixture is given in Figure 22 below. Careful scrutiny of the Figure suggests that *luffa cylindrica* has a pH buffering ability and that the tendency is towards a resultant pH of 4.8. It is observable that for the test solution where the initial dye pH was

below about 4.8 (i.e test numbers between 3-11) the pH of the resultant solution mixture i.e. final pH after 20 minutes of contact time was found to be always higher than the starting solution pH.

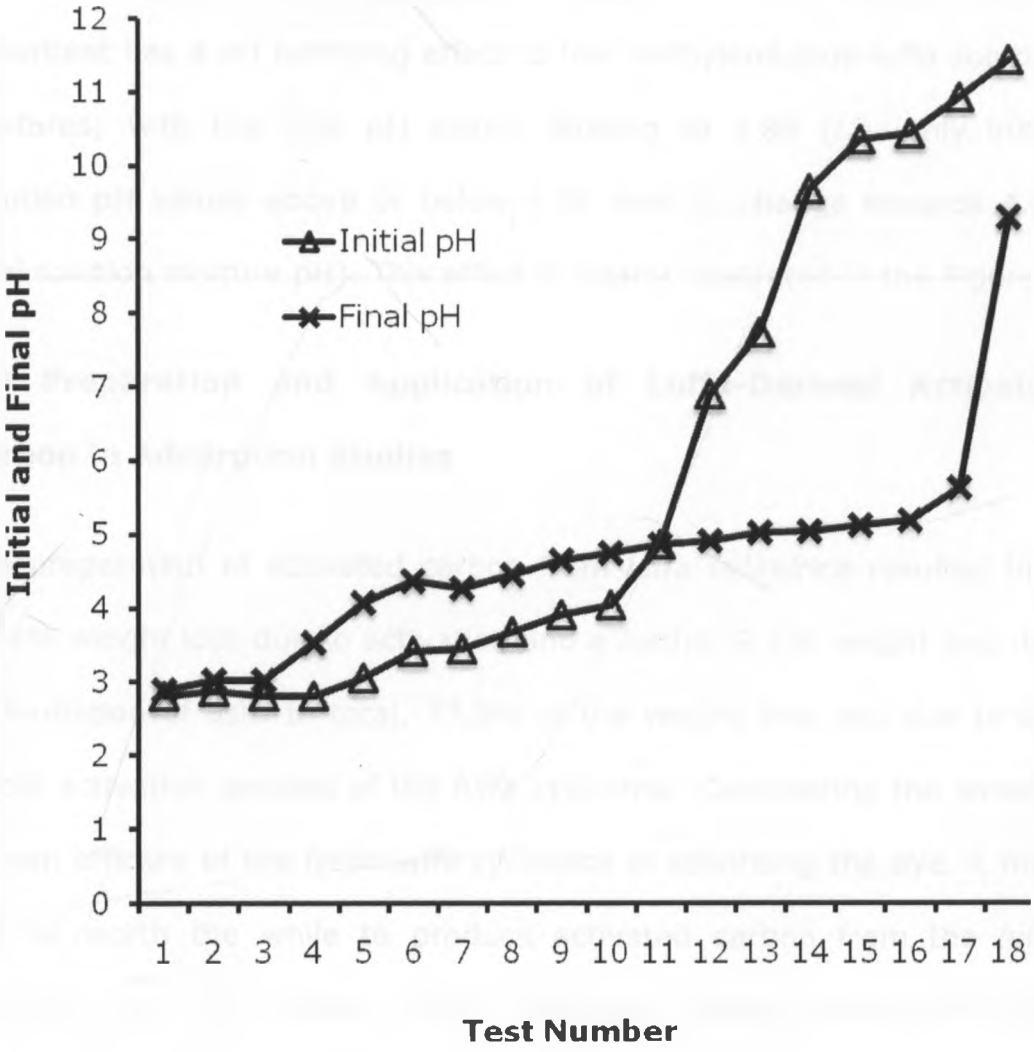

Figure 22: Initial and final solution pH against the test number

For solution mixtures whose initial pH values were above about 4.8 (i.e. the test numbers 11-17), the resulting solution mixture pH after 20 minutes of contact time was however, always found to be lower than

the initial solution pH values and hovering about 4.8. Overall, the final solution mixture pH after 20 minutes of contact time appears to hover between 4.2 and 5.0 despite the initial solution pH ranging from 3.0 to as high a pH as 11.0. This seem to suggest that the *luffa cylindrica* adsorbent has a pH buffering effect to the methylene blue-luffa solution mixtures; with the final pH values tending to 4.86 (i.e. only initial solution pH values above or below 4.86 tend to change towards 4.86 final solution mixture pH). This effect is clearly illustrated in the Figure.

4.9 Preparation and Application of Luffa-Derived Activated Carbon in Adsorption Studies

The preparation of activated carbon from *luffa cylindrica* resulted in a 68.4% weight loss due to activation and a further 9.1% weight loss due to formation of ash. In total, 77.5% of the weight loss was due to the whole activation process of the *luffa cylindrica*. Considering the already proven efficacy of the fresh *luffa cylindrica* in adsorbing the dye, it may not be worth the while to produce activated carbon from the *luffa cylindrica* for the purpose of dye removal, except perhaps for the purpose of regeneration. See appendix 9 for data on preparation of activated carbon from *luffa cylindrica*.

Studies were done using the luffa-derived activated carbon and the various studies and observations are recorded in the subsequent subsections.

4.9.1 Effect of Contact Time on % Adsorption of Dye by Luffa-Derived Activated Carbon

Figure 23 shows the effect of contact time between luffa-derived activated carbon and $2.5x10^{-5}$M concentration of methylene blue dye solution.

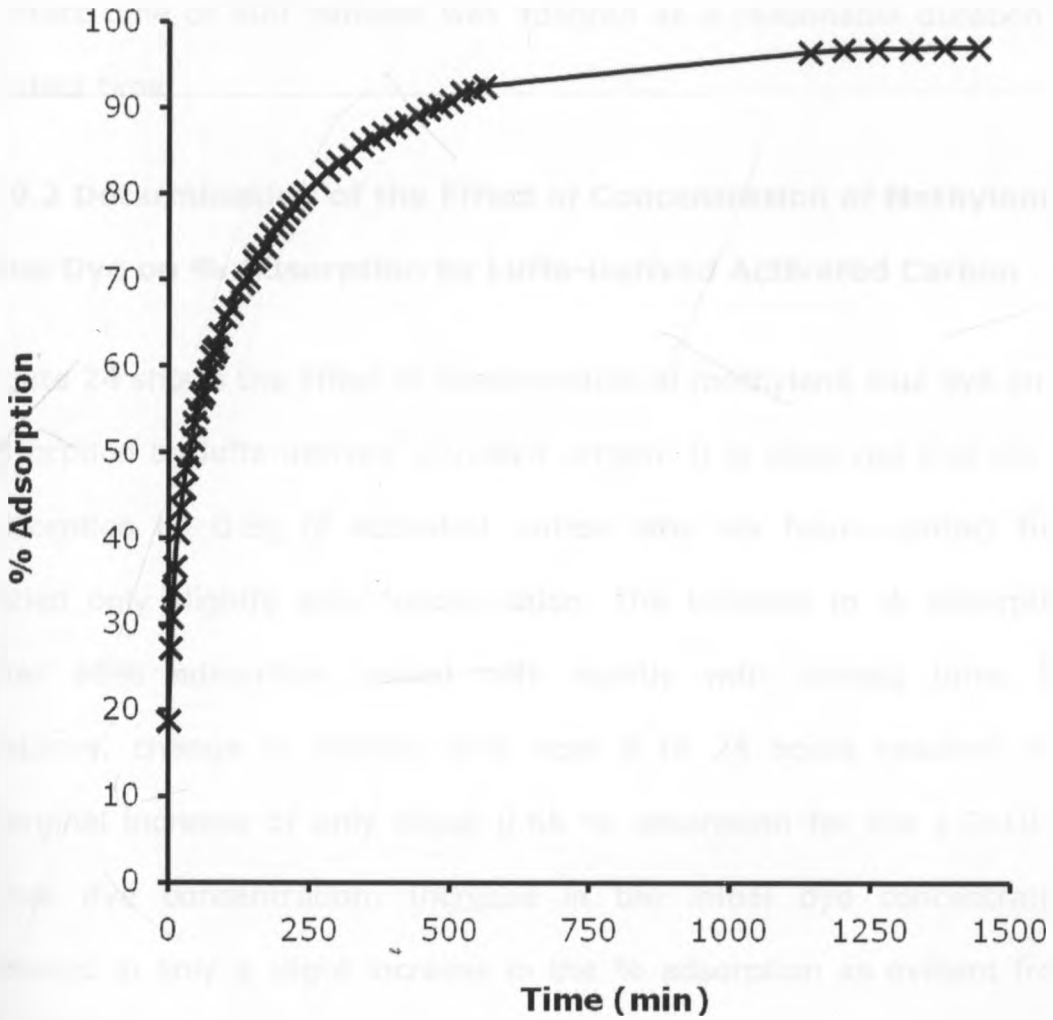

Figure 23: Effect of contact time between luffa-derived activated carbon and $2.5x10^{-5}$m methylene blue dye solution

It is observed from the Figure that a plateau was attained only after 800 minutes (over 13 hours) of contact and for practical purpose any further increase in the % adsorption after 800 minutes could be overlooked. The optimum contact time was a lot longer than expected. Although there was some change in the amount adsorbed from 800 minutes to 1400 minutes, the change was very gradual (Appendix 7). Hence contact time of 800 minutes was adopted as a reasonable duration of contact time.

4.9.2 Determination of the Effect of Concentration of Methylene Blue Dye on % Adsorption by Luffa-Derived Activated Carbon

Figure 24 shows the effect of concentration of methylene blue dye on % adsorption by luffa-derived activated carbon. It is observed that the % adsorption by 0.5g of activated carbon after six hours contact time varied only slightly with concentration. The increase in % adsorption after 95% adsorption varied only slightly with contact time. For instance, change in contact time from 6 to 24 hours resulted in a marginal increase of only about 0.65 % adsorption for the $1.0x10^{-5}$M initial dye concentration. Increase in the initial dye concentration resulted in only a slight increase in the % adsorption as evident from Figure 24.

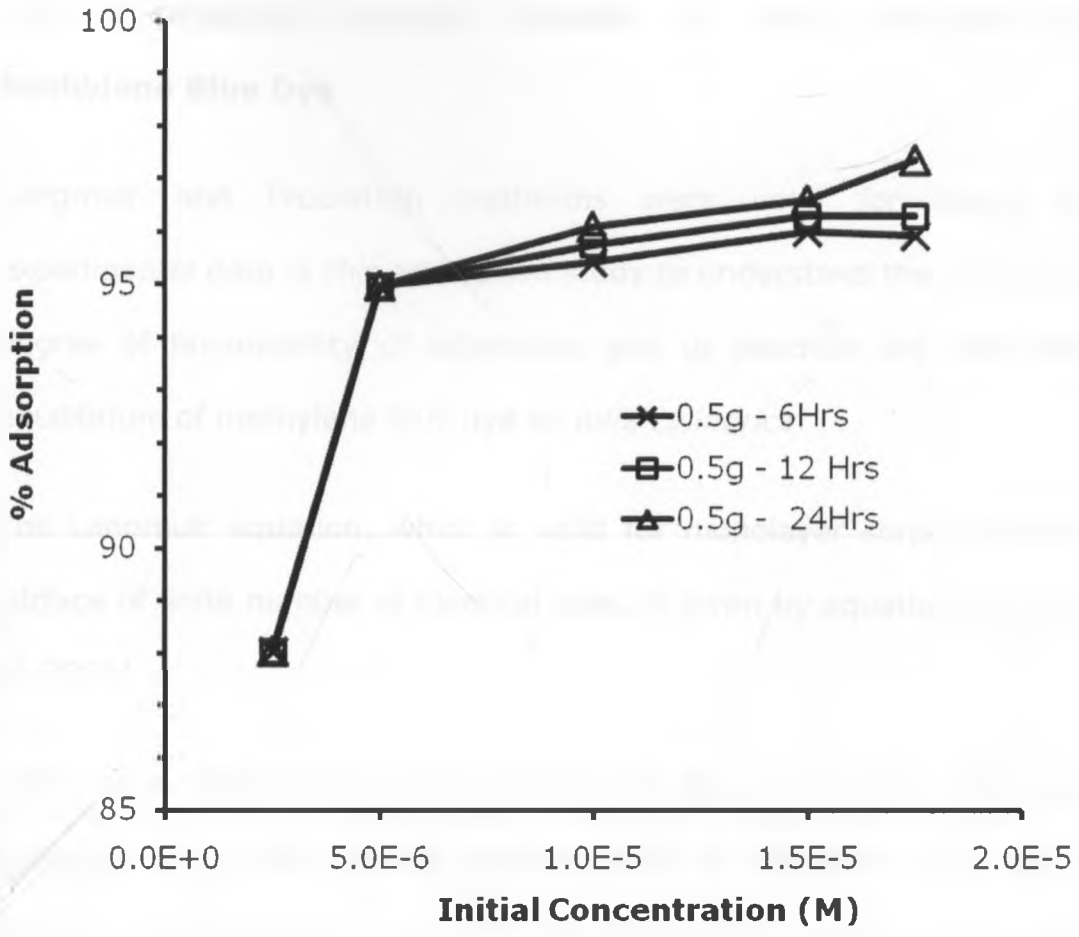

Figure 24: Effect of concentration on adsorption by luffa-derived activated carbon

From these observations, the change in % adsorption with increase in initial dye concentration is insignificant, may be due to the 0.5g luffa-derived activated carbon getting saturated by adsorbing about 95% of the dye from $5.0x10^{-6}$M initials dye concentration such that any further increase in initial dye concentration does not result in significant increase in % adsorption

4.10 Adsorption Isotherm Studies of *Luffa Cylindrica* for Methylene Blue Dye

Langmuir and Freundlich isotherms were used for fitting the experimental data in this adsorption study to understand the extent and degree of favourability of adsorption and to describe the adsorption equilibrium of methylene blue dye on *luffa cylindrica*.

The Langmuir equation, which is valid for monolayer sorption onto a surface of finite number of identical sites, is given by equation 1: (Ho *et al,* 2001).

where q_e is milligrams of dye accumulated per gram of the adsorbent material; C_{eq} is the residual concentration of methylene blue dye in solution at equilibrium; q_{max} is the maximum amount of the dye molecules adsorbed per unit weight of the adsorbent to form a complete monolayer on the surface, (q_{max} represents a practical limiting adsorption capacity when the surface is fully covered by dye molecules and assists in the comparison of adsorption performance); and b is the Langmuir constant related to the affinity of the binding sites.

When the initial dye concentration in the solution rises, adsorption increases till the binding sites are saturated. The linearised Langmuir isotherm allows the calculation of adsorption capacities and Langmuir

constants and is presented by equation 2 - see page 21, (Ho *et al*, 2001),

The essential characteristics of the Langmuir isotherms can be expressed in terms of a dimensionless constant, the separation factor or equilibrium parameter, R_L which is defined as:

$$R_L = \frac{1}{1 + bC_o}$$ ..... Equation 5,

where b is the Langmuir constant and C_o is the initial concentration of the methylene blue dye in solution. The R_L value indicates the descriptions of isotherm as shown in Table 1 below: An isotherm is favorable, if its fixation capacity grows rapidly with equilibrium concentration. The maximum for a highly favorable isotherm is irreversible adsorption, where the amount adsorbed does not depend on the decrease in concentration down to very low values, unlike unfavorable isotherms, which have a low adsorption capacity at low concentrations at equilibrium. The R_L value indicates the shape of the isotherm to be irreversible (R_L = 0), favourable ($0<R_L<1$); linear (R_L =1) or unfavourable ($R_L>1$)

The R_L for methylene blue dye adsorption on *luffa cylindrica* was found to be equal to 1.00 for both the initial concentrations of $2.5X10^{-6}$M and

$2.5X10^{-5}M$ methylene blue dye, indicating that the adsorption of methylene blue dye by 0.5g *luffa cylindrica* was linear.

Table1: Relationship between the Separation Factor (R_L) and the Type of Isotherm

R_L	Type of Isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0<R_L<1$	Favourable
$R_L = 0$	Irreversable

On the other hand, the Freundlich isotherm is represented by the Equation 3, (*Ho et al, 2001*) see page 2.

The linearised form of Freundlich adsorption isotherm (see Equation 4 – page 22) was used to evaluate the sorption data.

A perfect fit of the experimental data into the Freundlich isotherm implies that K_f, obtainable from the intercept, is roughly an indicator of the sorption capacity and the slope, 1/n, of the sorption intensity. These constants incorporate all the factors affecting the adsorption process.

The Freundlich constant, n also indicates the degree of favourability of adsorption. The Freundlich constant, n should have values lying in the range of 1 to 10 for classification as favourable adsorption. Smaller

values of (1/n) indicate a stronger bond between the adsorbate and the adsorbent.

4.10.1 Langmuir Adsorption Isotherm Studies for Methylene Blue Dye

The performance of *luffa cylindrica* in the removal of methylene blue dye solution was evaluated by comparing the adsorption isotherms of methylene blue dye onto the adsorbent under varying conditions of adsorbent weight and contact time. The Langmuir expression which is valid for monolayer sorption coverage onto a surface of finite number of adsorption sites is given by Equation 1 (*Ho et al, 2001*).

From Equation 3, q_e is expected to increase linearly with initial dye concentration at low adsorbate concentrations. However, when the equilibrium dye concentration in solution rises, adsorption of the dye onto the adsorbent increases until all the binding sites are saturated. In fact, a plot of q_e against equilibrium dye concentration (C_{eq}) is expected to plateau over the concentration range for which all binding sites are saturated (if monolayer coverage is exhibited). Note that at high C_{eq} values, the limit of denominator of Equation 1 becomes unity and hence $q_e = q_{max}$.

Figure 25 below shows superimposed plots of equilibrium sorption capacity q_e verses equilibrium dye concentration for varying contact

values of (1/n) indicate a stronger bond between the adsorbate and the adsorbent.

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Figure 25 below shows superimposed plots of equilibrium sorption capacity q_e verses equilibrium dye concentration for varying contact

times of 10, 20 and 60 minutes when 0.5g luffa is used as adsorbent. It is clearly evident from the Figure that; first, the magnitude of the equilibrium sorption capacity increases with contact time and the equilibration time between the adsorbate and adsorbent with 10 minutes contact time shows the least sorption capacity values.

Second, it is evident from the Figure that none of the plots shows evidence of saturation of the adsorption sites of the *luffa cylindrica*- exhibited by lack of plateauing of the profiles.

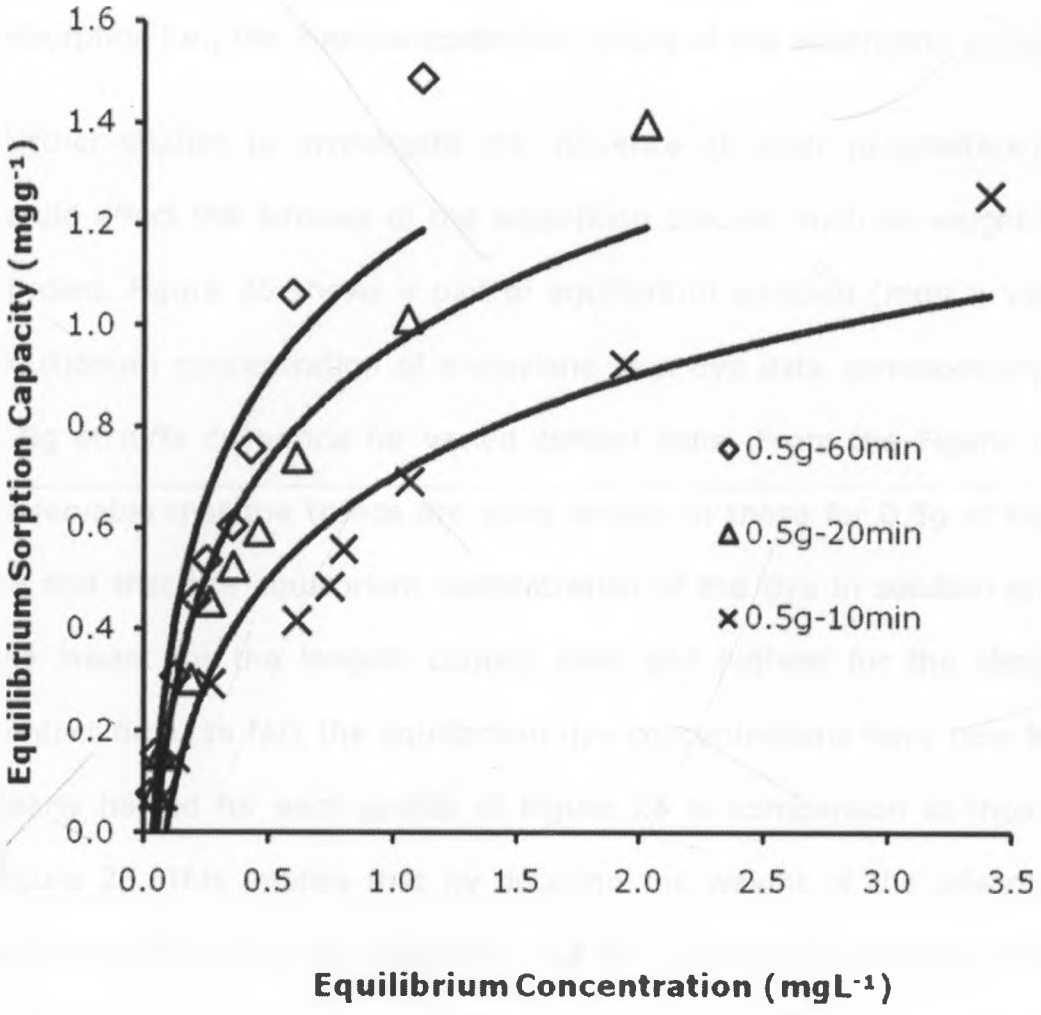

Figure 25: Plot of equilibrium sorption (mgg^{-1}) versus equilibrium concentration of methylene blue dye when 0.5g of *luffa cylindrica* was used for varied contact times

Third, it is also evident that the equilibrium dye concentration in solution increases with increasing contact time implying that increasing contact time affords the adsorbent more time for more dye molecules to

be adsorbed. This is indicative of the significance of contact time on adsorption i.e., the kinetics-controlled nature of the adsorption process.

Further studies to investigate the influence of other parameters that would affect the kinetics of the adsorption process such as weight was studied. Figure 26 shows a plot of equilibrium sorption (mgg^{-1}) verses equilibrium concentration of methylene blue dye data corresponding to 1.0g of *luffa cylindrica* for varied contact time. From the Figure, it is observable that the trends are quite similar to those for 0.5g of Figure 25 and that the equilibrium concentration of the dye in solution is still the lowest for the longest contact time and highest for the shortest contact time. In fact the equilibrium dye concentrations have now been nearly halved for each profile of Figure 26 in comparison to those of Figure 25. This implies that by doubling the weight of the adsorbent, more dye molecules are adsorbed and the residual dye becomes nearly halved. Absence of a plateau shows that equilibrium had not been fully attained even after 60 minutes of contact time.

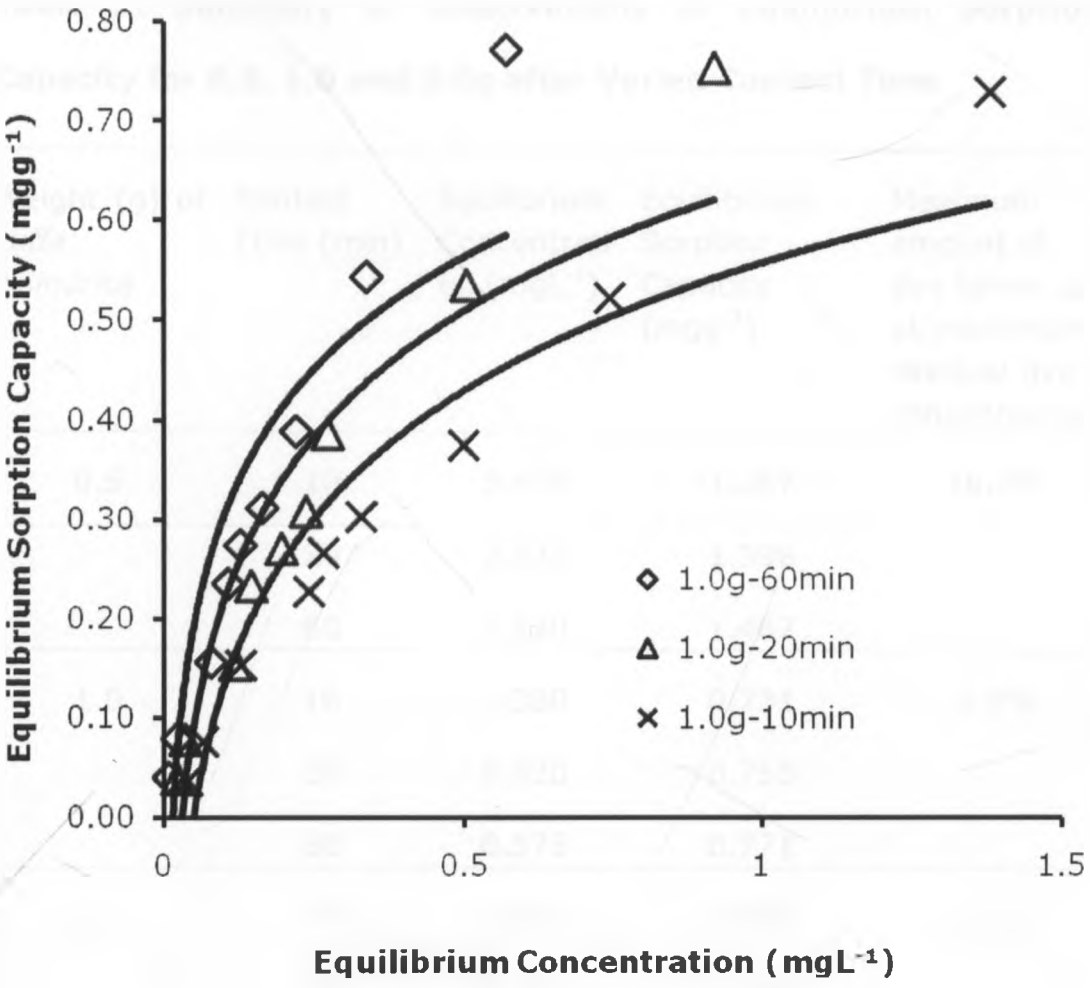

Figure 26: Plot of equilibrium sorption (mgg^{-1}) verses equilibrium concentration of methylene blue dye data corresponding to 1.0g of *luffa cylindrica* for varied contact time

In order to clearly examine and discern the behaviour of the *luffa cylindrica* – methylene blue dye solution mixture, in relation to variation in weight of the *luffa cylindrica* employed and varied contact time, a summary of the observations of equilibrium sorption capacity for 0.5g, 1.0g and 2.0g after varied contact time are tabulated in Table 2.

Table 2: Summary of Observations of Equilibrium Sorption Capacity for 0.5, 1.0 and 2.0g after Varied Contact Time

Weight (g) of *Luffa cylindrica*	Contact Time (min)	Equilibrium Concentration (mgL^{-1})	Equilibrium Sorption Capacity (mgg^{-1})	Maximum amount of dye taken up at maximum residual dye concentration
0.5	10	3.405	1.257	18.3%
	20	2.025	1.396	
	60	1.120	1.487	
1.0	10	1.380	0.731	5.5%
	20	0.920	0.753	
	60	0.573	0.771	
2.0	10	0.695	0.382	2.6%
	20	0.532	0.386	
	60	0.312	0.392	

Careful scrutiny of Table 2 and calculating the percentage change in maximum amount of dye adsorbed per unit weight of the adsorbent between contact times of 10 minutes and 60 minutes (i.e. amount adsorbed after 60 minutes (A_{60}) minus amount adsorbed after 10 minutes (A_{10}) divided by amount adsorbed after 10 minutes and then multiplying by 100%) i.e. $\frac{A_{60}-A_{10}}{A_{10}} \times 100\%$ shows a general reduction from 18.3% through 5.5% to 2.6%. This shows that with further increase in

adsorbent weight, 10 minutes would be deemed sufficient time to ensure 100% removal of residual dye.

Figure 27 below, which is a plot of equilibrium dye concentration (mgL^{-1}) versus contact time for three sets of weights of luffa is further proof of the combined effect of weight and time of contact on removal of dye from solution. It shows that for all the weights employed, the equilibrium concentration reduces as expected with increasing contact time: More contact time provides a better opportunity for more adsorption to take place. Increasing the weight of adsorbent also avails more adsorption sites resulting in reduced equilibrium dye concentration (i.e. residual dye concentration) for a particular period of contact time. From the Figure, it was also observed that allowing longer contact time resulted in a higher sorption capacity for a particular weight used.

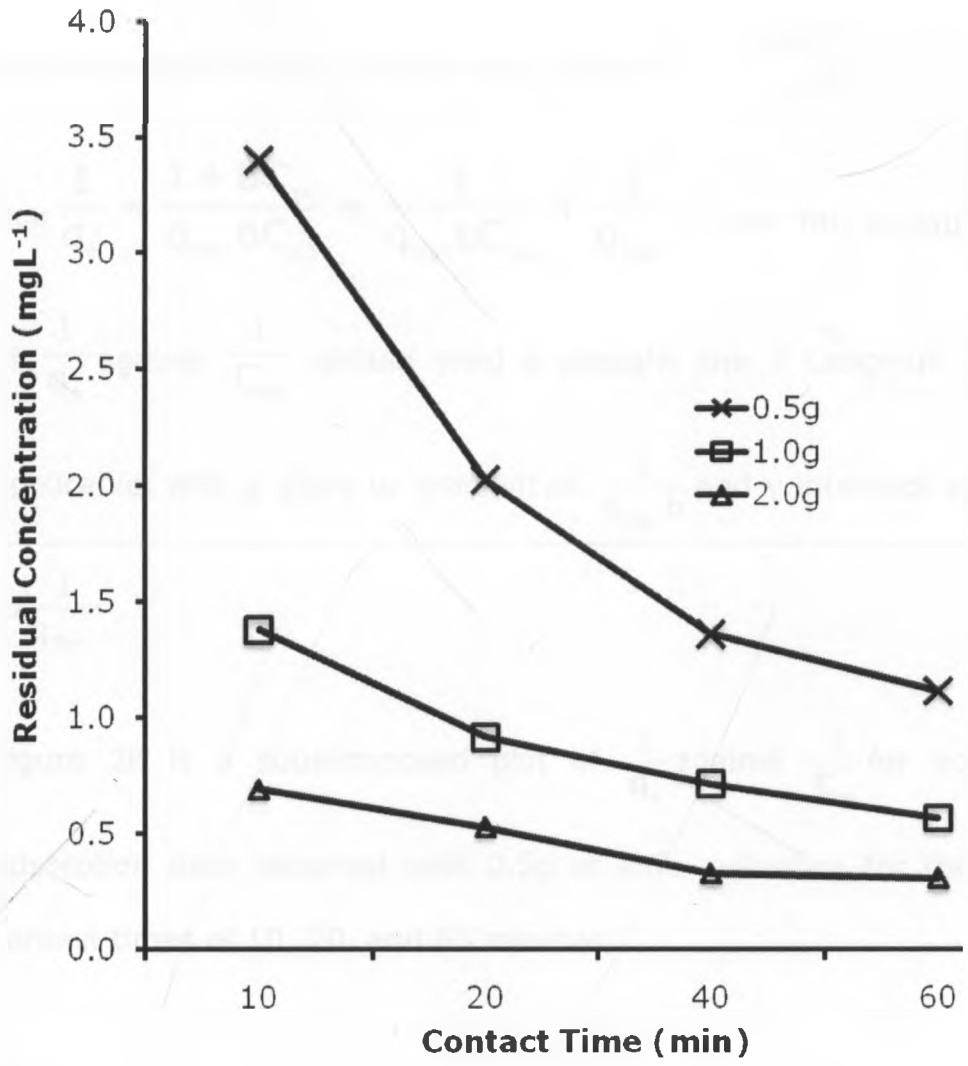

Figure 27: Residual dye concentration versus contact time

The equilibrium adsorption data was used to test conformity with the Langmuir adsorption isotherm. The data was fitted to the linearised form of Langmuir isotherm.

The linearised form of Langmuir expression $q_e = \frac{q_{max} bC_{eq}}{1 + bC_{eq}}$ is such that $\frac{1}{q_e} = \frac{1 + bC_{eq}}{q_{max} bC_{eq}} = \frac{1}{q_{max} bC_{eq}} + \frac{1}{q_{max}}$. From this equation a plot of $\frac{1}{q_e}$ against $\frac{1}{C_{eq}}$ should yield a straight line if Langmuir model is applicable, with a slope or gradient of $\frac{1}{q_{max} b}$ and y intercept equivalent to $\frac{1}{q_{max}}$.

Figure 28 is a superimposed plot of $\frac{1}{q_e}$ against $\frac{1}{C_{eq}}$ for equilibrium adsorption data obtained with 0.5g of *luffa cylindrica* for the various contact times of 10, 20, and 60 minutes.

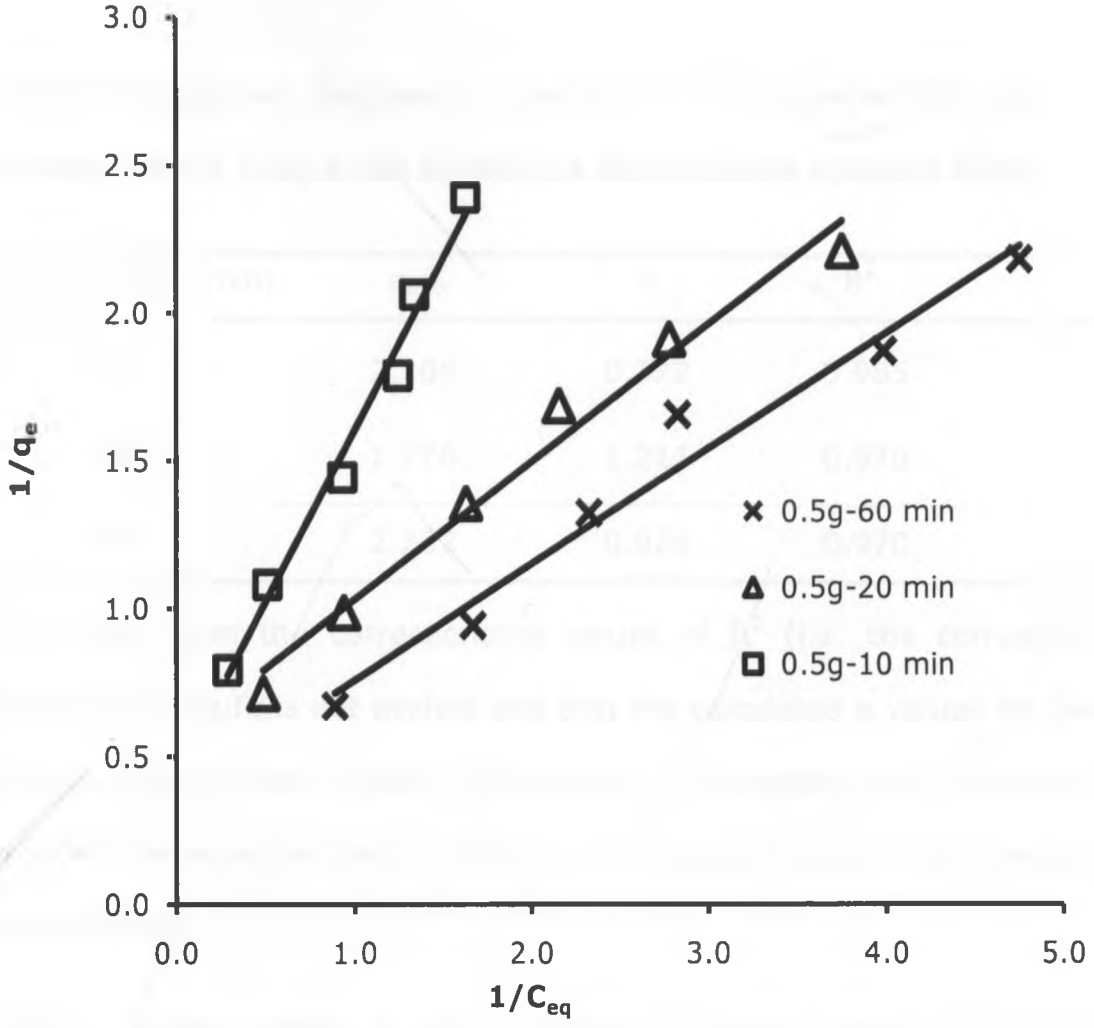

Figure 28: Langmuir adsorption isotherm for methylene blue dye on 0.5g *luffa cylindrica* after varied contact time.

The corresponding Langmuir constants are tabulated in Table 3 below.

Table 3: Langmuir Isotherm Constants for Methylene Blue Dye Adsorption on 0.5g *Luffa Cylindrica* after Varied Contact Time

Contact time (min)	q_{max}	b	R^2
10	2.309	0.372	0.985
20	1.776	1.211	0.978
60	2.752	0.928	0.970

It is clear from the corresponding values of R^2 (i.e. the correlation factor) that the fit is not perfect and that the calculated b values for the various contact times appear inconsistent, (i.e. smallest for 10 minutes as would be expected and highest for 20 minutes instead of 60 minutes contact time).

Using a larger weight of luffa however, provided better and more consistent results as depicted in Figure 29, a superimposed plot of $\frac{1}{q_e}$ versus $\frac{1}{C_{eq}}$ for adsorption data obtained with 1.0g weight of *luffa cylindrica* for the various contact times of 10, 20, and 60 minutes.

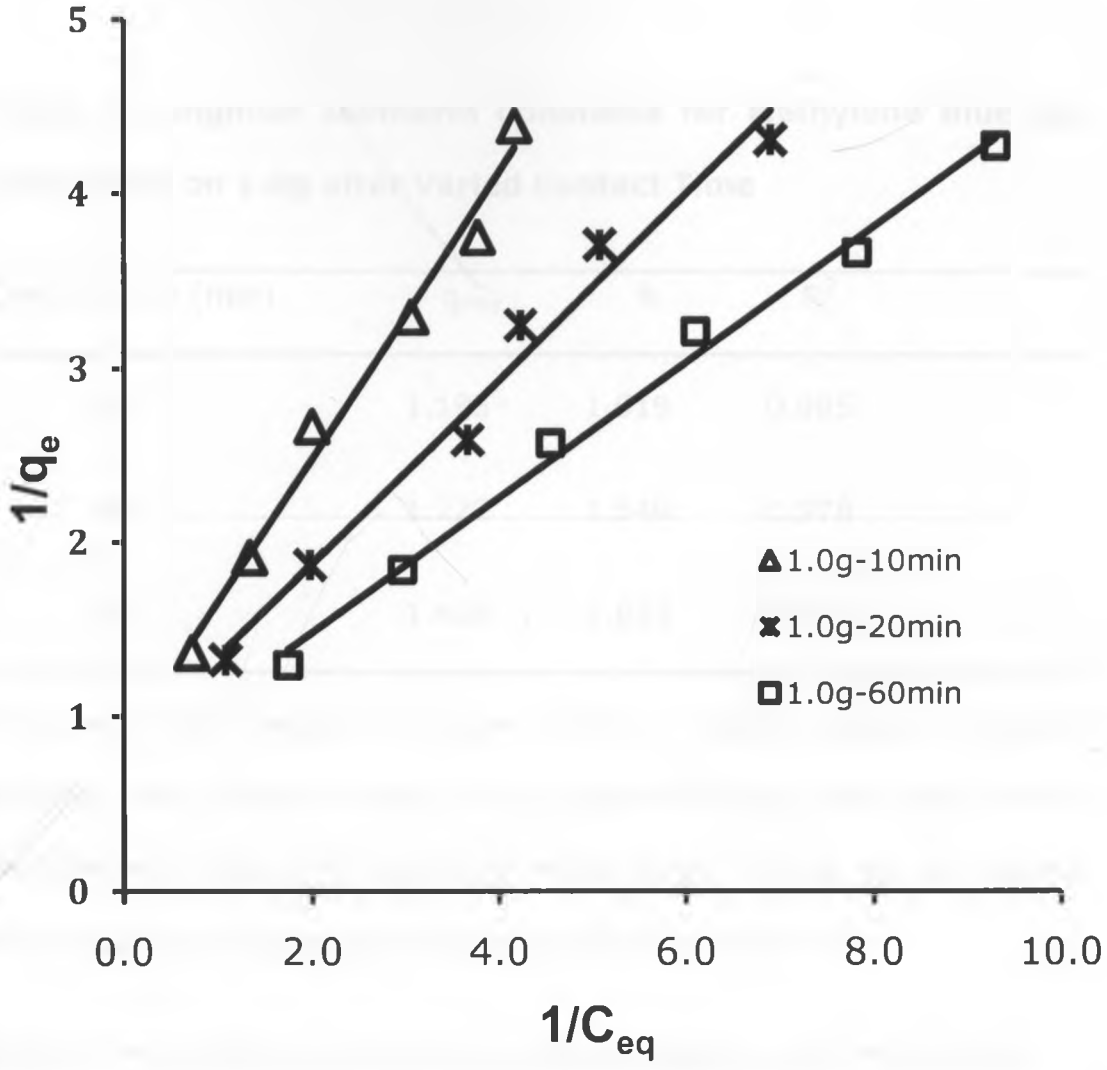

Figure 29: Langmuir adsorption isotherm for methylene blue dye on 1.0g *luffa cylindrica* after varied contact time

The corresponding Langmuir constants are given in Table 4. Here, more consistent results are observable with the b values increasing with contact time, (implying improved adsorption) and 60 minutes producing the highest R^2 value of 0.992.

Table 4: Langmuir Isotherm Constants for Methylene Blue Dye Adsorption on 1.0g after Varied Contact Time

Contact time (min)	q_{max}	b	R^2
10	1.195	1.019	0.985
20	1.222	1.549	0.978
60	1.408	1.835	0.992

It is clear from the plot of Figure 29 that a higher contact time of 60 minutes with a larger weight of 1.0g adsorbent provides data that fits the Langmuir adsorption isotherm model better. Hence we can assume monolayer coverage under these experimental conditions.

4.10.2 Freundlich Adsorption Isotherm Studies for Methylene Blue Dye

Experimental adsorption data was analysed further by subjecting it to the Freundlich isotherm model expressed as $Q_e = K_f C_e^{1/n}$, which is conveniently used in the linear form shown below:

$$\log_{10}(Q_e) = \log_{10}(K_f) + \frac{1}{n}\log_{10}(C_e)$$

Here, a plot of $\log_{10}(Q_e)$ against $\log_{10}(C_e)$ yielding a straight line indicates conformity with the Freundlich isotherm adsorption. The constants can be obtained from the slope and the intercept; where $\log(K_f)$ is the intercept and 1/n is the gradient of the plot. Figure 30 contains superimposed plots of $\log_{10}(Q_e)$ verses $\log_{10}(C_e)$ for 0.5g *luffa cylindrica* obtained at various contact times of 10, 20 and 60 minutes.

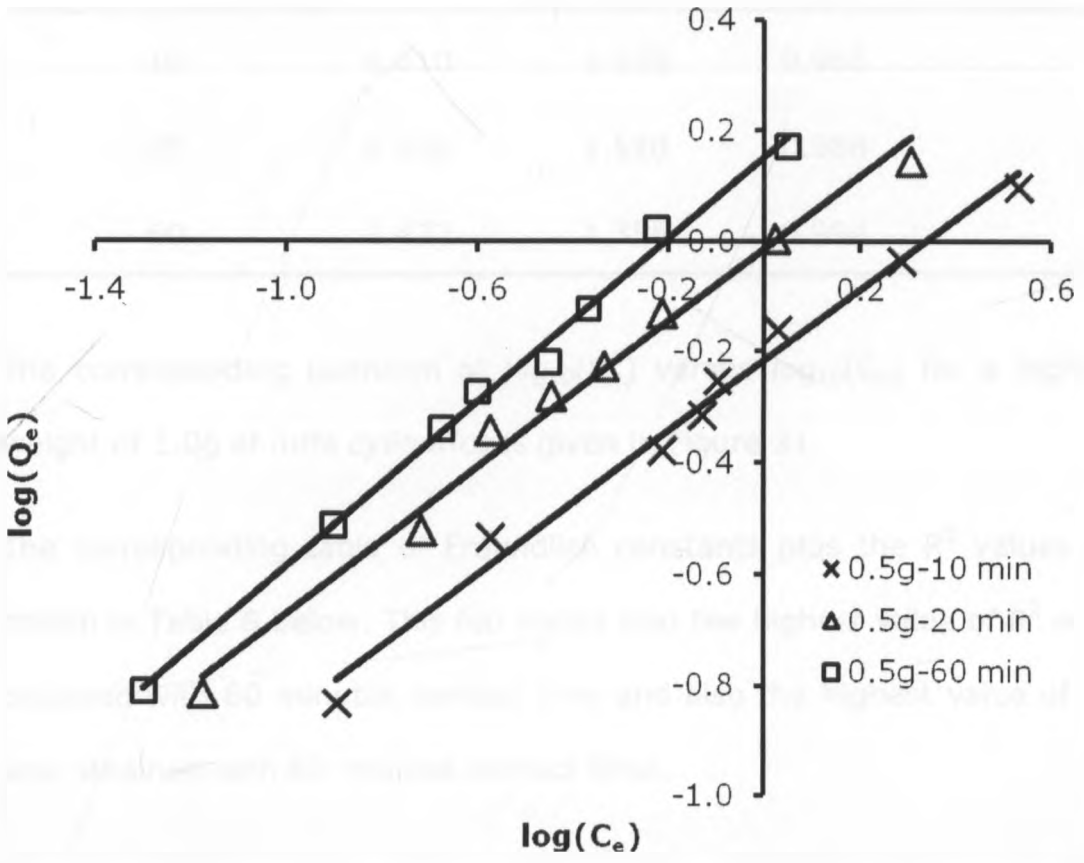

Figure 30: Freundlich adsorption isotherm for methylene blue adsorption on 0.5g of *luffa cylindrica* at varied contact time

The corresponding Freundlich isotherm constants are given in Table 5 with the R^2 values also presented. Again, just like in the case of the

Langmuir adsorption isotherm studies, a contact time of 60 minutes yields the highest R^2 value of 0.994. Hence, suggesting conformity with the Freundlich model.

Table 5: Freundlich Isotherm Constants for Methylene Blue on O.5g *Luffa Cylindrica* after Varied Contact Time

Contact time (min)	K_f (mg/g)	n	R^2
10	0.610	1.558	0.986
20	0.968	1.520	0.988
60	1.422	1.355	0.994

The corresponding isotherm of $\log_{10}(Q_e)$ versus $\log_{10}(C_e)$ for a higher weight of 1.0g of *luffa cylindrica* is given in Figure 31.

The corresponding table of Freundlich constants plus the R^2 values is shown in Table 6 below. This too shows that the highest value of R^2 was obtained with 60 minutes contact time and also the highest value of K_f was obtained with 60 minutes contact time.

The Freundlich constant K_f represents the predicted amount of dye adsorbed in mgg^{-1} of a sorbent at an equilibrium concentration. The results showed that *luffa cylindrica* exhibits good capacity to remove the bulky dye molecules without any pre-treatments.

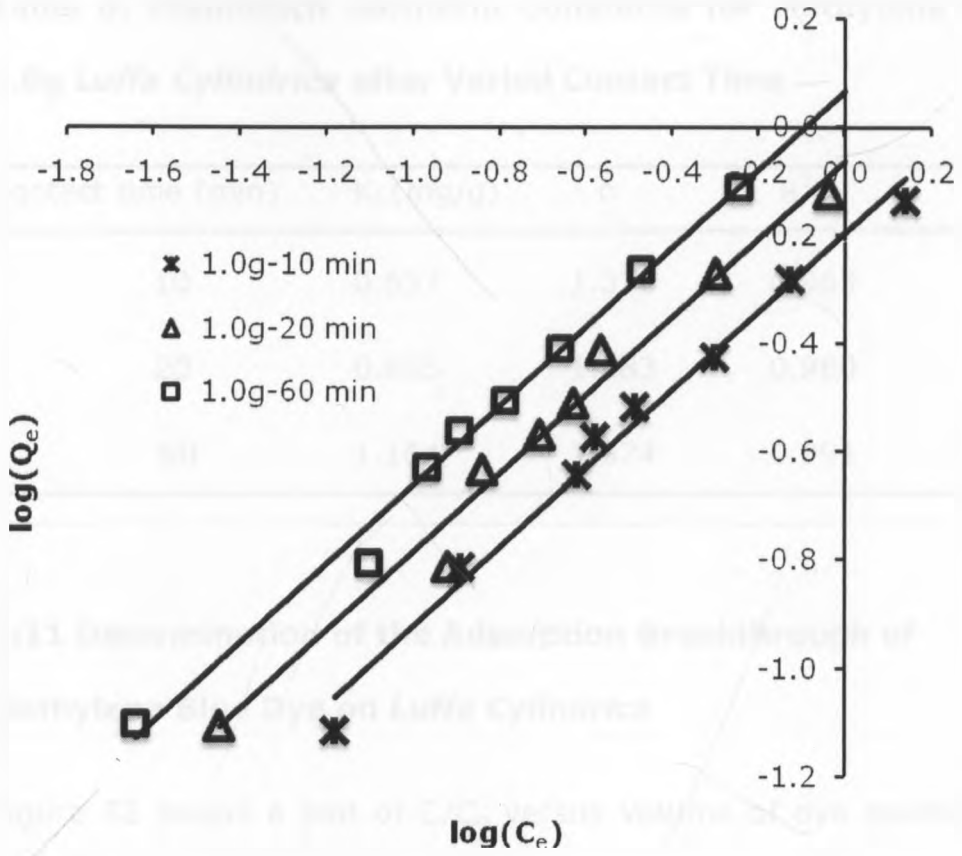

Figure 31: Freundlich adsorption isotherm for methylene blue dye adsorption on 1.0g *luffa cylindrica* at varied contact time

From Figure 31, the constants obtained are tabulated in table 6, which shows that the value of correlation coefficient R^2 is highest for 60 minutes contact time and the range between the highest and the lowest is only 0.011. The values of n are greater than one and k_f approximate to unity.

Table 6: Freundlich Isotherm Constants for Methylene Blue on 1.0g *Luffa Cylindrica* after Varied Contact Time

Contact time (min)	K_f (mg/g)	n	R^2
10	0.637	1.376	0.985
20	0.865	1.383	0.980
60	1.164	1.374	0.991

4:11 Determination of the Adsorption Breakthrough of Methylene Blue Dye on *Luffa Cylindrica*

Figure 32 shows a plot of C/C_o versus volume of dye solution eluted through the column, where C is the concentration of the dye eluting through the column at any time, t and C_o is the initial dye solution

concentration.

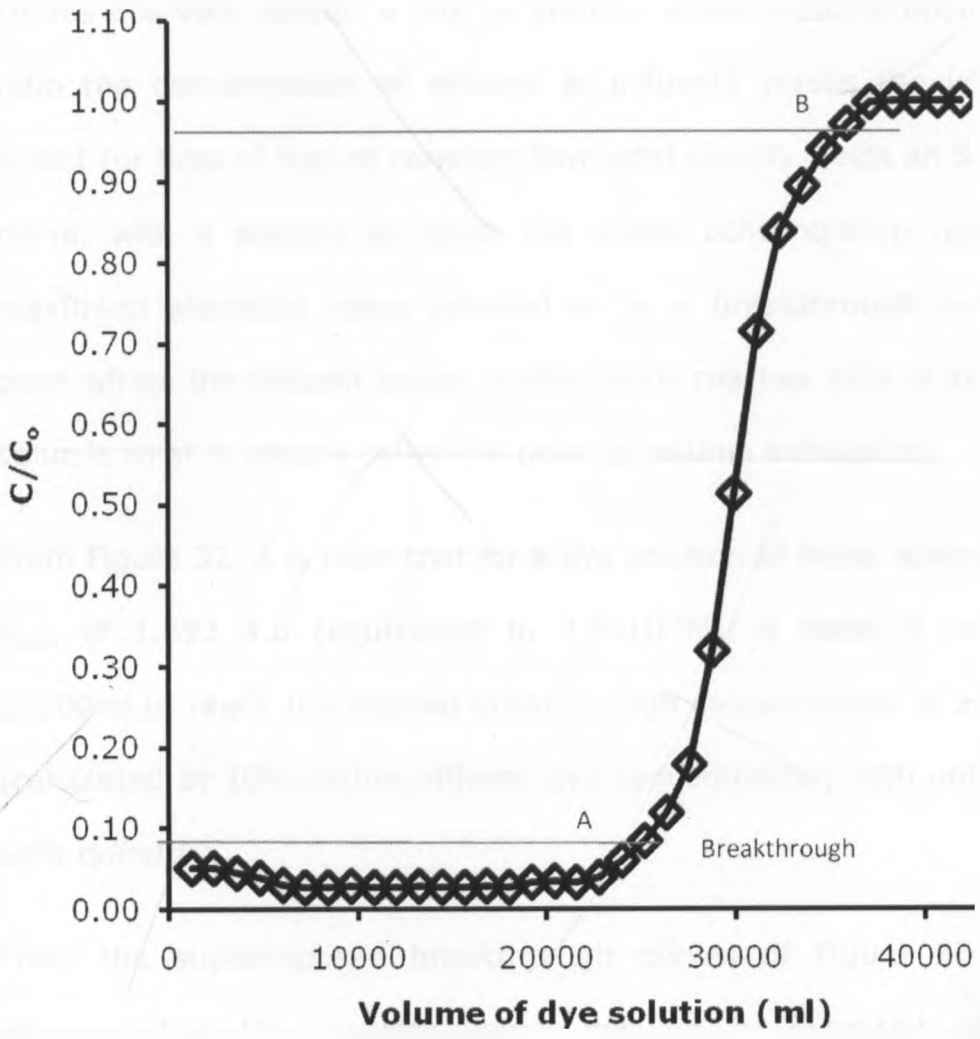

Figure 32: Breakthrough curve for methylene blue dye (of initial absorbance reading of 1.693 au) on 10g *luffa cylindrica*

This curve of C/C_o versus volume passed through between the effluent dye concentration at breakthrough (C_b) and effluent dye concentration at exhaustion (C_x), represented by point A and B, respectively on Figure 32, is called the breakthrough curve.

When working sorption experiments with columns, the breakthrough curves are very useful. A plot of effluent solute concentration (or the ratio the concentration of effluent to influent) versus the volume of eluent (or time of flow at constant flow rate) usually yields an S- shaped curve, with a plateau at which the solute concentration reaches its maximum allowable value referred to as a breakthrough curve. The point where the effluent solute concentration reaches 95% of its influent value is what is usually called the point of column exhaustion.

From Figure 32, it is clear that for a dye solution of initial absorbance at λ_{max} of 1.693 a.u (equivalent to $2.5x10^{-5}M$), it takes a volume of 25200ml to reach the desired breakthrough concentration of $2.5x10^{-6}M$ (calculated at 10% of the influent dye concentration) with only 10g of *luffa cylindrica*.

From the superimposed breakthrough curves of Figure 33, it was observed that the breakthrough is delayed, as expected, when the quantity of luffa is increased from 10 g to 40g. Such delayed breakthrough arises due to increased adsorption capacity of the bed.

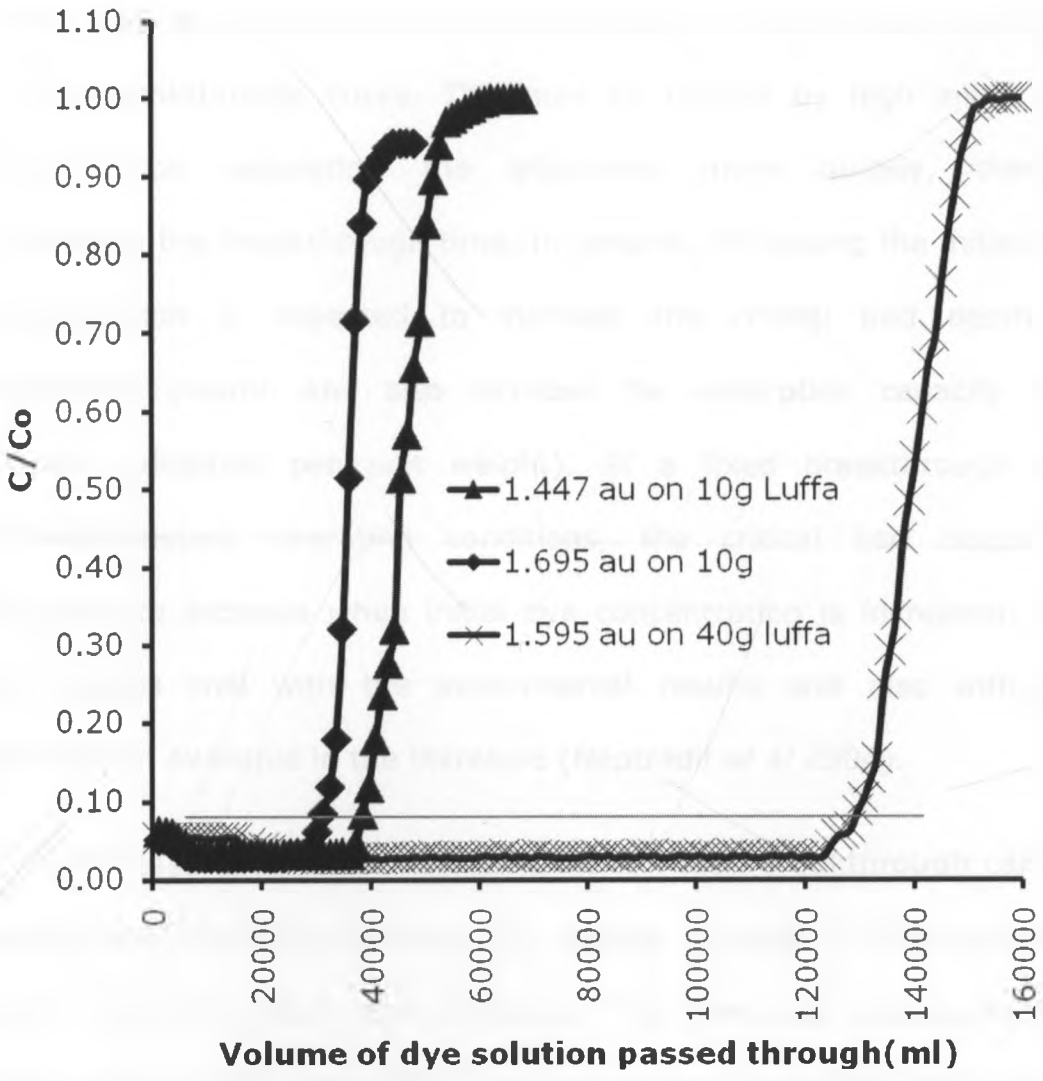

Figure 33: Superimposed adsorption breakthrough curves with methylene blue dye of slightly varying initial concentration on 10g and 40g *luffa cylindrica*

The initial concentration of dyes in the wastewater is an important parameter and a main limiting factor, since a given mass of adsorbent can only adsorb a fixed mass of dye. An increase in the initial dye concentration at a constant flow rate decreases the throughput (output

of the bed) before attainment of breakthrough and increases the slope of the breakthrough curve. This may be caused by high initial dye concentration saturating the adsorbent more quickly, thereby decreasing the breakthrough time. In general, increasing the initial dye concentration is expected to increase the critical bed depth of adsorption column and also increase the adsorption capacity (the amount adsorbed per unit weight). At a fixed breakthrough and defined/constant operating conditions, the critical bed height is expected to increase when initial dye concentration is increased, and this agrees well with the experimental results and also with the information available in the literature (Neptradit *et al* 2004).

The time (T_b) required for the effluent to reach breakthrough can be established from the volume (v_b) passed through at breakthrough point, since the flow rate is known. The flow rate represents the empty bed contact time (EBCT) in the column This affects the volume to the breakthrough and the shape of breakthrough curve. The EBCT is determined from Equation 6

$$\text{EBCT (min)} = \frac{\text{bed volume (cm}^3\text{)}}{\text{flow rate (cm}^3\text{/min)}} \quad \text{..... Equation 6}$$

When the adsorption zone moves down and the lower edge of this zone reaches the bottom of the column, the effluent concentration starts to rise rapidly. This point is the breakthrough point, which

indicates the Volume of dye solution passed through at breakthrough (V_b). It would be expected that a reduction in the flow rate at a constant bed depth would result in increased value of the V_b and hence the T_b, due to an increase in EBCT, since the front of adsorption zone takes a longer time to reach the bottom of the column. In designing a column, the length of the adsorption zone represents the minimum bed depth needed to produce a low effluent dye concentration. This result suggests that a lower flow rate or a longer contact time may be required for methylene blue dye adsorption in a column of *luffa cylindrica*.

From Figure 33, it is evident that the V_b or T_b increased with increased bed depth while the shape and gradient of the breakthrough curves were slightly different with the changed bed depth. The breakthrough curves of the longer bed tended to be a little more gradual, meaning that the column required slightly more time to be completely exhausted.

4.12 Assessment of Efficacy of *Luffa Cylindrica* on Industrial Effluent -Real Life Application

The potential of *luffa cylindrica* to clean up real industrial effluent was tested. An industrial effluent comprising of a direct red dye solution was used.

Figure 34 shows overlaid UV-Vis absorption spectra of the industrial direct red dye effluent upon subjection to different weights of *luffa cylindrica* in a batch mode. The contact time for each of the mixtures was 20 minutes.

The fact that the absorbance readings show a reduction when the dye is subjected to increasing weights of *luffa cylindrica* further confirms the efficacy of *luffa cylindrica* as potential material for removal of textile dyes from waste waters. A weight of 4.0g luffa removed 53.6% of the dye (as determined by the reduction in absorbance results measured at the wavelength of maximum absorbance – λ_{max}, 496nm), 4.5g removed 58.2% and 6g removed 77.9% of the dye from the fixed volume of 100ml dye solution. These results indicate that *luffa cylindrica* can be used effectively to remove the red dye from aqueous media.

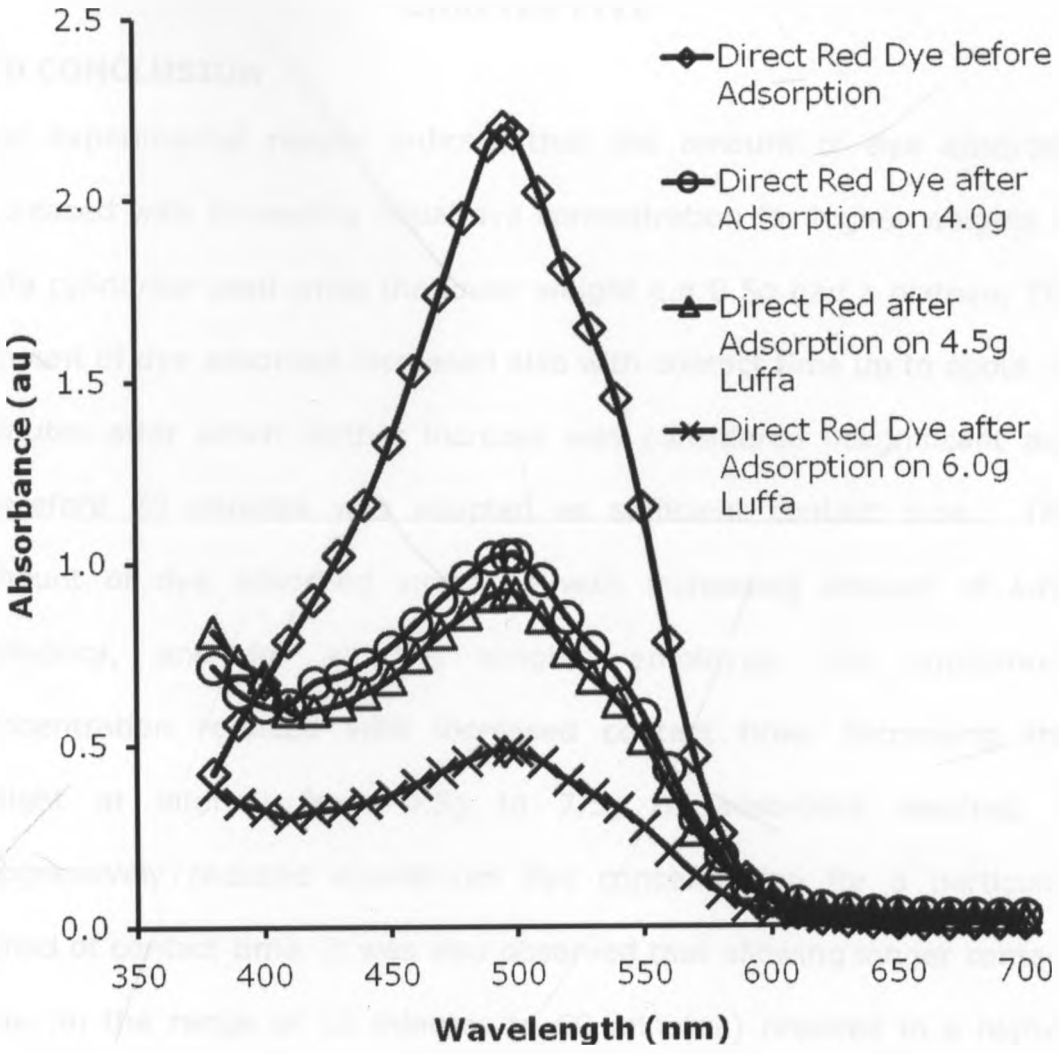

Figure 34: Overlaid UV-Vis Absorbance Spectra of Direct Red Dye Solution Before and After Treatment with Varying Weight of *Luffa Cylindrica*.

From these observations it can be concluded that by using larger weights of *luffa cylindrica* one may be able to remove all the Direct Red Dye from its solution.

CHAPTER FIVE

5.0 CONCLUSION

The experimental results indicate that the amount of dye adsorbed increased with increasing initial dye concentration for higher weights of *luffa cylindrica* used while the lower weight e.g 0.5g had a plateau. The amount of dye adsorbed increased also with contact time up to about 20 minutes after which further increase was considered insignificant and therefore 20 minutes was adopted as sufficient contact time. The amount of dye adsorbed increased with increasing amount of *luffa cylindrica*, and for all the weights employed, the equilibrium concentration reduced with increased contact time. Increasing the weight at interval from 0.5g to 7.5g of adsorbent resulted in progressively reduced equilibrium dye concentration for a particular period of contact time. It was also observed that allowing longer contact time (in the range of 10 minutes to 60 minutes) resulted in a higher sorption capacity for a particular weight employed. Rapid adsorption (up to 90%) took place during the first 5 minutes of contact and slowed down (95% after 20 minutes) as the contact time increased indicating a plateau in the %adsorption.

Langmuir isotherm model was applicable for the batch adsorption for the removal of methylene blue dye from its solution judging by the values of the Langmuir constant (b) 1.019-1.835 and R^2 values of

0.978-0.992 obtained for 1.0g *luffa cylindrica* in 10-60 minutes contact time range.

The breakthrough curves calculated from the adsorption of dyes by *luffa cylindrica* indicates that the dye removal is strongly dependent on the kinetics of adsorption of dyes. Freundlich adsorption equation reasonably describes the adsorption isotherms within the small concentration range of $2.5x10^{-6}$M -$2.0x10^{-5}$M. Freundlich parameter, 'K_f ' which is a measure of the adsorbent capacity was found to be independent of system ionic strength of the solution whereas the other Freundlich parameter 'n', which indicates the intensity of adsorption was greater than unity.

The potential of *luffa cylindrica* to clean up real industrial effluent was further tested using real industrial effluent comprising of a direct red dye solution. Here too the absorption spectra of the industrial direct red dye effluent, upon subjection to different weights of *luffa cylindrica* in a batch mode, showed a progressive reduction when the dye was subjected to increasing weights of *luffa cylindrica*; further confirming the efficacy of *luffa cylindrica* as potential material for removal of textile dyes from waste waters.

The results show *luffa cylindrica* is effective in the removal of methylene blue dye from effluents. This has particular significance to developing countries where the economies may not favour the use of expensive

materials for the cleaning of factory effluents containing dyes. Many developing countries suffer from contamination of water supplies, largely due to uncontrolled industrial activity since balancing between industrial development and environmental protection is not an easy choice to make and so a water treatment technique which is able to deal with such pollutants cheaply in an effective way using locally available resources is very valuable.

5.1 RECOMMENDATIONS

- It is recommended that further tests be done on the material using a variety of water soluble dyes to establish the efficacy of the material in each of the different dyes.
- Different particle sizes including finer particles or powder may yield different results owing to a bigger surface area and thus further tests using finer material is hereby recommended.
- Preparation of activated carbon at various temperatures could be investigated in order to establish the effect of temperature on activation and also as a way of re-using the spent luffa.
- The effect of flow rate on the breakthrough need to be further investigated in order to establish the optimum bed depth and the adsorptive capacity of the column.
- It is also recommended that a pilot effluent cleanup unit for textile dye removal be set up in order to establish the efficacy of *luffa cylindrica* in treating real effluent in an industrial set-up.

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APPENDICES

Appendix 1: Determination of the working wavelength of (λ max) with Methylene Blue Dye

Wave Length (nm)	Absor-bance (a.u.)	Wave Length (nm)	Absor-bance (a.u.)	Wave Length (nm)	Absor-bance (a.u.)	Wave Length (nm)	Absor-bance (a.u.)	Wave Length (nm)	Absor-bance (a.u.)
330	0.127	420	0.014	520	0.091	620	1.092	664	1.55
340	0.065	430	0.018	530	0.119	630	1.131	666	1.442
350	0.039	440	0.025	540	0.161	640	1.34	668	1.329
360	0.029	450	0.034	550	0.219	650	1.585	670	1.206
370	0.026	460	0.043	560	0.292	652	1.618	672	1.073
380	0.028	470	0.054	570	0.384	654	1.66	674	0.709
390	0.029	480	0.065	580	0.527	656	1.686	678	0.522
400	0.021	490	0.076	590	0.749	658	1.693	680	0.162
410	0.013	500	0.081	600	0.974	660	1.67	690	0.081
510	0.084	610	1.062	662	1.622	700	0.043		

Appendix 2: Determination of the optimum contact (equilibrium) time for adsorption

Blank 1.564

Time (min)	0	5	10	15	20	30	40	50	60
Absorbance readings (a.u.)	1.249	0.170	0.104	0.076	0.076	0.069	0.062	0.058	0.050
% Adsorption	20.1	89.1	93.4	95.1	95.1	95.6	96.0	96.3	96.8

Appendix 3A: Determination of the effect of initial concentration on adsorption of Methylene blue by *luffa cylindrica* after 10 minutes contact time

C_o(M)	A_o (a.u.)	0.5g (a.u.)	1.0g (a.u.)	2.0g (a.u.)
2.50×10^{-6}	0.165	0.019	0.021	0.027
5.00×10^{-6}	0.337	0.030	0.027	0.030
1.00×10^{-5}	0.619	0.055	0.038	0.038
1.50×10^{-5}	0.935	0.123	0.060	0.054
1.75×10^{-5}	1.092	0.149	0.065	0.055
2.00×10^{-5}	1.265	0.162	0.078	0.066
2.50×10^{-5}	1.559	0.212	0.111	0.080

Appendix 3B: Determination of the effect of initial concentration on adsorption of Methylene blue by *luffa cylindrica* - 20 minutes contact time

C_o(M)	A_o(a.u.)	0.5g(a.u.)	1.0g(a.u.)	2.0g(a.u.)
$2.50x10^{-6}$	0.192	0.018	0.017	0.022
$5.00x10^{-6}$	0.375	0.023	0.020	0.026
$1.00x10^{-5}$	0.706	0.048	0.037	0.038
$1.50x10^{-5}$	1.021	0.065	0.043	0.044
$1.75x10^{-5}$	1.092	0.081	0.052	0.044
$2.00x10^{-5}$	1.287	0.100	0.059	0.056
$2.50x10^{-5}$	1.572	0.129	0.066	0.057

Appendix 3C: Determination of the effect of initial concentration on adsorption of Methylene blue by *luffa cylindrica* - 40 minutes contact time

C_o(M)	A_o(a.u.)	0.5g(a.u.)	1.0g(a.u.)	2.0g(a.u.)
$2.50x10^{-6}$	0.172	0.018	0.017	0.022
$5.00x10^{-6}$	0.355	0.023	0.020	0.026
$1.00x10^{-5}$	0.663	0.048	0.037	0.038
$1.50x10^{-5}$	1.021	0.065	0.043	0.044
$1.75x10^{-5}$	1.132	0.081	0.052	0.044
$2.00x10^{-5}$	1.265	0.100	0.059	0.056
$2.50x10^{-5}$	1.572	0.129	0.066	0.060
$3.50x10^{-5}$	2.180	0.215	0.111	0.081
$5.00x10^{-5}$	3.112	0.404	0.192	0.122

Appendix 3D: Determination of the effect of initial concentration on adsorption of Methylene blue by *luffa cylindrica* - 60 minutes contact time

C_o(M)	A_o(a.u.)	0.5g(a.u.)	1.0g(a.u.)	2.0g(a.u.)
$2.50x10^{-6}$	0.172	0.009	0.012	0.030
$5.00x10^{-6}$	0.346	0.013	0.017	0.030
$1.00x10^{-5}$	0.687	0.028	0.026	0.030
$1.50x10^{-5}$	1.021	0.042	0.036	0.039
$1.75x10^{-5}$	1.132	0.049	0.036	0.044
$2.00x10^{-5}$	1.243	0.050	0.042	0.050
$2.50x10^{-5}$	1.594	0.074	0.056	0.065
$3.50x10^{-5}$	2.180	0.148	0.083	0.070
$5.00x10^{-5}$	3.112	0.270	0.147	0.098

Appendix 4: Effect of weight on adsorption

Weight (g)	Equilibrium Sorption (mg/g) $2.5x10^{-5}$	Equilibrium Sorption (mg/g) $(1.75x10^{-5})$	Equilibrium Sorption (mg/g) $(1.25x10^{-5})$	Absor-bance (a.u.), $(2.5x10^{-5})$	Absor-bance (a.u.), $(1.75x10^{-5})$	Absor-bance (a.u.), $(1.25x10^{-5})$
0.00				1.542	1.079	0.780
0.50	0.800	0.560	0.400	0.083	0.057	0.056
1.00	0.400	0.280	0.200	0.083	0.056	0.050
2.50	0.160	0.112	0.080	0.056	0.044	0.041
5.00	0.080	0.056	0.040	0.048	0.041	0.030
7.50	0.053	0.037	0.027	0.044	0.040	0.025

Appendix 5: Effect of ionic strength

	$2.5x10^{-5}M$					$1.25x10^{-5}M$				
0.1MKCl (ml)	1	2	3	4	5	1	2	3	4	5
Blank (A0)	1.553	1.551	1.535	1.535	1.548	0.803	0.803	0.803	0.803	0.803
Abs (A20)	0.058	0.062	0.066	0.066	0.062	0.056	0.056	0.056	0.056	0.056

Appendix 6: Effect of pH on adsorption

Initial Absor-bance	Initial pH	Absorbance (a.u.) after 20 min	pH after 20 min	% Equilibrium absorbance	% pH change	pH Controller
1.549	2.81	0.413	3.03	73.3376	-7.83	3ml 0.1mHCl
1.526	2.81	0.479	2.90	68.6107	-3.20	5ml 0.1mHCl
1.564	2.82	0.228	3.53	85.4220	-25.18	2ml 0.1mHCl
1.544	2.88	0.434	3.03	71.8912	-5.21	4ml 0.1MHCl
1.550	3.06	0.122	4.07	92.1290	-33.01	1ml 0.1MHCl
1.563	3.42	0.080	4.38	94.8816	-28.07	4ml 0.01MHCl
1.559	3.46	0.084	4.27	94.6119	-23.41	5ml 0.01MHCl
1.558	3.69	0.083	4.45	94.6727	-20.60	3ml 0.01MHCl
1.560	3.91	0.083	4.66	94.6795	-19.18	2ml 0.01MHCl
1.564	4.05	0.060	4.75	96.1637	-17.28	1ml 0.01MHCl
1.568	4.87	0.056	4.86	96.4286	0.21	0.5ml 0.01MHCl
1.573	6.91	0.060	4.92	96.1856	28.80	0
1.555	7.75	0.063	5.03	95.9486	35.10	0.5ml0.01MKOH
1.572	9.69	0.063	5.05	95.9924	47.88	1ml 0.01MKOH
1.572	10.36	0.056	5.13	96.4377	50.48	2ml 0.01MKOH
1.560	10.44	0.057	5.20	96.3462	50.19	3ml 0.01MKOH
1.552	10.94	0.050	5.64	96.7784	48.45	5ml 0.01MKOH
1.550	11.44	0.047	9.31	96.9677	18.62	1ml 0.2MKOH

Appendix 7: Determination of Optimum Contact Time for Luffa-derived Activated Carbon

Time (min)	Absorbance (a.u.)	Time (min)	Absorbance (a.u.)	Time (min)	Absorbance (a.u.)
0	1.135	35	0.254	80	0.175
3	0.703	40	0.242	85	0.171
5	0.598	45	0.226	90	0.169
7	0.527	50	0.22	95	0.164
10	0.449	55	0.207	100	0.162
15	0.383	60	0.198	105	0.162
20	0.326	65	0.188	110	0.162
25	0.3	70	0.186	160	0.143
30	0.272	75	0.184	238	0.142

Appendix 8: Effect of Concentration on Adsorption on Activated Carbon

Dye concentration (M)	Initial Absorbance (a.u.)	0.5g			1.0g			2.0g		
		6hrs	12hrs	24 hrs	6hrs	12hrs	24 hrs	6hrs	12hrs	24 hrs
$2.50x10^{-6}$	0.142	0.017	0.017	0.017	0.032	0.033	0.033	0.079	0.046	0.003
$5.00x10^{-6}$	0.339	0.017	0.017	0.017	0.052	0.058	0.074	0.120	0.071	0.076
$1.00x10^{-5}$	0.612	0.024	0.026	0.028	0.044	0.038	0.035	0.086	0.058	0.051
$1.50x10^{-5}$	0.972	0.069	0.036	0.033	0.040	0.054	0.055	0.059	0.063	0.065
$1.75x10^{-5}$	1.131	0.166	0.072	0.030	0.038	0.026	0.022			

Appendix 9: Data on preparation of activated carbon from *luffa cylindrica*

Crucible No.	Weight of crucible (g)	Weight of crucible + Sample(g) (before)	Weight of crucible + Sample(g) (After)	Weight(g) of sample used	Weight(g) of sample obtained
1	10.70	11.65	11.00	0.95	0.30
2	10.65	11.50	11.00	0.85	0.35
3	10.85	11.80	11.15	0.95	0.30
4	10.70	11.65	11.00	0.95	0.30
5	10.60	11.60	10.90	1.00	0.30
6	10.50	11.50	10.80	1.00	0.30
7	10.40	11.50	10.70	1.10	0.30
8	10.70	11.70	11.00	1.00	0.30
Average				0.98	0.31
Loss					68.39%
Ash Content					9.06%