DYE ADSORPTION CHARACTERISTICS BY TWO UNMODIFIED LIGNOCELLULOSIC BIOMASS MATERIALS *(T.pedata & L.cylindrica)* IN BATCH AND FIXED-BED SYSTEMS

By

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DECLARATION

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

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DEDICATION

For you, Stanley Mutali.

Love of my life.

And you, Sophia Mwenesi

Love in my life.

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ABSTRACT

Industrial dye wastewater is a major environmental concern in developing countries. This study investigated the viability of two low cost adsorbents (*L.cylindrica, T.pedata* and their mixture) in the adsorption of color from colored industrial effluent through experimenting with dyes.

The batch and fixed-bed modes of operation were utilized on the adsorbents while varying the adsorbate between Methylene blue and Congo red. The influence of different experimental parameters such as contact time, dye concentration, adsorbent dose, pH, temperature and ionic strength were studied in the batch mode.

Observations revealed that for maximum % adsorption of Methylene blue dye, a contact time of 30 minutes, 5 minutes and 55 minutes was required for *L.cylindrica, T.pedata,* and their equal weight mixture to achieve 99%, 97% and 100% adsorption, respectively. The optimum dye concentration was found to be the lowest concentration used (i.e., 1.0×10^{-6}M). The plant materials adsorbed 100% of the dye at this lowest concentration. The highest % adsorption was recorded when the maximum adsorbent dose of 3g was used for *L.cylindrica* and the mixture, at 99% and 100%, respectively. However, *T.pedata* removed the most dye with the least amount of adsorbent employed (0.5g). The % adsorption in this case was 99%. The optimum pH and temperature was found to be pH 10 and 20^0C, respectively for all the three types of adsorbents investigated. Observations made regarding the effect of temperature led to the conclusion that the adsorption process was exothermic. This further indicated that the rate-determining step of the adsorption process was intra-particle mass transfer. The % adsorption was found to be inversely proportional to ionic strength of solution. With Congo red dye employed as a representative acidic dye, the optimum contact time was observed to be at 120 minutes. 96% was recorded with *L.cylindrica*, while 57% and 76% was recorded with *T.pedata*, and the mixture, respectively. Similarly, the lowest concentration of dye used resulted in the highest % adsorption recorded: *L.cylindrica*, 84%, *T.pedata*, 39% and mixture, 61%. It was observed that at 3g, which was the highest adsorbent dose employed, *L.cylindrica, T.pedata* and the mixture adsorbed the most dye which varied in % adsorption as 83%, 48% and 65%, respectively. The optimum temperature was 20°C. pH studies revealed that *L.cylindrica* adsorbed best at pH 6.9 (78%), *T.pedata* at pH 3.82 (77%), and the mixture at pH 5 (57%). Observations made on effect of ionic strength revealed that when $9.5x10^{-4}$ M KCl was added to the dye solution, *L.cylindrica* and the mixture had the highest % adsorptions of 89% and 86%, respectively. However, *T.pedata* resulted in 96% adsorption; the highest recorded, after $4.0X10^{-3}$ M of KCl was added. Adsorption Isotherm studies indicated that the Freundlich model gave a better fit to the experimental data than the Langmuir equation.

Two parameters were investigated for the fixed bed mode of operation. Investigations on the effect of influent dye concentration with *L.cylindrica* showed breakthrough point at the volume of 2400 ml and 5000 ml, for $1.0x10^{-5}$ M and $5.0x10^{-6}$ M, respectively. The breakthrough point for *T.pedata* was at the volume of 1200 ml and 1500 ml, at dye concentrations of $1.0x10^{-5}$ M and $5.0x10^{-6}$ M respectively. Further experiments on the effect of adsorbent dose showed the breakthrough point of *L.cylindrica* to be at 2500 ml and 5000 ml, when 2.5 g and 5 g of adsorbent were used, respectively. Breakthrough for *T.pedata* was observed at 1000 ml and 1900 ml, when 2.5 g and 5 g of plant material were used, respectively.

CHAPTER 1

INTRODUCTION

Environmental degradation is fast getting global attention and the worrying trend is earning great concern. Air, land and water pollution is on the increase. The world water day on the 22nd of March 2008 (an event that occurs every year since its inception in 1992) brought special attention to one resource: Water. Press reports indicate that water scarcity in East Africa is fueling conflict and thwarting development while growing in step with local populations and rising global temperatures. One report continued to state that "though the actions of industrialized nations are primarily responsible for global warming, its effects are being felt most heavily in less developed regions of the world such as East Africa, where climate change can be tied to detrimental environmental issues such as droughts and melting snowcaps". Statistics have been presented at different fora to illustrate the need for the preservation of water. It is reported that nearly 1.1 billion people (roughly 20% of the world's population) lack access to safe drinking water (Water Aid, 2005). The lack of clean, safe drinking water is estimated to kill almost 4,500 children per day. In fact, out of the 2.2 million unsafe drinking water deaths reported in 2004, 90% were children under the age of five (Water for life, Making it Happen, 2005).

In view of this, it is important that water being utilized for purposes other than domestic be economized (reduced, reused and recycled) to ease pressure on competition for the resource. The author recognizes that there are many large scale uses of water including agricultural activities and for recreation. However, Industrial wastewater is the main target in this work, with emphasis on the dye wastewater. Among the different pollutants of aquatic ecosystems, dyes are a large and important group of industrial chemicals. Synthetic dyes are widely used in industries such as textiles, leather, paper, plastics, food, drug and cosmetics among others to color their final products (Khattri and Singh, 2000; Khanna and Das, 1991). In particular, printing and dyeing unit wastewaters contain several types of coloring agents, which are difficult to treat by biological methods (McKay, 1979). It is estimated that approximately 12% of the synthetic dyes used each year are lost during manufacture, processing and operations and 20% of these dyes lost, enter the environment through effluent that results from the treatment of the industrial wastewaters (Hwang and Cheng, 1993a,b; Nawar and Doma, 1989). Interest in the removal of dyes from wastewaters is prompted primarily by the fact that in developing countries, water pollution has become an issue. Unfortunately, the cost is quite high using conventional wastewater treatment chemicals like alum, ferric chloride, polymer flocculants and coal-based activated carbon (Attahiru *et al.*, 2003; Namasivayam and Kavitha, 2002; Namasivayam and Ranganathan, 1993). Low cost and easily available adsorbents would make the removal of pollutants an economically viable alternative. Besides this, colored compounds are the most easily recognizable pollutants in the environment because of their appearance. The presence of very low concentrations of dyes in effluents is highly visible and undesirable (Nigam *et al.*, 2000). Due to their good solubility, synthetic dyes are common water pollutants and they may frequently be found in trace quantities in industrial wastewater. However, the discharge of dye-bearing wastewater into natural streams and rivers pose a severe problem, as dyes impart toxicity to aquatic life – when dyes are broken down aerobically in the sediment, they lead to production of toxic amines that affect the aquatic system and associated flora and fauna- and are a damage to the aesthetic nature of the environment. In addition, the presence of dyes in water reduces light penetration and has a derogatory effect on the process of photosynthesis (Willmott *et.al.*, 1998; Abdullah *et al.*, 2005). Toxicity of dyes results from the various chemicals from which they are manufactured. Generally during manufacture, organic compounds such as naphthalene are reacted with an alkali or an acid along with an intermediate (such as nitrating or sulfonating compound) and a solvent to form a dye mixture. The following sub-section introduces dyes and their classification.

1.1 DYES

A dye is a colored substance that has an affinity for the substrate to which it is applied, and is usually adsorbed to a certain extent by that material. The colors from some dyes are more stable than others depending on the kind of material which they are used on (Evans *et.al.*, 1984). Correlation of chemical structures with color has been accomplished in the synthesis of dyes using a chromogen-chromophore with auxochrome. Chromogen is the aromatic structure containing benzene, naphthalene or anthracene rings. A chromophore group provides color and is represented by the following functional groups, which form basis for the classification of dyes when coupled with the Chromogen: azo (-N=N), Carbonyl (=C=O), Carbon (=C=C=), Carbon-Nitrogen(-C=NH or –CH=N-), nitroso (-NO or N-OH), nitro (-NO_2 or =NO-OH), Sulfur (-C=S) and other carbon-sulfur groups. The Chromogen chromophore structure is often not sufficient to impart solubility and cause adherence of dye to the fiber. The auxochromogen or bonding affinity groups are amine, hydroxyl, carbonyl and sulfonic groups. These auxochromes are important in the classification of dyes as Acetate rayon dyes, Acid dyes, Azoic dyes, Basic Dyes, Direct dyes, Mordant (Chrome) dyes, Lake (Pigment) dyes, Sulphur (Sulphide) dyes and Vat dyes.

Among the various classes of dyes, basic dyes are found to be the brightest class of soluble dyes used by the textile industry as their tinctorial value is very high (Hema and Arivoli, 2007). The textile industry is worth a mention because it accounts for 67% of the total dyestuff market (Robinson *et al*., 2002).

It has been established that dye wastewater is considered a problematic pollutant because of its color and organic content. A combination of several processes is generally necessary to achieve adequate removal of all contaminants (Annadurai, 2002). Industries that discharge dyes in their wastewaters should treat them before directing these waters away from the industry to remove organic wastes and coloring agents. In fact, the environmental regulation body in Kenya-National Environment Management Authority (NEMA)-has provided in section 147 of the Environmental Management and Co-ordination Act, 1999, stringent measures that are to be taken against those industries that choose not to sufficiently treat wastewaters before discharge. In the case of dye wastewaters, adsorption has evolved as one of the most effective and economical physical processes for its decolourisation. Adsorption techniques are not only efficient in the removal of pollutants too stable for conventional methods-as are many dyes which are difficult to decolorize due to their complex structure and synthetic origin- but it is also a process that produces a high quality product and is a process which is economically feasible (Willmott *et al.*, 1998; Choy *et al.*, 1999). The following sub-section gives an insight into the process of adsorption.

1.2 ADSORPTION

Adsorption can be described as the adhesion or retention of a thin layer of molecules of a gas or liquid mixture brought into contact with a surface resulting from the force field at the surface. It is a property of surfaces of contact between two phases, such as solid and liquid, solid and gas, liquid and liquid, or liquid and gas. Adsorption either increases or decreases the concentration of some constituent of the system in this interface.

There are two types of adsorption: Physical adsorption and Chemisorption. The two types of adsorption differ in the extent of how tightly the adsorbate (A substance that becomes adsorbed at the interface or into the interfacial layer of another material, or adsorbent) molecules are held on the surface of the adsorbent (An adsorbent is the substrate material onto which a substance is adsorbed).

In both types of adsorption, weak Van der Waal's forces of attraction hold the atoms in a solid. The unbalanced forces on the surface of the solid make it very reactive. When a solid substance is broken into smaller and smaller pieces, the number of unbalanced forces increases. These unbalanced forces tend to take up the molecules of liquids or gases when the solid is placed in the liquid or a gas. Solid substances in the finely divided state therefore act as good adsorbents.

Any solid is capable of adsorbing a certain amount of gas or liquid with the extent of adsorption at equilibrium depending on temperature, pressure of the gas or liquid concentration and the effective surface area of the solid. The most notable adsorbents are therefore, highly porous solids such as charcoal and silica gel. The most efficient and commonly used adsorbent in the removal of dyes from wastewater is activated carbon (McKay, 1964). However, activated Carbon is costly and has regeneration problems. In-depth investigations have been carried out by various workers with focus on the use of low cost materials such as rice husks (Vadivelan and Kumar, 2005; Hawar and Uma, 1989); coconut husks (Low and Lee, 1990), giant duckweed (Waranusantigul *et al.*, 2003), sewage sludge (Garg *et al.*, 2004), waste orange peel (Namasivayam *et al.*, 1996); neem dust (Otero *et al.*, 2003), maize cobs (Nasar *et.al.*,1991), banana pith (Namasivayam and Kanchana,1992; Namasivayam and Kanchana,1993; Namasivayam *et al.*, 1993), saw dust (Lin S.H, 1993), fly ash (Sunil *et al.*, 1987 ; Khare *et al.*, 1987), spent bleaching earth (Lee *et al.*, 1996; Lee *et al.*, 1999), chrome sludge (Lee *et al.*, 1997) and chitin (Annadurai and Krishnan,1996; Nawar and Doma, 1989; McKay *et al.*, 1983) to remove dyes with varying degrees of success. In recent years, agricultural by-products such as peat and pith, waste cellulose, apple pomace and wheat straw have been widely studied for dyes removal from wastewater (Ho and McKay, 2003; Annadurai *et al.*, 2002; Robinson *et al.*, 2002).

Adsorption is usually described through isotherms, that is, the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature. The quantity adsorbed is nearly always normalized by the mass of the adsorbent to allow comparison of different materials. Adsorption Isotherms will be discussed in detail in the next chapter.

1.3 STATEMENT OF THE PROBLEM

Synthetic dyes used in various industries are common water pollutants due to their good solubility. Many dyes are difficult to degrade due to their complex structures and properties (Willmott *et al.*, 1998). The presence of dyes in water reduces light penetration and has a derogatory effect on photosynthesis. When dyes are broken down aerobically in the sediment, they lead to production of toxic amines that affect the aquatic system and associated flora and fauna.

Besides that, dyes damage the aesthetic nature of the environment. There is definite need for dye removal technologies that work and that are cost effective. Dyes must be removed from polluted streams in order to alleviate their associated problems and to meet increasing environmental quality standards. Although microbial biomass is utilized, they are largely ineffective because most dyes are toxic to organisms used in the process. Flocculation effectively decolorizes insoluble dyes but fails to work with soluble dyes (Grimshaw and Harland, 1974). Chemical destruction by oxidation is effective but the oxidizing agents are utilized in high quantity hence expensive. The use of oxygen is effective and economical only in cases where the solute concentrations are relatively high. Photochemical degradation in aqueous solution is likely to proceed slowly as synthetic dyes are in principal, designed to exhibit high stability in light.

Adsorption is the procedure of choice for dye removal as it can be used to remove different types of coloring material. Activated carbon is the most widely used adsorbent because it has excellent adsorption efficiency for organic compounds, to an efficiency of 100% (Raghavacharya, 1997; Rao *et al.*, 1994); but its use is usually limited due to its high cost (*Appendix 3*). The present work investigated the possibility of utilizing low cost adsorbents in the form of two lignocellulosic materials, *Telfairia pedata* and *Luffa cylindrica,* for dye removal from aqueous solutions in both batch and fixed-bed systems.

1.4 JUSTIFICATION

The environmental implications of discharging dye-bearing wastewater into natural water systems is immense, as dyes impart toxicity to aquatic life and are damaging the aesthetic nature of the environment. NEMA has done well to introduce stringent measures and subsequent penalties that would ensure that water being discharged from industries is of acceptable quality. However, the industries incur overhead costs in the use of adsorbent carbon. In order to decrease the cost of treatment, attempts have been made to find inexpensive alternative adsorbents. The two lignocellulosic materials will be tested and their potential to solve multiple concerns evaluated such as the fact that the plant materials require no modification prior to the adsorption process. The cost of preparation and therefore the eventual cost of treatment reduce drastically.

Secondly, the fact that the plants can be grown locally offers the greatest potential for increased employment, poverty reduction, rural development and generation of increased incomes in arid and semi-arid areas of the country. This offers opportunity for rapid economic development in the country.

Thirdly, the country could receive income in terms of foreign exchange from exporting the plant materials to other countries and save money used in the importation of other alternatives and expensive adsorbents such as activated carbon (*appendix 3*).

Fourthly, growing plants sequester Carbon from the atmosphere in the form of carbon dioxide gas (CO_2), which is used in the process of photosynthesis. The plant part in utilization as an adsorbent in both cases is the fruits (*section* 2.2.1). The fruits contain the mesh-like material that can be ground and used for adsorption. The leaves and the rest of the plant remain intact after harvesting of the fruits. Consequently, in the process of growth and even after achieving maturity, these plants grown in large scale is an approach to mitigate global warming by capturing carbon dioxide. Further, these plant materials are typically grown in arid and semi arid regions (*section 2.2.1*) and will therefore not replace food crops.

Finally, the careful reuse of water in the industries, at an affordable cost of recycling by use of alternative adsorbents in the form of plant materials such as these; will ease on competition and effectively reduce pressure on this very valuable and increasingly scarce resource: water.

1.5 OBJECTIVES OF THE STUDY

The study had the following overall and specific objectives:

1.5.1 Overall Objective

To test the efficacy of two lignocellulosic materials and their mixture, as low cost adsorbents for dye removal from aqueous solutions in both batch and fixed-bed systems.

1.5.2 Specific Objectives

Specifically, the study sought:

1. To determine, compare and contrast the adsorption efficiencies by studying the effects of dye concentration, contact time, adsorbent dose, pH, temperature and ionic strength on the removal of dyes from representative aqueous solutions of Methylene blue dye and Congo red dye solutions, separately by *T. pedata, L.cylindrica* and their equal-weight mixture, separately in batch mode of operation.
2. To test the adsorption behavior of *T.pedata, L.cylindrica* and their equal-weight mixture, separately against Langmuir and Freundlich Adsorption Isotherms.
3. To determine the effects of bed depth and adsorbent concentration on breakthrough curves of dye sorption by *T.pedata, L.cylindrica* and their equal-weight mixture in continuous flow mode of operation.

CHAPTER 2

LITERATURE REVIEW

2.0 INTRODUCTION

Environmental pollution may be defined as the contamination of air, water and land as a result of human activities, primarily by wastes (Krantz and Kifferstein, 2001). Water pollution is the discharge of organisms or substances into water, which limits its use as a natural resource. Different forms of pollution can affect water quality: chemical, biological and physical pollution (Krantz and Kifferstein, 2001). Polluting factors introduced in water in the form of either chemicals or organisms can influence natural and human environment whether directly or indirectly by creating conditions that limit water utilization for specific purposes.

Indicators of water quality degradation include physical, chemical and biological parameters. Examples of biological parameters include species diversity and abundance. Examples of physical and chemical parameters include pH, turbidity, temperature and color (Krantz and Kifferstein, 2001).

Color is a visible pollutant. The discharge of highly colored effluents into natural water bodies is not only aesthetically displeasing, but it also impedes light penetration, thus upsetting biological processes in a stream. In addition, many dyes are toxic to some organisms causing direct destruction of aquatic communities. Some dyes can cause allergic dermatitis, skin irritation, cancer and mutation in man (Hema and Arivoli, 2007). Two dyes, Methylene blue and Congo red, were used as sample dyes in this work. Their structures and uses are discussed below:

2.1 DYES

2.1.1 Methylene blue

Methylene blue is a heterocyclic aromatic chemical compound with molecular formula: $C_{16}H_{18}ClN_3S$ (IUPAC: 3,7-bis(dimethylamino)phenothiazin-5-ium chloride). It has many uses in a range of different fields, such as biology and chemistry. At room temperature it appears as a solid, odorless, dark green powder that yields a blue solution when dissolved in water (Linz *et al.*, 2006). Its chemical structure is shown in Figure 1 below.

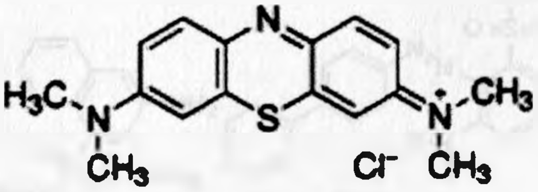


Figure 1: Structure of Methylene Blue dye

Methylene blue is widely used as a redox indicator in analytical chemistry. Solutions of this substance are blue when in an oxidizing environment, but will turn colorless if exposed to a reducing agent (Harvey and Keitt, 1983).

Methylene blue is a basic dye: a group of dyes which are found to be the brightest class of soluble dyes used by the textile industry as their tinctorial value is very high (Hema and Arivoli, 2007; Weber and Stickney, 1993). Methylene blue has wider applications that include coloring paper, temporary hair colorant, dyeing cottons, wools, and coating for paper stock (Han *et al.*, 2006).

2.1.2 Congo red

Congo red is the sodium salt of benzidinediazo-bis-1-naphtylamine-4-sulfonic acid (formula: $C_{32}H_{22}N_6Na_2O_6S_2$; molecular weight: 696.66 g/mol). It is a secondary diazo dye. Congo red is water soluble, yielding a red colloidal solution; its solubility is better in organic solvents such as ethanol. Figure 2 below shows its chemical structure.

Figure 2: Structure of Congo red dye

Due to a color change from blue to red at pH 3.0-5.2, Congo red can be used as a pH indicator.

Congo red has a propensity to aggregate in aqueous and organic solutions. The proposed mechanisms suggest hydrophobic interactions between the aromatic rings of the dye molecules, leading to a pi-pi stacking phenomenon. Although these aggregates are present under various sizes and shapes, the "ribbon-like micelles" of a few molecules seem to be the predominant form. This aggregation phenomenon is more important for high Congo red concentrations, at high salinity and/or low pH.

As suggested by its intense red color, Congo red has important spectrophotometric properties. Aggregation of the dye tends to red-shift the absorption spectrum, whereas binding to cellulose fibers or amyloid fibrils has the opposite effect. It has a strong, though apparently non-covalent affinity to cellulose fibers.

2.2 DYE REMOVAL FROM AQUEOUS BODIES

There are several methods that can be used in the removal of dyes from water.

These include biological processes which is the use of microbial biomass to remove color from dye wastewater. However, they are largely ineffective because most dyes are toxic to organisms used in the process (Brahimi-Horn *et.al.*, 1992). Coagulation (Flocculation) process is defined by IUPAC as a process of contact and adhesion whereby the particles of dispersion form larger-size clusters. It is also known as agglomeration .This effectively decolorizes insoluble dyes. The main disadvantage of the process is that it fails to work with soluble dyes (Grimshaw and Harland, 1974). Chemical destruction by oxidation is an effective method but the oxidant requirements are very high hence expensive (McKay *et al.*, 1987a). Photochemical degradation in aqueous solution is likely to proceed slowly as synthetic dyes are in principal, designed to exhibit high stability in light (Willmott *et al.*, 1998). Photocatalytic oxidation and ozone treatment methods are effective and economical, but only in cases where the solute concentrations are relatively high (Evans *et.al.*, 1984). Adsorption, therefore, remains the procedure of choice. This is because it can be used to remove different types of coloring material. Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a film of molecules or atoms (the adsorbate).

In the following sub-sections, the characteristics and general requirements of adsorbents will be discussed.

2.2.1 ADSORBENTS

Characteristics and General Requirements

Adsorbents are used usually in the form of spherical pellets, rods, moldings, or monoliths with hydrodynamic diameters between 0.5 and 10 mm. They must have high abrasion resistance, high thermal stability and small pore diameters, which results in higher exposed surface area and hence high surface capacity for adsorption.

Most industrial adsorbents fall into one of three broad classes which include Oxygen-containing compounds which are typically hydrophilic and polar. These include materials such as silica gel and zeolites; Carbon-based compounds which are hydrophobic and non-polar, including materials such as activated carbon and graphite; and Polymer-based compounds which are polar or non-polar functional groups in a porous polymer matrix.

This study focuses on materials that would typically replace carbon-based activated carbon in the removal of dyes from aqueous solutions via the process of adsorption.

Activated Carbon

Activated carbon is a highly porous, amorphous solid consisting of micro crystallites with a graphite lattice, usually prepared in small pellets or a powder. It is non-polar and cheap. One of its main drawbacks is that it is combustible.

Activated carbon can be manufactured from carbonaceous material, including coal (bituminous, sub-bituminous, and lignite), peat, wood, or nutshells (that is, coconut). The manufacturing process consists of two phases, carbonization and activation. The carbonization process includes drying and then heating to separate by-products, including tars and other hydrocarbons, from the raw material, as well as to drive off any gases generated. The carbonization process is completed by heating the material at 400-600°C in an oxygen-deficient atmosphere that cannot support combustion.

The carbonized particles are "activated" by exposing them to an oxidizing agent, usually steam or carbon dioxide at high temperature. This agent burns off the pore blocking structures created during the carbonization phase and so, they develop a porous, three-dimensional graphite lattice structure. The size of the pores developed during activation is a function of the time that they spend in this stage. Longer exposure times result in larger pore sizes. The most popular aqueous phase carbons are bituminous based because of their hardness, abrasion resistance, pore size distribution, and low cost, but their effectiveness needs to be tested in each application to determine the optimal product (Asfour *et al.*,1985)

Activated carbon is used for adsorption of organic substances and non-polar adsorbates and it is also usually used for waste water (and waste gas) treatment. It is the most widely used adsorbent. Its usefulness is derived mainly from its large micropore and mesopore volumes and the resulting high surface area.

Activated carbon is the most commonly used method of dye removal by adsorption (Nasser and El-Geundi, 1991) and is very effective for adsorbing cationic, mordant & acid dyes and to a slightly lesser extent, dispersed, direct, vat, pigment and reactive dyes- to an efficiency of 100% for the former and 94-99% for the latter. (Raghavacharya, 1997; Rao *et al.*, 1994). Performance is dependent on the type of carbon used and the characteristics of the wastewater. Removal rates can be improved by using massive doses, although regeneration or re-use results in a steep reduction in performance, and efficiency of dye removal becomes unpredictable and dependant on massive doses of carbon (Robinson *et.al.*, 2001).

Activated carbon (Sigworth and Smith, 1972; Nelson *et.al.*, 1974), although widely used as an adsorbent, is usually limited to developed countries due to its high cost (*Appendix 3*). In order to decrease the cost of treatment, attempts have been made to find inexpensive alternative adsorbents. Consequently, a number of low cost and easily available materials, such as waste biomass, are being studied for the removal of different dyes from aqueous solutions under different operating conditions. Biomass decolorizes wastewater by adsorption and ion exchange mechanisms. A description of the performance characteristics of an ideal dye adsorbent would be for it to have high capacity and rapid binding kinetics; be easily and inexpensively regenerated; and have binding properties, which are insensitive to dye bath electrolytes, other additives, and pH (Lazlo, 1994).

Forest and agricultural production by-products have been long considered as potential dye adsorbents (Abdullah *et.al.*, 2005). Dye adsorption studies have been carried out using Chitin and Chitosan; Microbial biomass; Chemically-modified cellulose and lignocelluloses; and Unmodified lignocellulose biomass as biomass for decolorization of solutions containing dyes (Lazlo, 1994; Robinson *et al.*, 2001).

Chitin and Chitosan

Chitin, a polymer of N-acetyl glucosamine obtained from shellfish waste, has been examined for its dye-binding ability (McKay *et.al.*, 1982; Smith *et.al.*, 1993). The dye –binding kinetics of chitin were found to be very slow. In addition, the effects of temperature on binding capacity varied among the various dyes tested. The influence of electrolyte concentration and solution pH on dye binding was however, not investigated.

Treatment of chitin with strong base produces the deacylated form of chitin called chitosan. A particulate form of chitosan gave low dye binding values under non-equilibrium conditions of packed beds reflecting the poor binding kinetics of particulate chitosan. Chitosan can be spun into fibers (Qin, 1993), which apparently have much improved adsorption kinetics. Chemically cross-linking the chitosan fibers allows the fibers to be used at low pH, which improves their dye binding capacity, without solubilizing the chitosan (Yoshida *et al.*, 1991; 1993). The cross-linked fibers were regenerated by treatment with NaOH.

Chitosan also can be cast into membranes and then cross-linked to produce filters with good physical and chemical stability and high water permeability

(Yisong *et al.*, 1990). Chitosan membranes thus would be expected to have very rapid dye adsorption kinetics.

Microbial Biomass

Fungi

Many industrially used fungi contain chitin and chitosan in their cell walls (Volesky, 1990). Hence, the fungal biomass by-products of industrial fermentation processes can serve as an alternative to crustaceans as a source of chitin-based dye adsorbents. In another study, the cell wall of *Myrothcium verrucaria* was shown to bind azo dyes. Dye binding to fungal material was moderately slow (Brahimi-Horn *et al.*, 1992). The white-rot fungus, *Phanerochaete chysosporium* has been widely studied with regards to xenobiotic degradation. It was shown (Paszczynski and Crawford, 1995) that although azo dyes, the largest class of commercially produced dyes, are not readily degraded by micro-organisms, they can however be degraded by *P.chysosporium*. Other fungi such as *Hirschioporus larincinus, Inonotus hispidus, Phlebia tremellosa* and *Coriolus versicolor* have been shown to decolorize dye-containing effluent (Banat *et al.*, 1996; Kirby, 1999).

Bacteria

Bacterial biomass has also been shown to adsorb dyes (Hu, 1996). In the study by Hu, adsorption of eleven dyes reactive to *Aeromonas* biomass was examined. Dye binds to the bacteria cell wall fraction. The dye adsorption kinetics was moderately fast, but no method to regenerate the biomass was indicated. In other investigations, mixed bacterial cultures from a wide variety of habitats have been shown to decolorize the diazo-linked chromophore of dye molecules in 15 days (Knapp and Newby, 1995). Nigam and Marchant (1995) and Nigam *et al.*, (1996) demonstrated that a mixture of dyes was decolorized by anaerobic bacteria in 24-30 hours, using free growing cells or in the form of biofilms on various support materials. Ogawa and Yatome (1990) also demonstrated the use of bacteria for azo dye biodegradation. These microbial systems have the drawback of requiring a fermentation process, and are therefore unable to cope with larger volumes of effluents.

Other bacterial strains that have been shown to be able to degrade certain azo dyes are *Pseudomonas* strains (Kulla, 1981) and a strain of *Sphingomonas* (Keck *et al.*, 1997).

Yeasts

Yeasts, such as *Klyveromyces marxianus,* are capable of decolorizing dyes. Banat et al. (1999) showed that *K. marxianus* was capable of decolorizing Remazol Black B by 78-98%. Zissi *et al.*, (1997) showed that *Bacillus subtilis* could be used to break down *p*-aminoazobenzene, a specific azo dye. Further research using mesophilic and thermophilic microbes have also shown them to degrade and decolorize dyes (Nigam *et al.*, 1996; Banat *et al.*, 1997).

Dead Microbial Biomass

Dead bacteria, yeast and fungi have been used for the purpose of decolorizing dye-containing effluents (Robinson *et al.*, 2001).

Dyes vary greatly in their chemistry, and therefore their interactions with microorganisms depend on the chemistry of a particular dye and the specific chemistry of the microbial biomass (Polman and Brekenridge, 1996).

The use of biomass has its advantages, especially if the dye-containing effluent is very toxic. Biomass adsorption occurs when conditions are not always favorable for the growth and maintenance of the microbial population (Modak and Natarajan, 1995).

Biosorption tends to occur reasonably quickly: a few minutes in algae to a few hours in bacteria (Hu, 1996). This is likely due to an increase in surface area caused by cell rupture during autoclaving (Polman and Brekenridge, 1996).

Chemically-Modified Cellulose and Lignocellulose

As discussed (*see section* 2.2), chemical modification of chitin improves its dye adsorption characteristics. In much the same way, derivatization of cellulose or lignocellulosic biomass can dramatically improve their dye binding properties. In studies (Hwang and Cheng 1993a,b) carried out, the grafting of polyamide-epichlorohydrin (PAE) polymer onto cellulose was described. This material, which composed of 10-30% cellulose, was found to have a high adsorption capacity. However, the rate of dye adsorption was found to be very low. An added disadvantage is that no studies show if PAE-Cellulose can be regenerated, neither is it known to what extent dye bath electrolytes influence dye binding (Lazlo, 1994).

In another study (Youssef, 1993), chemical modification of cellulose (cotton) with N-methyl derivatives of tris- and bis- (2-carbamoylethyl) ethylamine to enhance dye adsorption was described. It was found that dye adsorption decreased with increasing pH, as would be expected for a weak, tertiary amine ion exchanger. Dye was readily removed from the cellulose derivative with NaOH.

Quaternary ammonium groups can be introduced into cellulose and lignocellulosic materials using the same chemistry as employed for cotton fabrics (Evans *et al.*, 1984). The quaternary ammonium group introduces a permanent positive charge into the substrate, making the materials very effective dye adsorbents. This was demonstrated in various studies (Gangneux *et al.*, 1976 a,b) Quaternized cellulose was shown to bind unidentified azo dyes, and to be readily regenerated by desorbing bound dye with a solution containing NaCl and NaOH (Jorgensen, 1979). A major draw back of this material is its high cost due to the cost of preparing pure cellulose.

Low cost adsorbents can be prepared by quaterization of lignocellulosic materials such as maize cob (McKay *et al.*, 1987b), sawdust (Asfour *et al.*, 1985) and sugarcane bagasse (McKay *et al.*, 1987a, 1988). The dye adsorption and desorption characteristics of the quaternized lignocelluloses should be comparable to the cationic materials prepared from pure cellulose. Thus, relatively inexpensive and moderately high capacity dye adsorbents can be prepared from lignocellulose biomass.

Formaldehyde and concentrated sulphuric acid-treated sawdust and dilute acid-hydrolyzed charred sawdust have been successfully used as adsorbents for a variety of dyes (Shukla *et al.*, 2002; Garg *et al.*, 2003). Cellulose-based anionic dye adsorbents have been prepared from agricultural residues treated with cross-linked polyethylenimine (Ibrahim *et al.*, 1997); also, carbonized agricultural wastes such as coir pith (Namasivayam *et al.*, 2001a), cassava peel (Rajeshwarisivaraj *et al.*, 2001), bagasse (Tsai *et al.*, 2001) and kudzu (Allen *et al.*, 2003) have been utilized successfully for the removal of dyes from aqueous solutions.

Unmodified Lignocellulose Biomass

Forest and agricultural production by-products have long been considered as potential dye adsorbents (Lazlo, 1994). Unfortunately, without chemical modification these materials uniformly have shown very low adsorption capacities for acidic dyes. An examination was carried out on wood bark, rice husks, and cotton waste for their ability to bind Congo red (a divalent anion) (McKay *et al.*, 1982). Negligible amounts of adsorption were observed.

Other studies carried out (Abo-Elela and El-Dib, 1987; McKay *et al.*, 1988; Nawar and Doma, 1989) on wood shavings, maize cob, peat moss and rice hulls, came to the same conclusion.

Among the untreated materials that have been investigated, wood shavings are commonly used as an adsorbent especially for basic dyes, with capacity varying according to the structure of the dye and the mesh size (Abo-Elela and El-Dib, 1987). Many agricultural residues, such as wheat straw, wood chips and corncobs, have been used successfully to adsorb individual dyes and dye mixtures in textile effluent (Nigam *et al.*, 2000). Removal of Methylene blue and other basic dyes has been carried out using coir pith, an unwanted product from the coir processing industry (Namasivayam *et al.*, 2001b), banana/orange peels (Annadurai *et al.*, 2002) and palm-fruit bunch particles (Nassar and Magdy, 1997; Nassar, 1999).

The commercial potential of raw lignocellulosic materials for the treatment of colored wastewater has not been fully realized. Indeed, there is need for continued trials in the discovery of other materials, whose results could be successful. The present study is undertaken to evaluate the efficiency of two lignocellulosic materials, *Telfairia pedata* and *Luffa cylindrica*, for removal of Methylene blue and Congo red dyes in aqueous solution. The following sub-sections give a brief description of each of these materials.

Telfairia pedata

Telfairia pedata (T.pedata) is also known as the oyster nut. It is a perennial dioecious member of the Cucurbitaceae family grown in Central and East Africa. It is drought tolerant, can grow at elevations up to 2,000 m. The vines will climb for up to 30 meters. The flowers are pinkish-purple (*plate 1*). The nuts are relished by people in Tanzania and are normally planted directly in the drip line of existing trees (*plate* 2). The species is cultivated in Meru (Kenya), Kabale (Uganda), Mauritius, Mozambique, Tanzania, Zanzibar and Malawi. The seed is rich in fats and minerals and is part of the traditional food of breastfeeding mothers, now primarily eaten by children. The nuts (seeds) are sold by vendors in Tanzanian markets (Jeffrey, 1967).

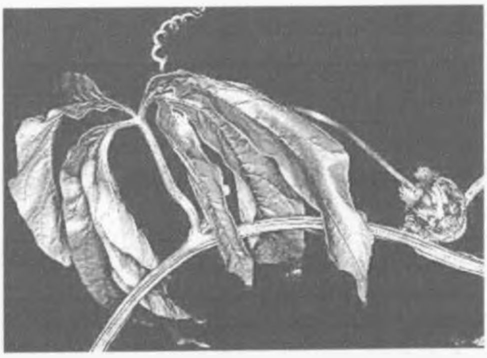


Plate 1: *T.pedata* plant.

Seeds are typically 3 cm in diameter, yellow or brown in color, flat and nearly circular and covered with a network of fibrous material (*see plate 2 below*). It is the network of fibrous material which covers the seeds that was crushed (*plate* 3) and was the subject of testing in this work.

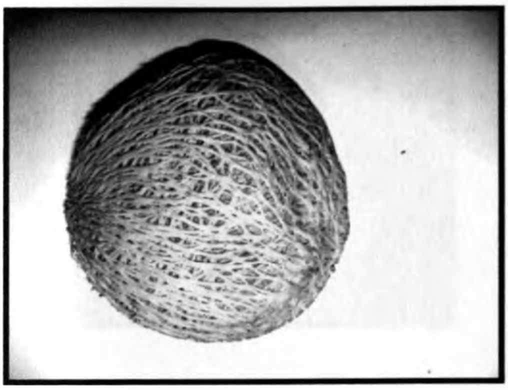


Plate 2: ***T.pedata*** **seed.**

Diameter= 3-5.5 cm.

Plate 3: ***T.pedata*** **crushed husks.**

Size= ≥ 300 microns.

Luffa cylindrica

Luffa cylindrica (L.cylindrica) is also known as Loofah, Dishcloth Gourd or Vegetable Sponge Gourd. It is 1-2ft long, cylindrical, smooth skinned gourd (*plate 4 and 5*). The interior contains white flesh as well as a fibrous structure that is dried and used as a sponge.

Plate 4: ***L.cylindrica*** **plant**

(Immature plant)

Plate 5: ***L.cylindrica*** **mature plant**

This is ready for harvesting.

Its fruits can be eaten, but the vine is most commonly grown for the fibrous interior of the fruits, which when dried, can be used as a sponge (*see Plate 6*).

The crop can be found in Shinyanga area in Tanganyika, west Usambara Mountains, Ulanga District and Makuyuni in Tanzania; and in Uganda it is grown in Ankole, Mbale (Tororo & Nloy) and Mengo districts. In Kenya, *L.cylindrica* is grown in Kwale and Machakos (Mtito Andei) Districts. These regions are semi arid. The crop therefore will not replace food crops.

It is a very fast growing vine to 10-15ft. The vines may be ground dwelling, but grow best when given upward support. The interior, whose fibrous structure when dried can be used as a sponge, was the subject of testing in this work.

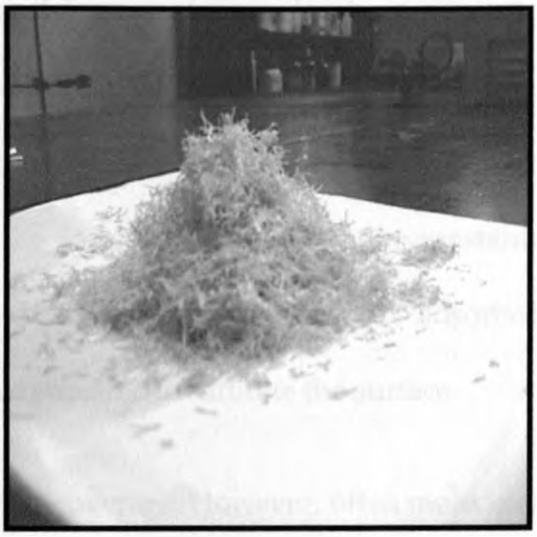


Plate 6: ***L.cylindrica*** **after harvesting** **Plate 7:** ***L.cylindrica*** **crushed fruit**

2.3 ADSORPTION

2.3.1 Adsorption Isotherms

Adsorption isotherms describe the equilibrium conditions for the adsorbate (Weber, 1972).

Generally, there are five adsorption isotherms depending on whether the surface coverage is mono or multilayer (Henderson *et. al.*, 2009):

The first mathematical fit to an isotherm was published by Freundlich and Küster (1894) and is a purely empirical formula for gaseous adsorbates,

$$\frac{x}{m} = kP^{\frac{1}{n}}$$

where x is the quantity adsorbed, m is the mass of the adsorbent, P is the pressure of adsorbate and k and n are empirical constants for each adsorbent-adsorbate pair at a given temperature. The function has an asymptotic maximum as pressure increases without bound. As the temperature increases, the constants k and n change to reflect the empirical observation that the quantity adsorbed rises more slowly and higher pressures are required to saturate the surface.

The Langmuir isotherm assumes monolayer coverage. However, often molecules do form a multilayer (some are adsorbed on already adsorbed molecules) and the Langmuir isotherm is not valid. In 1938 Stephan Brunauer, Paul Emmett, and Edward Teller developed a model isotherm that takes that possibility into account. Their theory is called BET theory, after the initials in their last names. They modified Langmuir's mechanism. The Langmuir isotherm is usually better for chemisorption and the BET isotherm works better for physisorption for non-microporous surfaces.

In other instances, molecular interactions between gas molecules previously adsorbed on a solid surface form significant interactions with gas molecules in the gaseous phase. Hence, adsorption of gas molecules to the surface is more likely to occur around gas molecules that are already present on the solid surface, rendering the Langmuir adsorption isotherm ineffective for the purposes of modelling. This effect was studied in a system where nitrogen was the adsorbate and tungsten was the adsorbent by Paul Kisliuk in 1957, giving rise to the Kisliuk adsorption isotherm.

The Henderson-Kisliuk adsorption isotherm was developed for use with the new field of Self Assembling Monolayer (SAM) adsorption. SAM molecules adsorb to the surface of an adsorbent until the surface becomes saturated with the SAM molecules' hydrocarbon chains lying flat against the adsorbate.

The Freundlich Isotherm will be revisited in a short while but first, there is going to be a brief discussion on the other main isotherm: The Langmuir Isotherm.

The Langmuir Isotherm

The Langmuir Isotherm (Langmuir, 1916) is the simplest isotherm and is based on three assumptions:

1. That adsorption cannot proceed beyond monolayer coverage
2. That all sites are equivalent and the surface is uniform
3. That the ability of a molecule to adsorb at a given site is independent of the occupation of neighboring sites.

Langmuir derived the relationship for weight adsorbed per unit weight of adsorbent, q, and concentration in fluid C, based on the assumptions above.

The rate of attachment to the surface should be proportional to the driving force multiplied by the area. The driving force is the concentration of the fluid, and the area is the amount of bare surface (Langmuir, 1916). If the fraction of covered surface is Φ:

Rate going in= $k_1 C (1-\Phi)$ (Samuelson, 1963)...................... ....eq.2.1

The evaporation or adsorption from the surface is proportional to the amount of surface covered.

Rate leaving= $k_2 \Phi$..eq.2.2

Where k_1 and k_2 are the rate coefficients for adsorption and desorption processes respectively, C is the concentration in the fluid and Φ is the fraction of the surface covered.

At equilibrium, the two rates are equal and it can be shown that:

$$\Phi = \frac{k_1 C}{k_2 + k_1 C} \qquad \text{.........eq.2.3}$$

By dividing the numerator and the denominator of equation 2.3 by k_1 we find that:

$$\Phi = \frac{C}{[k_2 / k_1] + C} \qquad \text{.........eq.2.4}$$

Since q (unit weight of adsorbent) will be proportional to Φ, the useful form of the equation is:

$$q = \frac{q_m k_a C}{(1 + k_a C)} \quad \text{...eq.2.5}$$

where $q_m = q$ for a complete layer and k_a is a coefficient.

Taking reciprocals and rearranging:

$$\frac{1}{q} = \frac{1}{q_m} + \frac{1}{k_a q_m C} \quad \text{...eq.2.6}$$

A plot of $\frac{1}{q}$ vs. $\frac{1}{C}$ should yield a straight line of slope $\frac{1}{k_a q_m}$ and an intercept of $\frac{1}{q_m}$ (Berrueta *et al.*, 1990), if the Langmuir model is applicable.

Freundlich (Classical) Adsorption Isotherm

The Freundlich Isotherm (Freundlich, 1906) is a reliable model for interpreting adsorption beyond one layer. This is an empirical expression used to connect the quantity of a substance adsorbed and the concentration of the adsorbate in solution at a given temperature. It assumes the logarithmic fall in the enthalpy of adsorption with the surface coverage. The equilibrium relationship proposed by Freundlich is only valid when the adsorption is purely a physical process. The equilibrium model is:

$$q_e = k_f C_e^{1/n} \quad \text{...eq.2.7}$$

Where q_e is the equilibrium adsorbed amount of analyte on the adsorbent, C_e is the equilibrium concentration of the analyte and k_f and n are constants depending on the nature of the adsorbent and adsorbate (Weber, 1972).

k_f is an approximate constant that indicates adsorption capacity while $\frac{1}{n}$ is the function of the strength of adsorption. The constant can be obtained by introducing logs on the above equation i.e.

$$Log\ q_e = Log\ k_f + \frac{1}{n} Log\ C_e \qquad \text{eq.2.8}$$

A plot of $Log\ q_e$ versus $Log\ C_e$ gives a linear graph with a slope of $\frac{1}{n}$ and intercept of $Log\ k_f$ if the Freundlich model is applicable (McKay et.al, 1982).

CHAPTER 3

MATERIALS AND METHODS

3.1 Adsorbent Preparation

Preparation of the adsorbent material involved the processes of grinding & sieving; and cleaning.

3.1.1 Grinding and Sieving

The subject of testing in *T.pedata* is the network of fibrous material which covers the seeds (*see Plate* 2). This material had to be separated from the rest of the seed by use of a sharp, knife-like object.

L.cylindrica, on the other hand, was obtained from a local (Gikomba market in Nairobi, Kenya) market already dried and ready to be used by the locals as a sponge. The "sponge" is a fibrous structure which connects from 1 to 2 feet long and is cylindrical (*see Plate* 6). The structure was cut into small pieces by use of sharp scissors. Both the cut pieces from the *L.cylindrica* and the fibrous material of *T.pedata* were separately subjected to grinding in a mechanical grinder: *The Wiley Mill model no.2.*

The ground substance from the two materials was separately sieved using the number 52 sieve, with pore size of $\geq$ 300 microns. Subsequently, the size of material achieved through the process was $\geq$ 300 microns for to expose maximum adsorption sites. The material was also sieved to achieve uniform size of adsorbent.

3.1.2 Cleaning

Cleaning of the plant materials was necessary to remove oil and other substances that could interfere with the adsorption process. The ground substance from the two materials was separately washed copiously following the procedure outlined below:

The material was placed in a 20 L bucket. Deionised water was then poured in making sure that the material was completely soaked. The mixture was thoroughly stirred using a rod and left to soak for two hours. The water was then decanted and fresh deionised water introduced. The mixture was again thoroughly stirred and left to soak for another two hours. This process was repeated five times (ten hours in total).

The resultant material was then soaked in hot water and decanted every two hours for ten hours every day for fourteen days. During this time, the material was left to soak overnight.

On the fifteenth day, the material was soaked in distilled water for 48 hours. The distilled water was decanted and replaced every 24 hours.

The material was dried in an oven at 100 ^{0}C for 3hours. The material was sieved again using the number 52 sieve and then the portions were subjected to sonication by soaking in distilled water contained in a 500 ml beaker and placed in a sonicator for 5 hours in the case of *T.pedata* and 2 hours in the case of

L.cylindrica. Distilled water in the beaker was poured out and replaced every hour.

Finally, the sonicated material was dried in an electric oven at 100 ^{0}C for 4 hours.

3.2 BATCH ADSORPTION EXPERIMENTS

Batch adsorption experiments were carried out using different composition feed mixtures taken in various flasks placed in an orbital shaker (*Thermolyne Type 65800*) at 200 rotations per minute (200 rpm). The orbital shaker functioned to regenerate laboratory conditions analogous to natural water systems. At the end of predetermined periods of time, the supernatant was withdrawn by means of a syringe and the level of adsorption was determined using a UV-Visible Spectrophotometer (*Turner Model SP-850*). These studies were carried out using *Telfairia pedata, Luffa cylidrica* and a mixture of both in various proportions. The procedure for the study of each of the parameters is discussed below:

3.2.1 Effect of Contact Time

Part 1

A solution of 1.0×10^{-5} M Congo red dye was prepared from a stock solution using the dilution formula $C_1V_1=C_2V_2$. Where C_1 is the stock solution of known concentration, V_1 is the volume to be drawn from the stock solution, C_2 is the concentration of the intended solution and V_2 is the volume of the volumetric flask used to make the stock solution.

The absorbance measurement for this solution was obtained. 1.0 gram portions of *L.cylindrica* were weighed out into a 100 ml conical flask. Into the 100 ml conical flask containing the 1.0 gram portion of *L.cylindrica*, 30 ml of the dye solution was introduced. The clock was started at this time. The mixture was swirled very fast and a few ml was withdrawn from the mixture by means of a syringe. The withdrawn solution was introduced into a sample cell of a UV/ VIS. spectrophotometer. The remaining solution mixture was placed on the orbital shaker pre-set at 200 rpm. The absorbance reading was recorded at λ_{max}=499 nm (Congo red). This was the wavelength used for all other readings involving this dye unless otherwise stated. The sample in the sample cell (cuvette) was returned back into the conical flask mixture. The next aliquot was withdrawn after a five minute interval and its absorbance measured then returned to the mixture. This process was repeated over a period of two hours and the mixture then left to equilibrate for an additional four hours. The last aliquot was withdrawn at the 6th hour and an absorbance reading was obtained.

The entire procedure was repeated using 1 gram portions of *T.pedata* instead of *L.cylindrica.*

The entire procedure was also repeated using a mixture of 0.5g portions of *L.cylindrica* and 0.5g portions of *T.pedata.*

Part 2

The procedure above was repeated using a solution of 1.0×10^{-5} M Methylene blue dye instead of Congo red dye.

The absorbance reading was recorded at λ_{max}=664nm (Methylene Blue). Absorbance readings for this dye were made at this wavelength in the subsequent studies unless stated otherwise.

3.2.2 Effect of Dye Concentration

Part 1

Congo red solution of varying concentrations (1.0×10^{-6} M, $2.5\text{X}10^{-6}$ M, $5.0\text{X}10^{-6}$ M, $7.5\text{X}10^{-6}$ M and 1.0×10^{-5} M) were prepared by serial dilution. The absorbance of each of the solutions was determined by use of a UV/VIS spectrophotometer. 1.0 gram portions of *L.cylindrica* were weighed out into a 100 ml conical flask. Into the 100 ml conical flask containing the 1.0 gram portion of *L.cylindrica*, 30 ml of 1.0×10^{-6}M solution of Congo red was introduced. The mixture was left to equilibrate in the orbital shaker for 30 minutes. A few ml was withdrawn from the mixture by means of a syringe. The withdrawn solution was introduced into a sample cell of a UV/VIS. Spectrophotometer and the corresponding absorbance value obtained. After recording the absorbance reading, the sample in the sample cell (cuvette) was returned back into the conical flask mixture. The mixture was left to equilibrate for a further 30 minutes. A few ml was withdrawn from the mixture by means of a syringe. The withdrawn solution was introduced into a sample cell and the absorbance recorded.

This procedure was repeated for the 2.5X10^{-6}M, 5.0X10^{-6}M, 7.5X10^{-6}M and 1.0x10^{-5}M solutions.

The entire procedure was repeated using 1 gram portions of *T.pedata* instead of *L.cylindrica.*

The entire procedure was also repeated using a mixture of 0.5g portions of *L.cylindrica* and 0.5g portions of *T.pedata.*

Part 2

The procedure was repeated using dye working concentrations of Methylene Blue solution (1.0 x10^{-6} M, 2.5X10^{-6} M, 5.0X10^{-6} M, 7.5X10^{-6} M and 1.0x10^{-5} M) that were prepared by serial dilution instead of Congo red dye.

3.2.3 Effect of Adsorbent Dose

Part 1

Different weights (0.5 g, 1.0 g, 1.5 g, 2.0 g, 2.5 g and 3.0 g) of *L.cylindrica* were separately placed in 100 ml conical flasks. A 30 ml aliquot of 1x10^{-5} M Congo Red solution was introduced into the conical flask containing 0.5 g of *L.cylindrica.* The mixture was left to equilibrate in the orbital shaker for 30 minutes. A few ml was withdrawn from the mixture by means of a syringe and was introduced into a sample cell (cuvette). The absorbance reading was recorded. The sample in the cuvette was returned back into the conical flask mixture. The mixture was left to equilibrate for a further 30 minutes. The absorbance was measured following equilibration.

This procedure was repeated for the other weights: 1.0 g, 1.5 g, 2.0 g, 2.5 g and 3.0 g.

The entire procedure was repeated using 0.5 g, 1.0 g, 1.5 g, 2.0 g, 2.5 g and 3.0 g portions of *T.pedata* instead of *L.cylindrica.*

The entire procedure was also repeated using mixtures comprising of 0.25 g of *L.cylindrica* and 0.25 g of *T.pedata;* 0.5g of *L.cylindrica* and 0.5 g of *T.pedata;* 0.75 g of *L.cylindrica* and 0.75 g of *T.pedata* ; 1 g of *L.cylindrica* and 1 g of *T.pedata* ; 1.25 g of *L.cylindrica* and 1.25 g of *T.pedata* ; and 1.5 g of *L.cylindrica* and 1.5 g of *T.pedata.*

Part 2

The procedure was repeated using a solution of $1.0\text{x}10^{-5}$ M Methylene Blue solution instead of Congo red solution.

3.2.4 Effect of pH

Part 1

30 ml of $1.0\text{x}10^{-5}$ M Congo Red dye solution was pipetted into a 50 ml volumetric flask. This solution was topped to the mark with distilled water. 30 ml of $1.0\text{x}10^{-5}$ M Congo Red dye solution was pipetted into a 50 ml volumetric flask. This solution was mixed with 1 ml of 1 M HCl and topped to the mark with

distilled water. This process was repeated with 2 ml, 3 ml, 4 ml and 5 ml of 1 M HCl. The pH and absorbance of each of the solutions were obtained prior to mixing with the sorption material. 1.0 gram portions of *L.cylindrica* were weighed out into 100 ml conical flasks. Into the 100 ml conical flask containing the 1.0 gram portion of *L.cylindrica*, 30 ml of the 1.0×10^{-5} M Congo red solution containing 1 M HCl was introduced. The mixture was left to equilibrate in the orbital shaker for 30 minutes. A few ml was withdrawn from the mixture for the absorbance reading to be taken. The pH of the withdrawn solution was also obtained and recorded. The sample in the cuvette was returned back into the conical flask mixture. The mixture was left to equilibrate for a further 60 minutes, and thereafter its absorbance was recorded. The pH of the withdrawn solution was also obtained and recorded. This procedure was carried out using the unmodified and the 1 ml, 2 ml, 3 ml, 4 ml and 5 ml of 1 M HCl pH-modified solutions of 1.0×10^{-5} M Congo Red dye solutions.

The entire procedure was repeated using 1 gram portions of *T.pedata* instead of *L.cylindrica.*

The entire procedure above was also repeated using a mixture of 0.5g portions of *L.cylindrica* and 0.5g portions of *T.pedata.*

Part 2

The procedure was repeated using 30 ml of 1.0×10^{-5}M Methylene Blue dye solution instead of Congo red solution.

3.2.5 Effect of Temperature

Part 1

1.0 gram portions of *L.cylindrica* were weighed out into six separate 100 ml conical flasks. Into one of the 100 ml conical flasks containing the 1.0 gram portion of *L.cylindrica*, 30 ml of 1x 10^{-5} M Congo Red was introduced. The mixture was left to equilibrate at 20 ^{0}C in a thermostat oven (*Gallenkamp Brand Thermostat shaker at 120 rpm*) for 30 minutes. An aliquot sample was measured for absorbance after which it was returned back into the conical flask mixture. The mixture was left to equilibrate for a further 30 minutes followed by its absorbance measurement. The procedure was repeated at different temperatures (30 ^{0}C, 40 ^{0}C, 50 ^{0}C, 60 ^{0}C and 70 ^{0}C).

The entire procedure above was repeated using 1 gram portions of *T.pedata* instead of *L.cylindrica.*

The entire procedure above was also repeated using a mixture comprising of 0.5g portions of *L.cylindrica* and 0.5g portions of *T.pedata.*

Part 2

The procedure was repeated using 30 ml of 1x 10^{-5} M Methylene Blue instead of Congo red dye.

3.2.6 Effect of Ionic Strength

Part 1

A stock solution of 0.1 M KCl was prepared by calculating the dilution required using the following formula $C_1V_1=C_2V_2$ (*section 3.2.1*)

1.0 gram portions of *L.cylindrica* were weighed out into six separate 100 ml conical flasks. KCl, water and Congo red solution were mixed in labeled conical flasks. Each conical flask contained 20 ml Congo red solution. In the conical flask labeled 1, 10 ml of water was introduced. In the conical flask labeled 2, 2ml of water and 8 ml of KCl was introduced. In flask 3, 4ml of water and 6 ml of KCl was introduced. In the 4th flask, 6ml of water and 4 ml of KCl was added. 8ml of water and 2ml of KCl was added to the 5th flask. Finally, 10 ml of KCl was added to the 6th flask.

Each solution was shaken and poured into labeled flasks containing *L. cylindrica.* The mixture was left to equilibrate in the orbital shaker for 30 minutes. Once the absorbance was recorded, the sample was returned into the conical flask mixture. The mixture was left to equilibrate for a further 30 minutes and its absorbance recorded.

The entire procedure was repeated using 1 gram portions of *T.pedata* instead of *L.cylindrica.*

The entire procedure was further repeated using a mixture comprising of 0.5g portions of *L.cylindrica* and 0.5g portions of *T.pedata.*

Part 2

The procedure was repeated using 1.0×10^{-5} M solution of Methylene Blue instead of Congo red dye and the absorbance was recorded.

3.3 FIXED-BED EXPERIMENTS

3.3.1 Effect of Initial Dye Concentration

Continuous flow sorption experiments were conducted in a glass column (Sigma chemical company, 3 cm in diameter and 23 cm in height). 2.5 g of *L.cylindrica* was tightly packed into the glass column with the aid of a spatula. This measured to 7.5 cm of bed height. Methylene blue solution, whose concentration was $1.0\text{X}10^{-5}$ M, was pumped from a 20 L capacity container, filled to the 5 L mark, into the column in a down-flow direction by a pump at a known flow rate. The flow rate was established to be 20 ml/min after taking an average from 3 trials. Solution eluates were collected after exiting the column at regular time intervals (after every 100 ml) throughout the process.

The procedure was repeated using 2.5 g of *T.pedata*, then a mixture of 1.25 g *L.cylindrica* and 1.25 g of *T.pedata*.

The procedure outlined above was repeated using a dye concentration of $5.0\text{X}\ 10^{-6}$ M instead of $1.0\text{X}10^{-5}$ M.

3.3.2 Effect of Adsorbent Dose (Bed Height)

The procedure described in section 3.3.1 (first paragraph) was repeated.

The procedure was repeated using 2.5 g of *T.pedata*, then a mixture of 1.25 g *L.cylindrica* and 1.25 g of *T.pedata*.

The procedure was repeated using 5.0 g of both the adsorbents separately and a mixture of 2.5 g of each adsorbent that made up a mixture. The bed height in this case was 14.8 cm.

The set up is represented in Plate 8

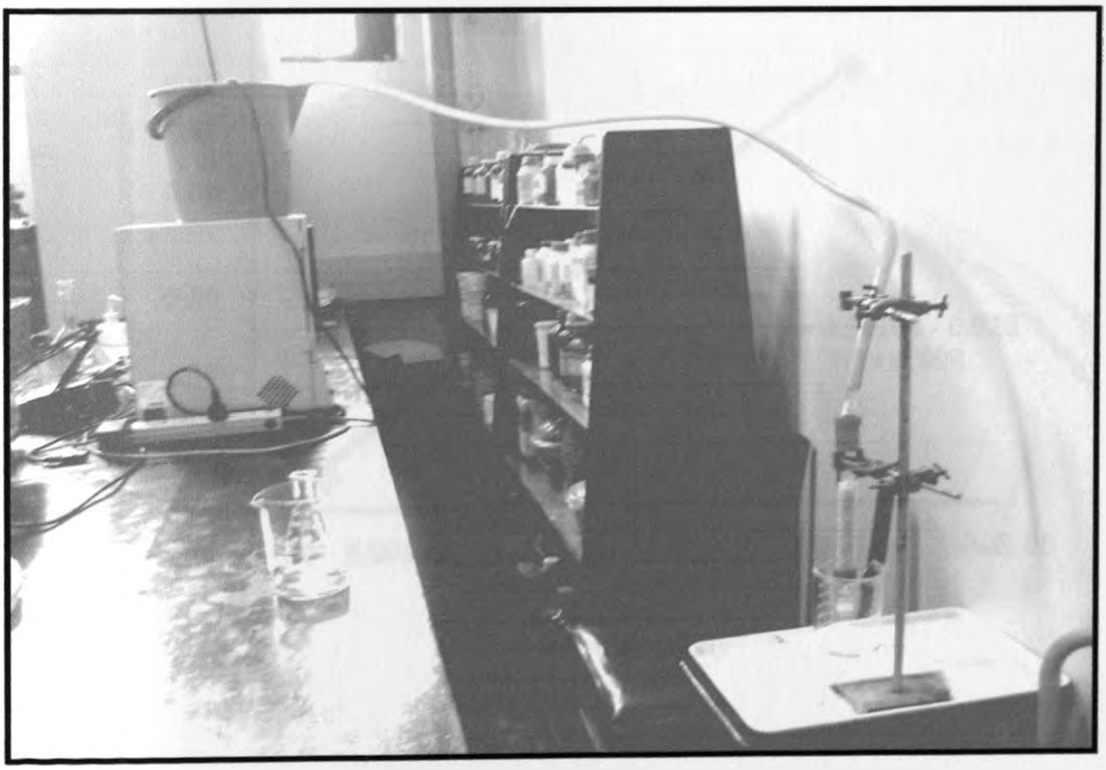


Plate 8: Set-up for Fixed-bed studies. The column (23cm in height and 3cm in diameter) contains 5.0g of *L.cylindrica*.

CHAPTER 4

RESULTS AND DISCUSSION

4.0 Generation of a Calibration Plot and Its Usage

In order to determine the exact concentration of the residual dye from a dye-adsorbent mixture, it was necessary to obtain a calibration plot (a plot of analytical signal versus the concentration of dye) from which the response of an unknown sample could be interpolated to obtain its corresponding concentration. Figures 3 and 4 represent the typical concentration calibration plots drawn for Congo red and Methylene blue dyes, respectively.

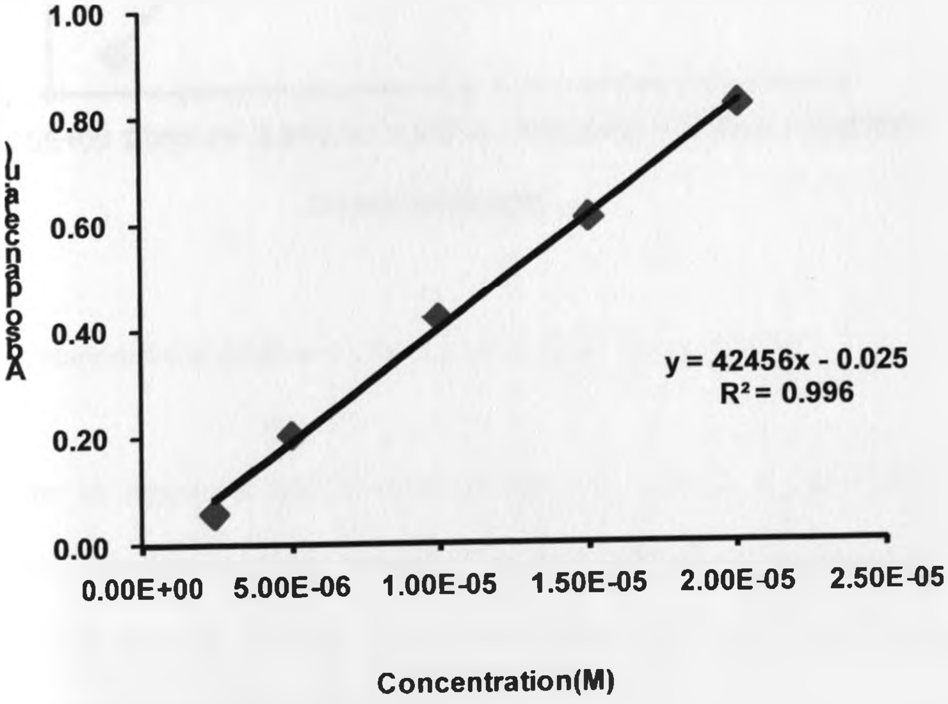


Figure 3: Standard Calibration curve for Congo red Solution.

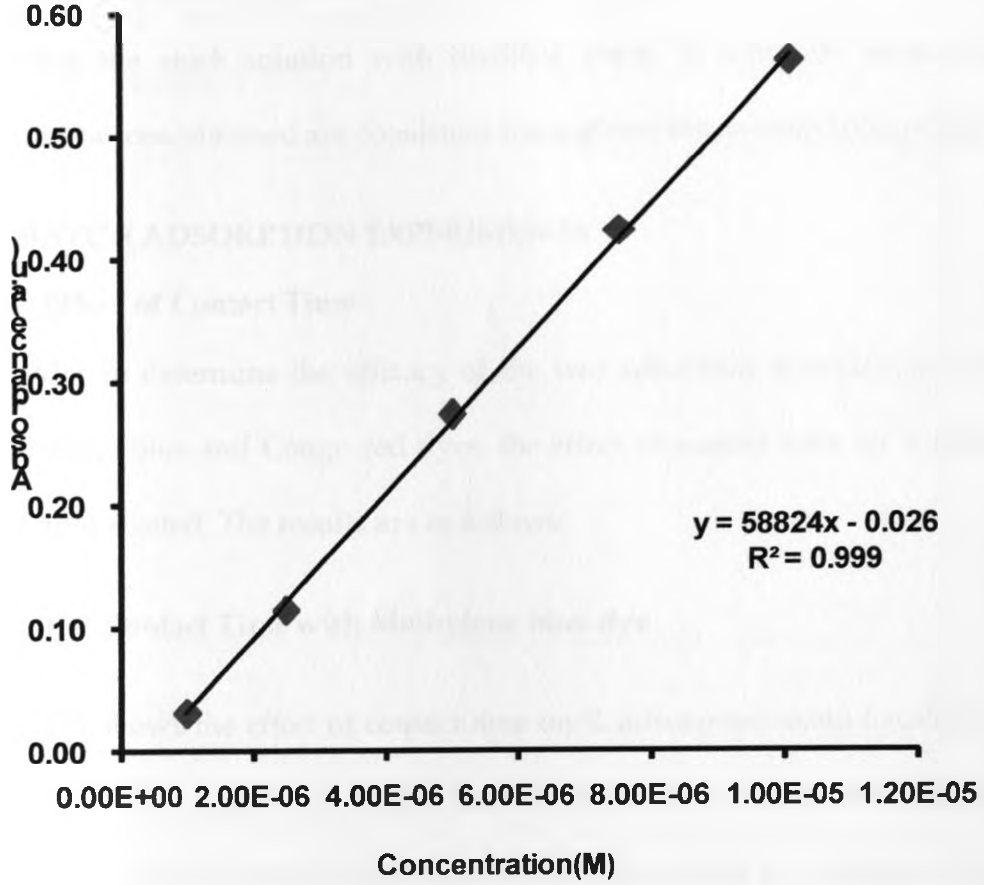


Figure 4: Standard Calibration Curve for Methylene Blue solution

The points in figures 3 and 4 were obtained by getting the absorbance of solutions that had been diluted serially. The first absorbance measurement was taken at 1.00x10^{-6} M, making this the automatic start point of the graph. Absorbance reading at 0 M was not undertaken.

The significance of this exercise in generating the calibration plots becomes clear in the advanced stages of the experimental process where one has to repetitively prepare solutions of certain or various concentrations (working solutions) by diluting the stock solution with distilled water. It serves to ensure that the concentrations obtained are consistent throughout the investigation period.

4.1 BATCH ADSORPTION EXPERIMENTS

4.1.1 Effect of Contact Time

In order to determine the efficacy of the two adsorbent materials in adsorbing Methylene blue and Congo red dyes, the effect of contact time on % adsorption was investigated. The results are as follows:

Effect of Contact Time with Methylene blue dye

Figure 5 shows the effect of contact time on % adsorption using *L.cylindrica*. The plot shows that *L.cylindrica* rapidly adsorbed the dye solution and within the first 5 minutes, approximately 97% of it had been adsorbed. On contact, within the first few seconds, 87% of the dye had been adsorbed. This indicates instantaneous adsorption of the dye by the adsorbent. The change in percentage adsorption after the 5th minute became relatively gradual with the equilibrium being reached at the 100th minute, when 99% of the dye solution had been adsorbed. The % adsorption increased with increase in contact time before attainment of equilibrium (exhibited by the plateau profile).

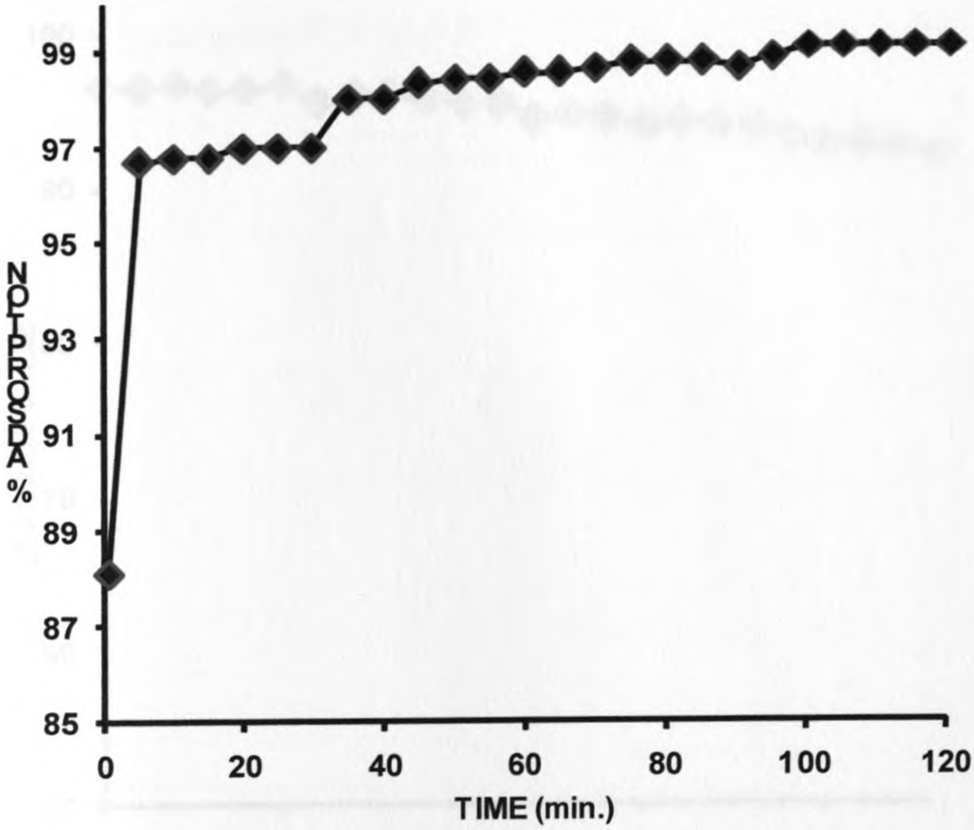


Figure 5: Plot of % adsorption of Methylene blue dye by *L.cylindrica* versus contact time

Similar experiments were conducted using *T.pedata* and the results are shown in Figure 6. From the figure, % adsorption decreased with increase in contact time. An adsorption efficiency of 97% was recorded within the first 5 minutes which decreased to 93% by the 120th minute. The decrease is thought to be due to the presence of interferents from the adsorbent, which are increasingly released with the lapse of time. The interferents either compete with the dye cations for the adsorption sites or interfere with the absorbance measurements.

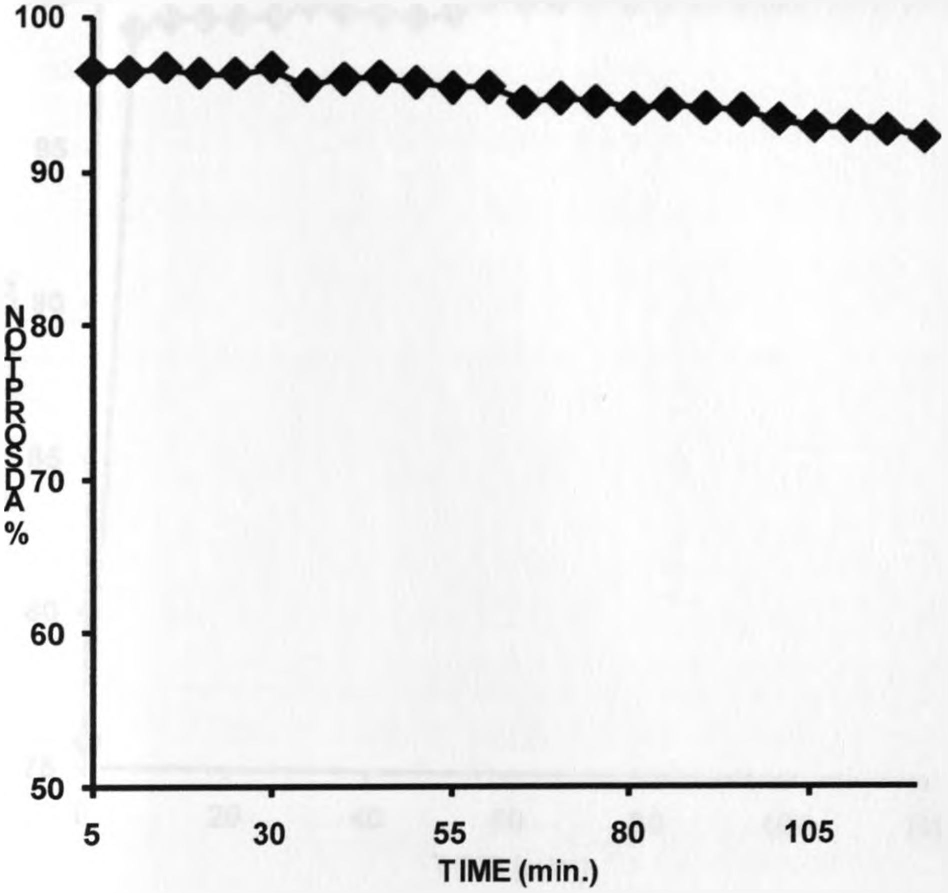


Figure 6: Plot of % adsorption of Methylene blue dye by *T.pedata* versus contact time

Figure 7 below shows the % adsorption versus contact time results for the mixture.

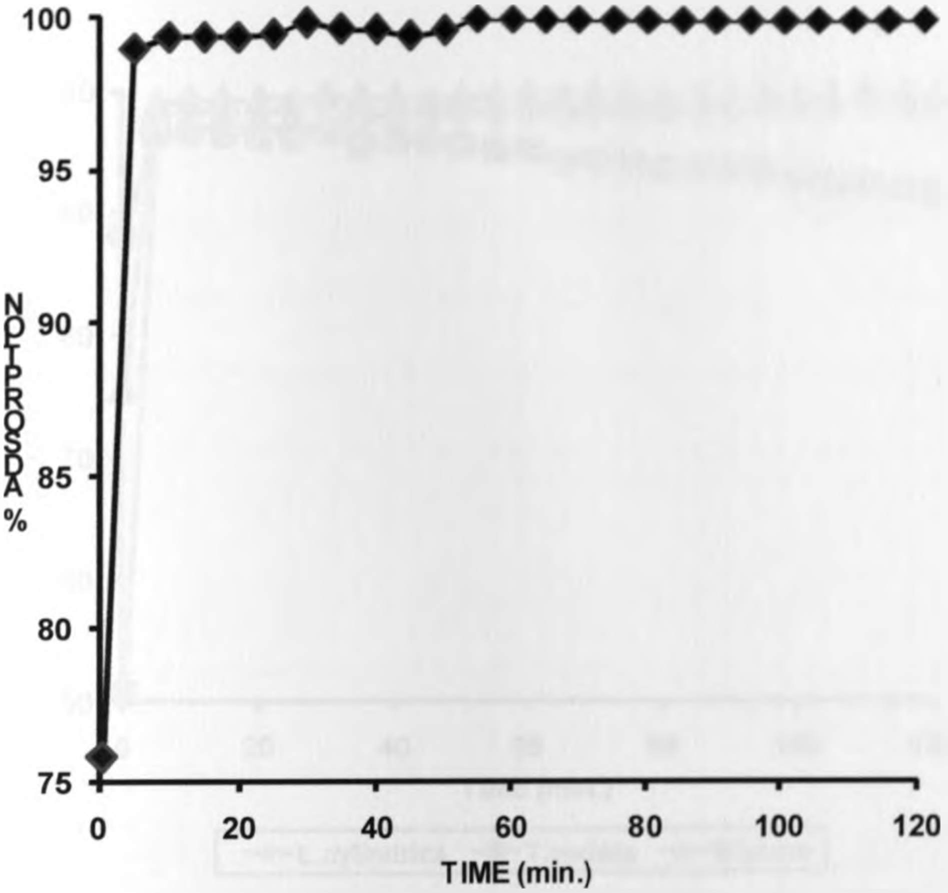


Figure 7: Plot of % adsorption of Methylene blue dye by the equal weight mixture of *L.cylindrica* and *T.pedata* versus contact time

The figure shows that within the first 5 minutes, 99% of the dye solution had been taken up. By the 55th minute, the % adsorption was determined to be 100%.

In order to clearly observe the differences and similarities on how contact time affected the adsorption properties of *L.cylindrica, T.pedata* and their mixture, a superimposed plot of % adsorption versus contact time is given in Figure 8 below.

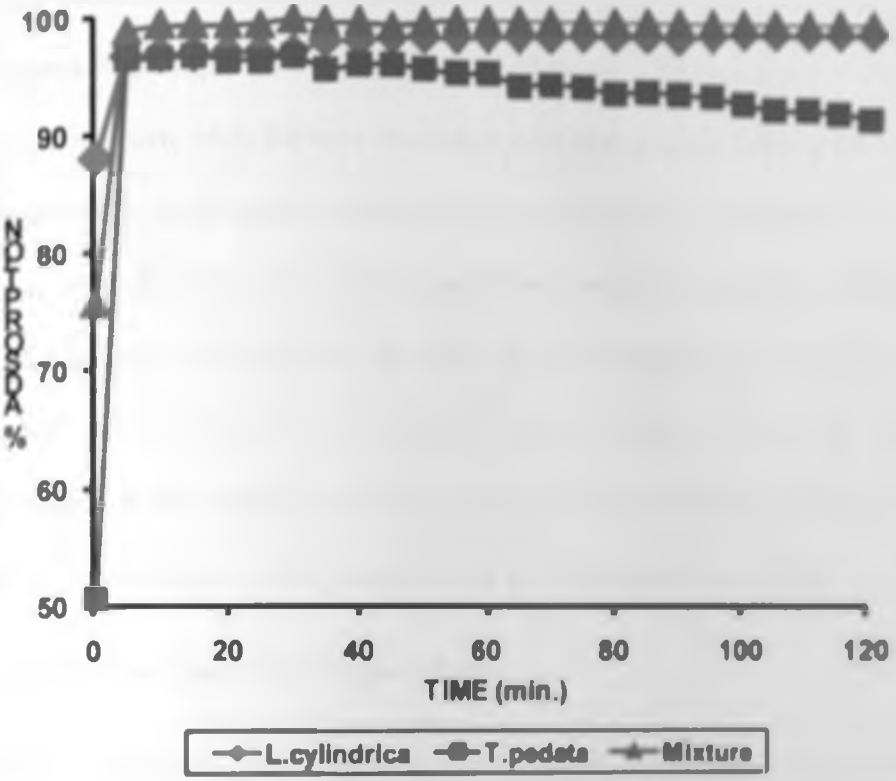


Figure 8: Superimposed plots of % adsorption of Methylene blue dye by *L.cylindrica*, *T.pedata* and their equal-weight mixture versus contact time

From the figure, it can be seen that at initial contact time of t=0, the % adsorption is higher using *L.cylindrica* than with either the mixture or *T.pedata*. By the 120th minute, the mixture adsorbed slightly better than either *L.cylindrica* or *T.pedata*. With the exception of *T.pedata*, the increase of contact time resulted to a corresponding increase in % adsorption until a saturation point was reached.

Overall, the removal of Methylene Blue by adsorption on the various materials was found to be rapid in the initial period of contact time and then to become slow and stagnate with increase in contact time ([illegible], 2007). The study shows that the uptake of the dye at the active sites of adsorbent is a rapid process, hence initial contact with the adsorbent removes a significant amount of dye. This leads to the conclusion that more dye can be efficiently removed over a period of time with the rate of adsorption being mainly governed by either a liquid phase mass transfer or an intra-particle mass transfer rate ([illegible], 1998; Kannan and Sundaram, 2001; Annadurai et al. 2002; Mohan et al. 2002).

Effect of Contact time with Congo red dye

Figure 9 below gives an account of the results found when *[illegible]* was used. As per the plot, there is a general increase in % adsorption with increase in contact time. 57% of the dye was adsorbed within the first 5 minutes. By the 120th minute, the % adsorption had increased to 96%.

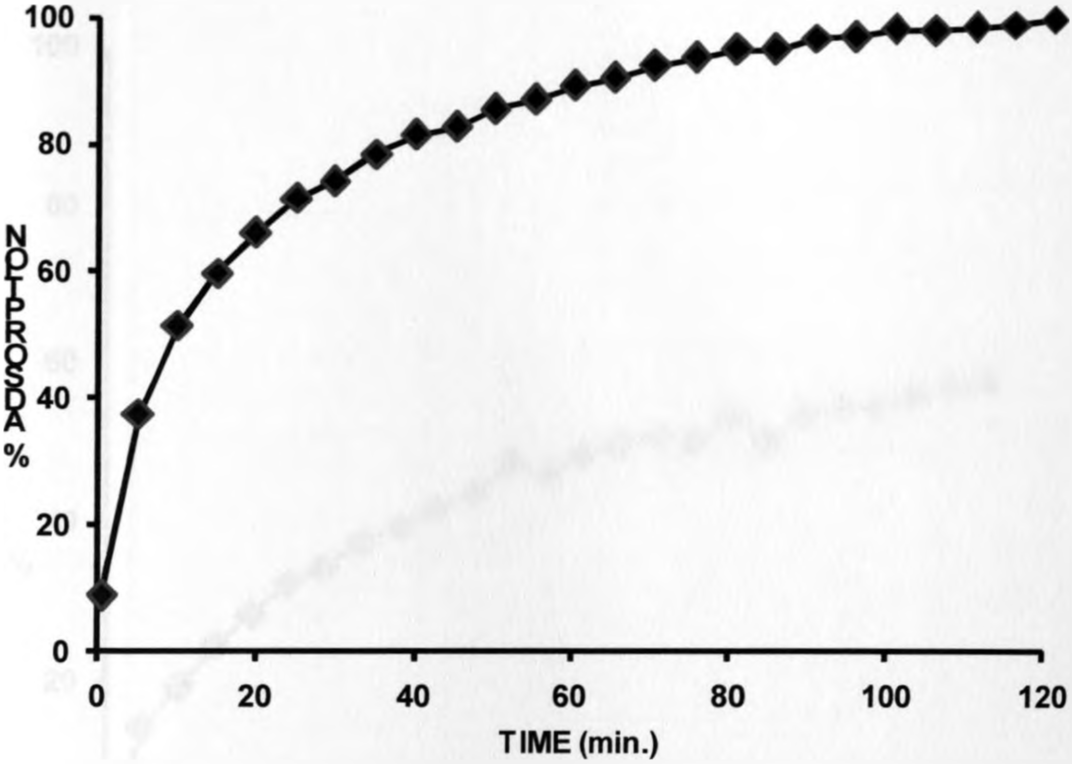


Figure 9: Plot of % adsorption of Congo red dye by *L.cylindrica* versus contact time

Studies that utilized *T.pedata* resulted in similar findings with respect to the trend of adsorption. Figure 10 reveals that % adsorption increased with increase in contact time. At the 120th minute, the % adsorption had increased to 57% up from 14% at the 5th minute. Comparatively, the affinity of *T.pedata* for Congo red dye is significantly lower than that of *L.cylindrica* for Congo red dye.

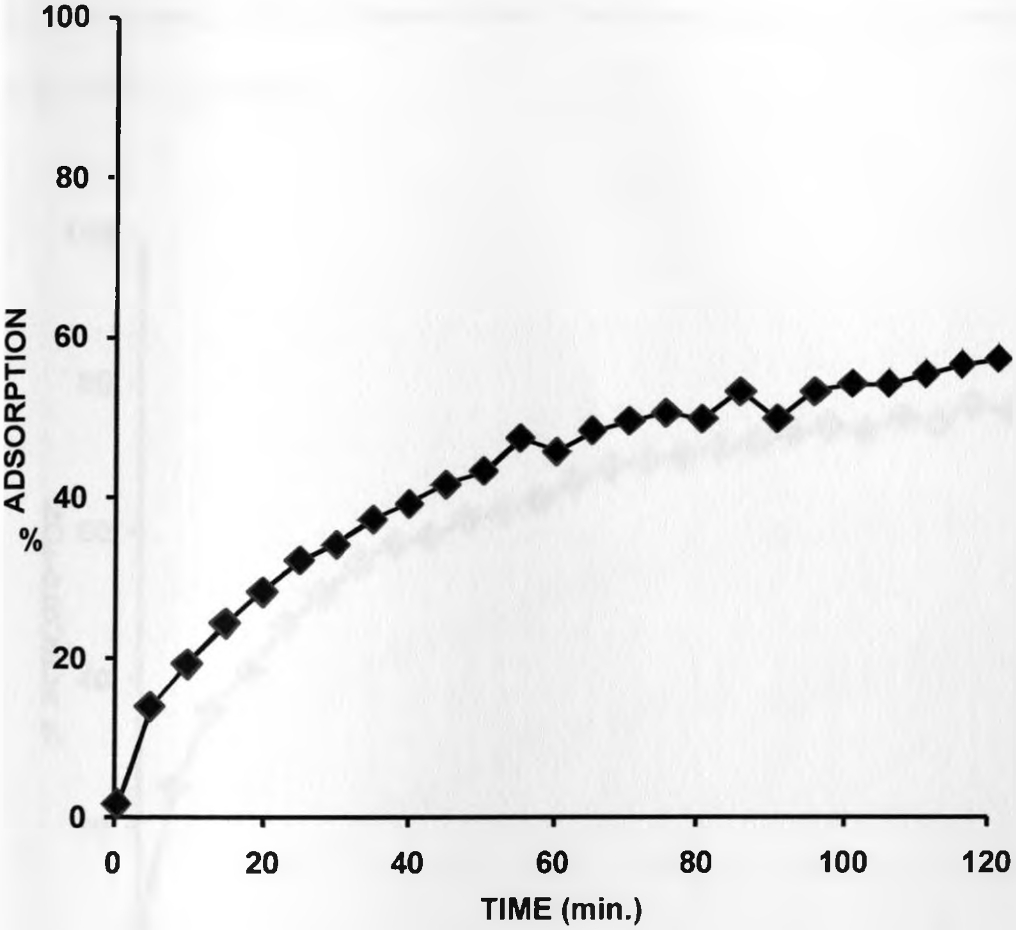


Figure 10: Plot of % adsorption of Congo red dye by *T.pedata* versus contact time

Experiments were also carried out using the mixture of the two adsorbents in equal proportions of 0.5g each. Figure 11 shows a gradual increase in % adsorption with contact time. It is evident that the increase is from 26% at the 5th minute to about 86% at the 120th minute. The % adsorption values obtained were higher compared to those obtained when *T.pedata* was employed but lower when compared to *L.cylindrica*.

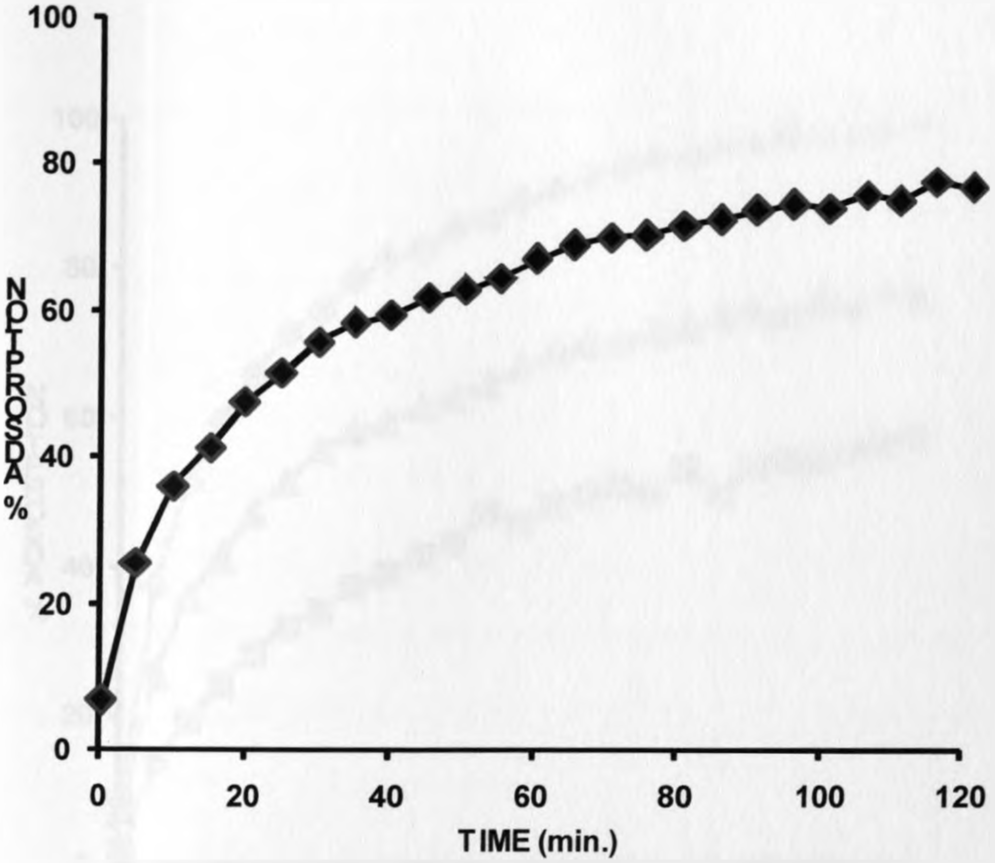


Figure 11: Plot of % adsorption of Congo red dye by the equal-weight mixture of *L.cylindrica* and *T.pedata* versus contact time

A comparison of the % adsorption profiles of the three sets of adsorbents is shown as superimposed plots in Figure 12. It is clearly evident that *L.cylindrica* adsorbs Congo red dye best as compared to either the mixture or *T.pedata.* This indicates that *L.cylindrica* has the better sorption affinity for Congo red dye followed by the mixture of the remaining two adsorbents.

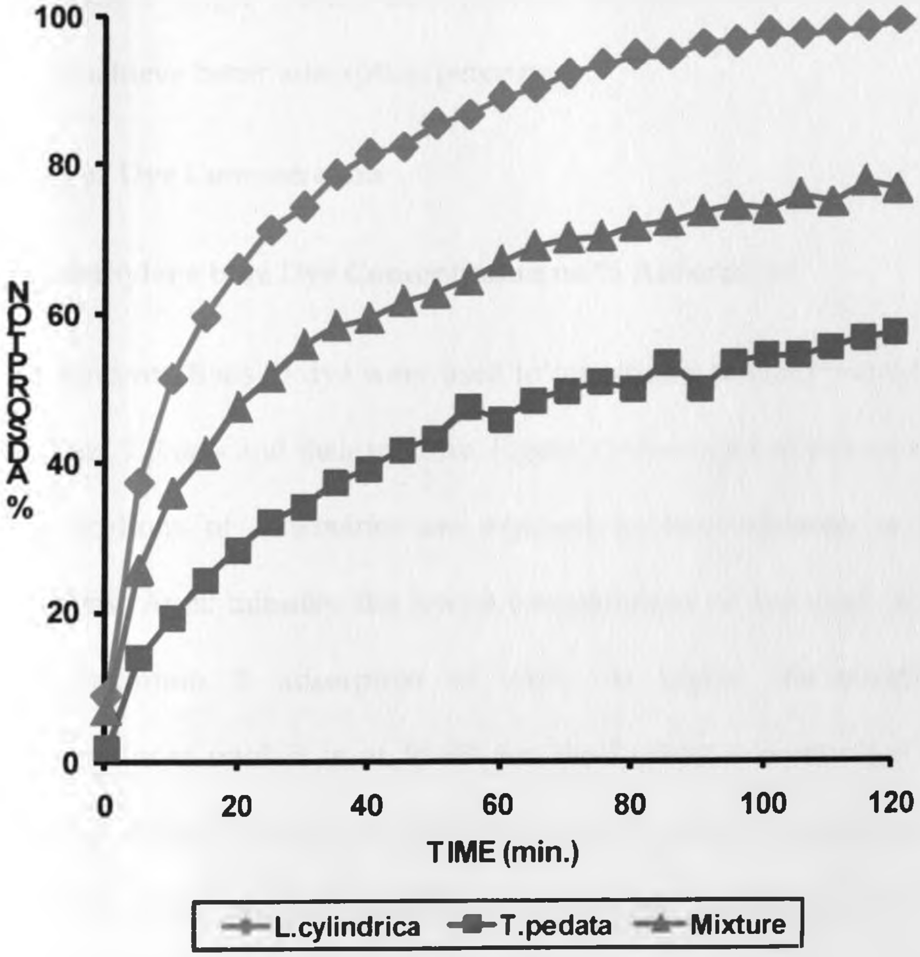


Figure 12: Superimposed plots of % adsorption of Congo red dye by *L.cylindrica, T.pedata* and their equal-weight mixture versus contact time

The adsorbents exhibit weaker sorption affinity for Congo red dye. This can be attributed to the possible difference in the chemical nature of the adsorbents in solution as well as that of the dye solution in interaction with the adsorbents. The results show that, to uptake an acidic adsorbate, or one with a structure similar to Congo red, a longer contact time between the adsorbate and adsorbent is required to achieve better adsorption percentage.

4.1.2 Effect of Dye Concentration

Effect of Methylene blue Dye Concentration on % Adsorption

Different concentrations of dye were used to investigate the sorption properties of *L.cylindrica*, *T.pedata* and their mixture. Figure 13 shows the observations made when 1g portions of *L.cylindrica* are exposed to dye solutions of various concentrations. At 30 minutes, the lowest concentration of dye used ($1X10^{-6}$ M) recorded maximum % adsorption of 100%. At higher concentrations, % adsorption reduces until it is at 96.8% for the highest concentration of dye solution used ($1.0X10^{-5}$ M). The % dye removal at equilibrium decreased from 100% to 96.8% as the dye concentration was increased 10-fold from $1X10^{-6}$ M to $1.0X10^{-5}$ M. At 60 minutes, *L.cylindrica* still exhibited 100% dye removal efficiency for the lower dye concentration. A higher % removal of 99% was now recorded with the higher dye concentration. These results further corroborate findings observed during the study on effect of contact time (*section 4.1.1*); that removal efficiency increases with increase in contact time until a level of saturation is reached.

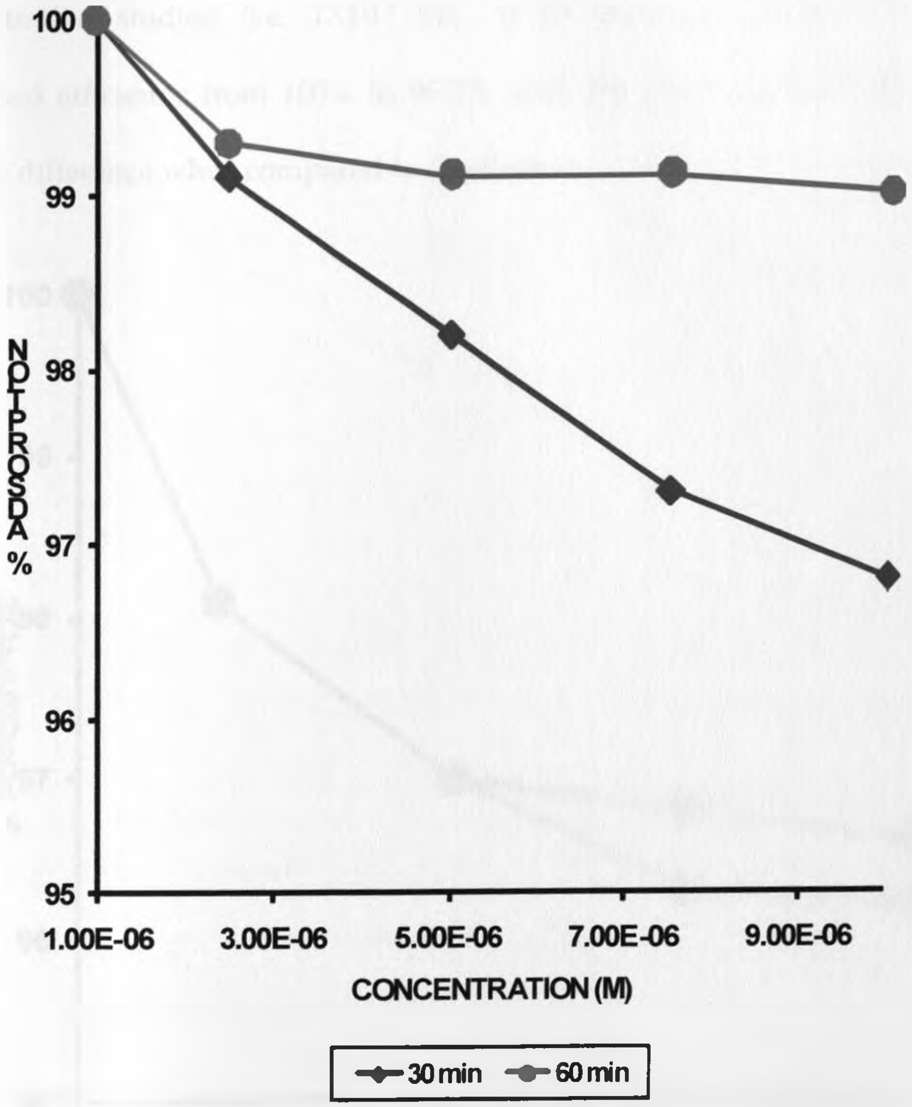


Figure 13: Plot of % adsorption of Methylene blue dye by *L.cylindrica* versus initial concentration of dye

Similar observations were made with *T.pedata*. However, there are marked differences with this adsorbent as is evident from Figure 14. In comparison to

L.cylindrica, *T.pedata* exhibited 100% removal efficiency at the lowest concentration (i.e. $1X10^{-6}$ M), which decreased to 96.6% with the highest dye concentration studied (i.e. $1X10^{-5}$ M). At 60 minutes, *T.pedata* exhibited a decreased efficiency from 100% to 96.2%, with the lower dye concentration; a notable difference when compared to *L.cylindrica*.

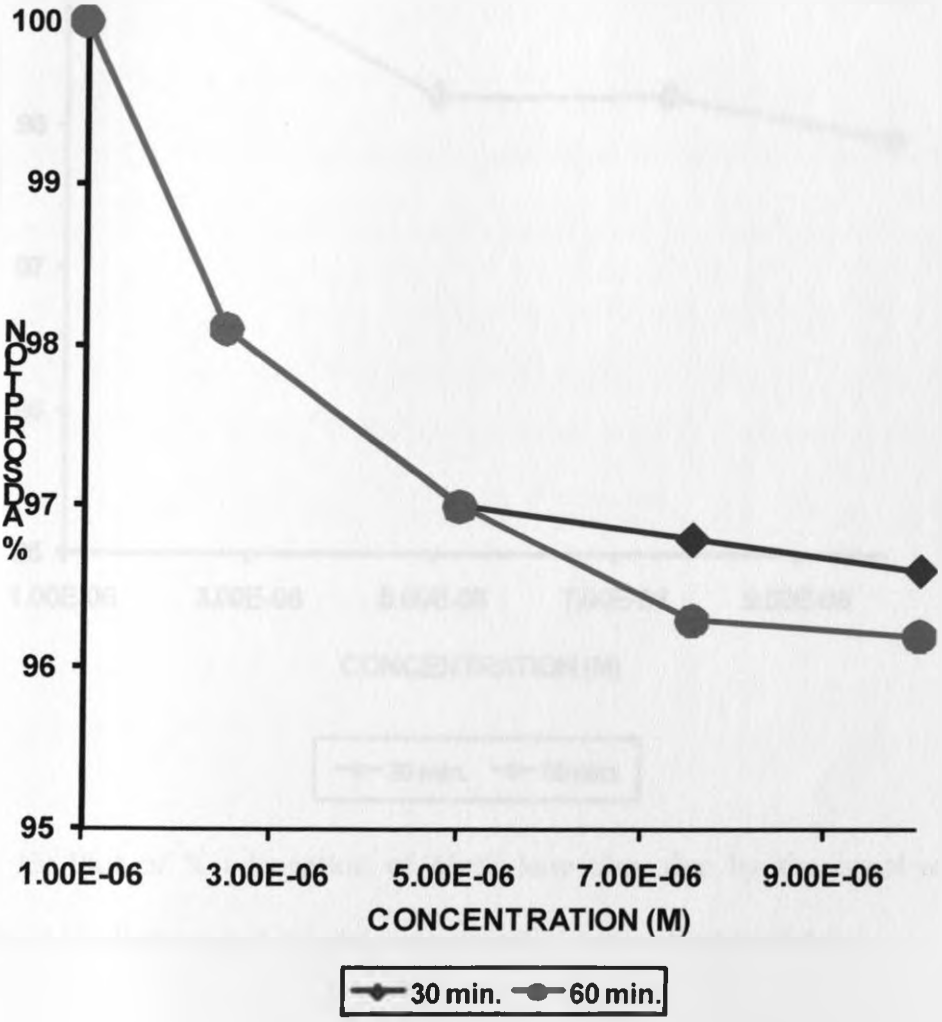


Figure 14: Plot of % adsorption of Methylene blue dye by *T.pedata* versus initial concentration of dye

Figure 15 is a plot of the % adsorption of Methylene blue by the mixture of *T.pedata* and *L.cylindrica* versus different dye concentrations.

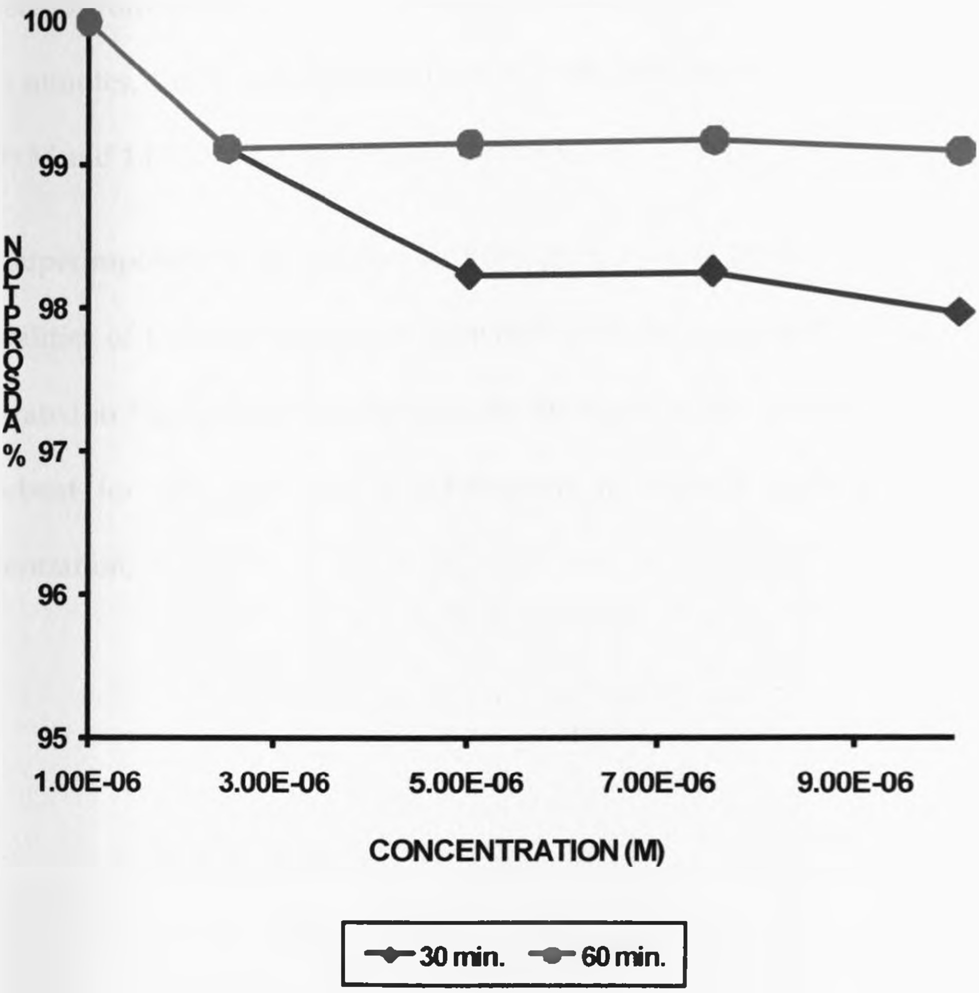


Figure 15: Plot of % adsorption of Methylene blue dye by the equal-weight mixture of *L.cylindrica* and *T.pedata* versus initial concentration of dye

Figure 15 is a plot of the % adsorption of Methylene blue by the mixture of *T.pedata* and *L.cylindrica* versus different dye concentrations.

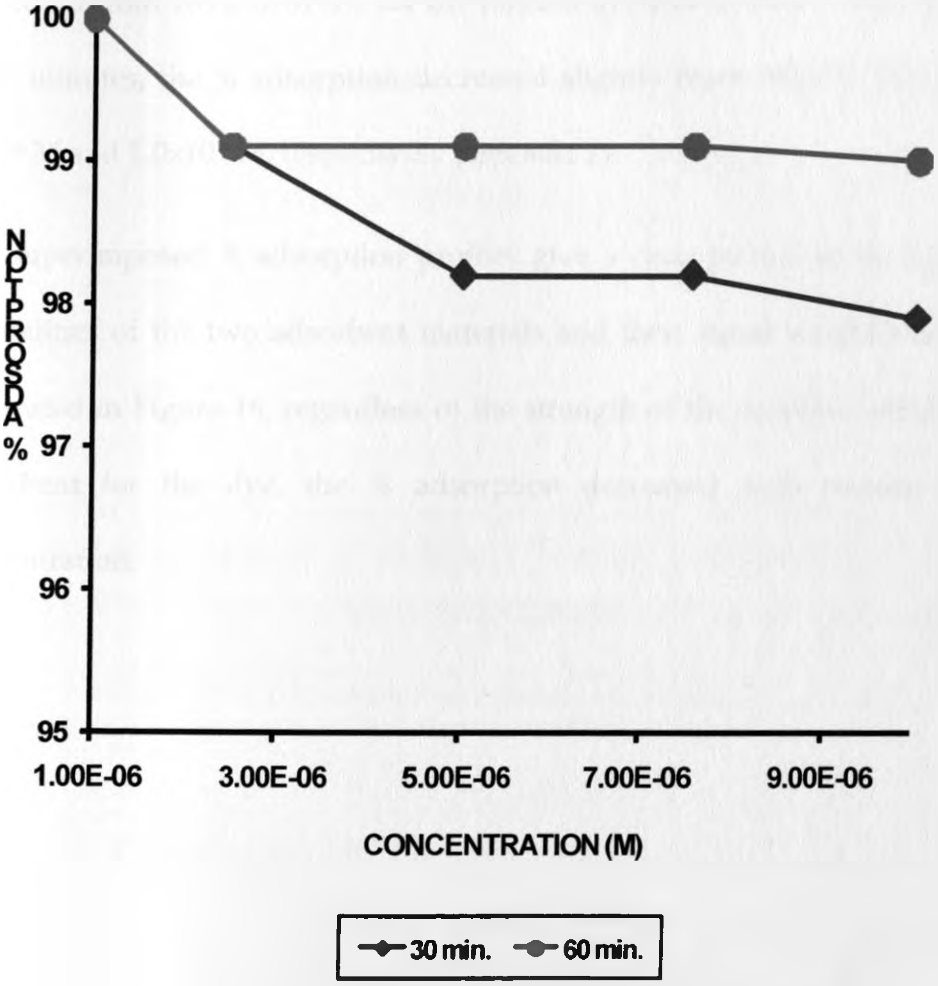


Figure 15: Plot of % adsorption of Methylene blue dye by the equal-weight mixture of *L.cylindrica* and *T.pedata* versus initial concentration of dye

Here, the mixture produced the same adsorption pattern as the individual adsorbents, with the highest % adsorption being observed at the lowest concentration when the contact time was 30 minutes. The removal efficiency decreased from 100% to 97.9% for the highest dye concentration used. However, at 60 minutes, the % adsorption decreased slightly from 100% to 99% between $1x10^{-6}$ M and $1.0x10^{-5}$ M, respectively (*appendix* 2).

The superimposed % adsorption profiles give a clear picture of the adsorption capabilities of the two adsorbent materials and their equal weight mixture. As illustrated in Figure 16, regardless of the strength of the sorption affinity of the adsorbent for the dye, the % adsorption decreased with increase in dye concentration.

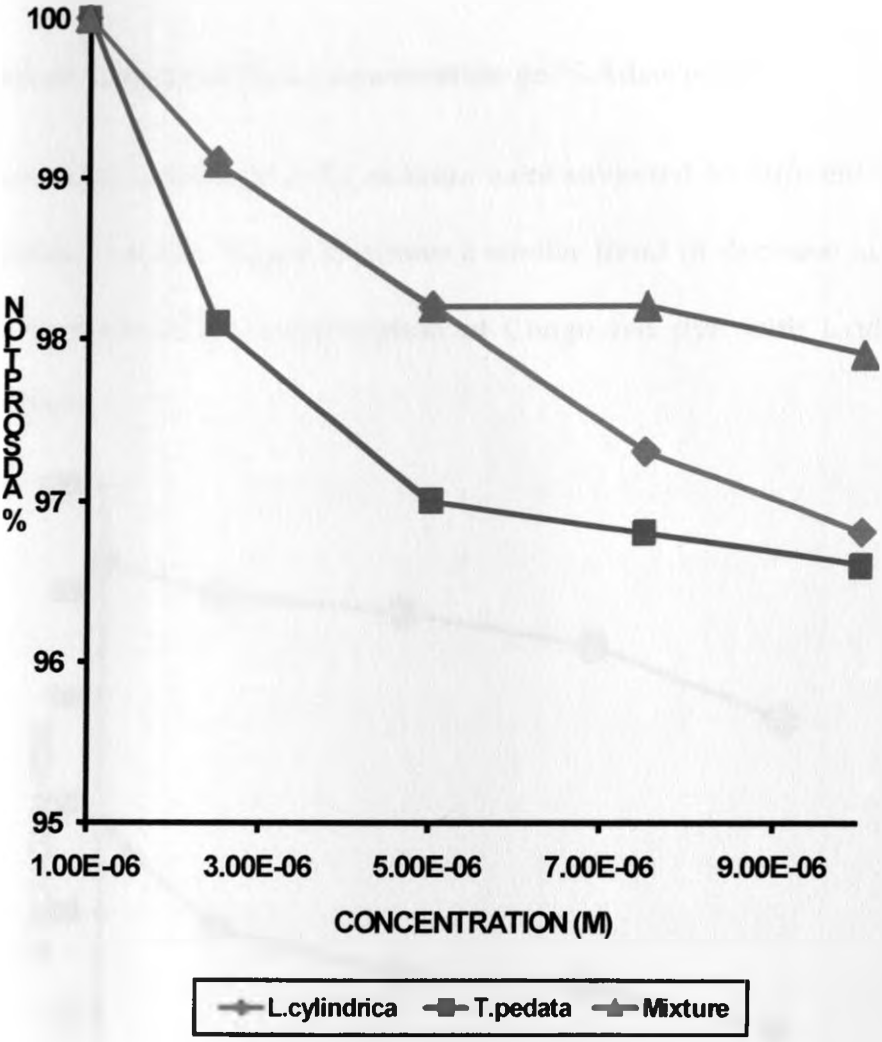


Figure 16: Superimposed Plot of % adsorption of Methylene blue dye by *L.cylindrica, T.pedata* and their equal-weight mixture versus initial concentration of dye after a contact time of 30 minutes

According to this study, percent adsorption decreased with increase in dye concentration. The adsorbents investigated adsorbed a minimum of slightly over 96% at the highest dye concentration used ($1.0\text{x}10^{-5}$ M).

Effect of Congo red Dye Concentration on % Adsorption

L.cylindrica, T.pedata and the mixture were subjected to different concentrations of Congo red dye. Figure 17 shows a similar trend of decrease in % adsorption with increase in the concentration of Congo red dye with *L.cylindrica* as the adsorbent.

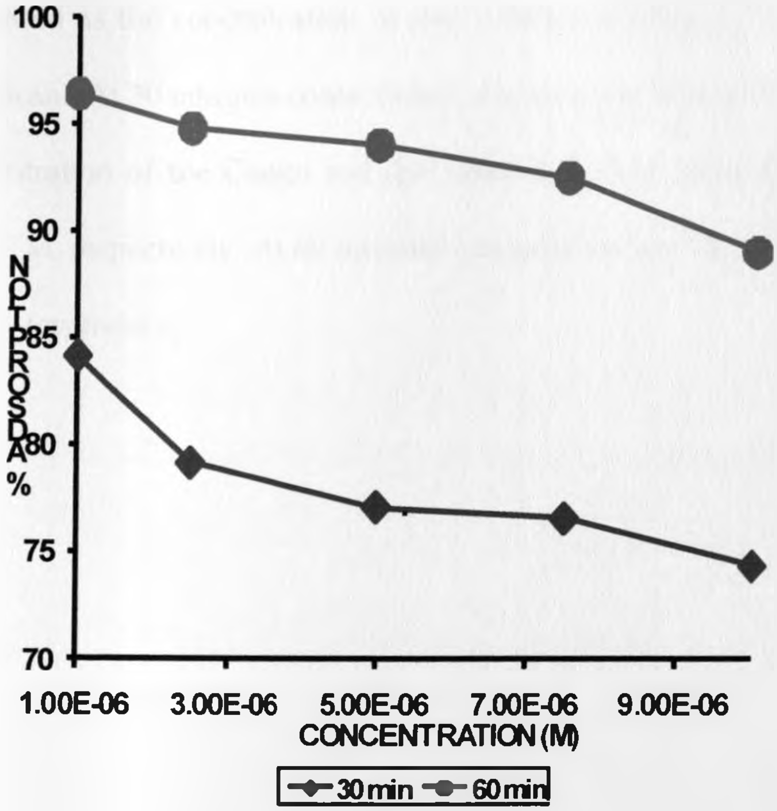


Figure 17: Plot of % adsorption of Congo red dye by *L.cylindrica* versus initial concentration of dye.

For instance, *L.cylindrica* adsorbed 74.4% and 84.2% Congo red dye after contact time of 30 minutes from the initial dye concentration of 1.0×10^{-5} M and 1×10^{-6} M, respectively. Further, after 60 minutes of contact time, the removal efficiency decreased from 96.4% to 89% as the initial concentration of the dye was increased from $1.0x10^{-6}$M and $1x\ 10^{-5}$M, respectively (*appendix* 2).

Figure 18 shows % adsorption trends of different concentrations of Congo red by *T.pedata*. From the figure, it can be deduced that although % adsorption decreased as the concentration of dye solution increased, the decrease was not significant. At 30 minutes contact time, the decrease is from 38.5% to 34.5% as the concentration of the Congo red dye solution was increased from $1.0x10^{-6}$ M to $1x\ 10^{-5}$ M, respectively. At 60 minutes contact time, the decrease was from 48.7% to 46% (*appendix* 2).

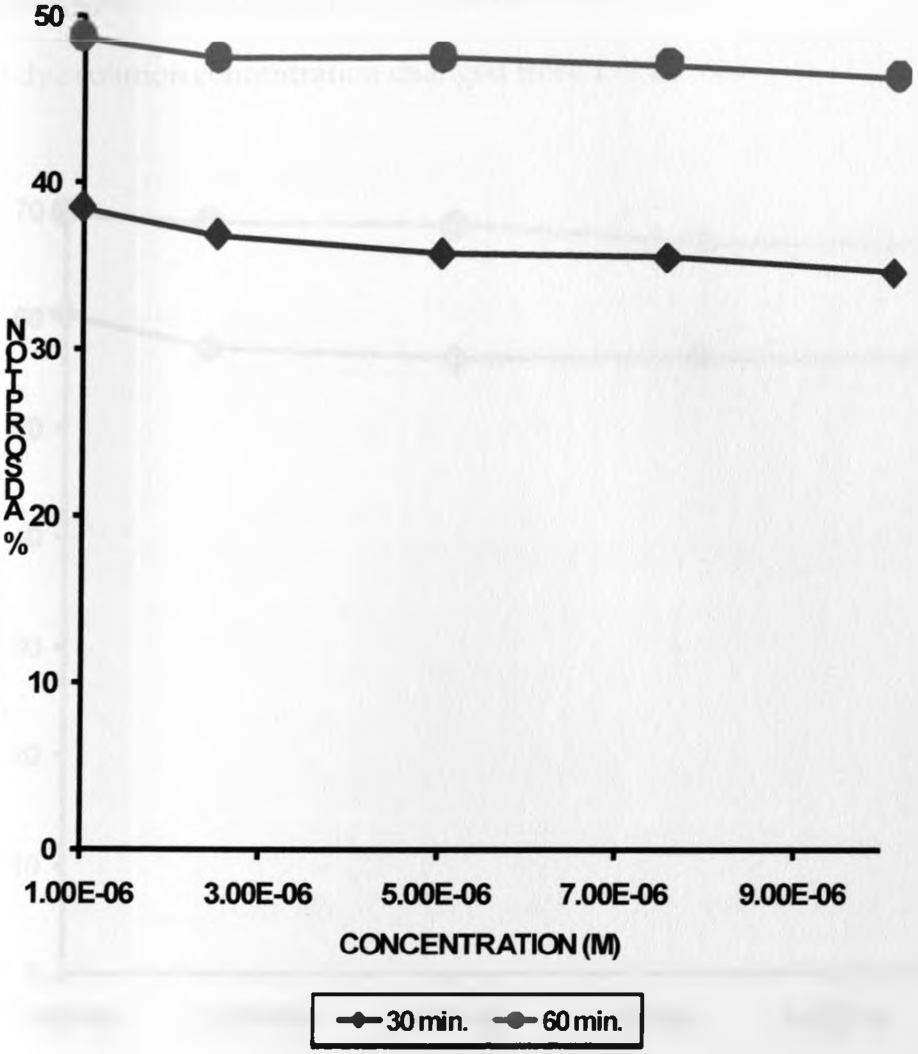


Figure 18: Plot of % adsorption of Congo red dye by *T.pedata* versus initial concentration of dye.

The mixture, whose results are displayed in Figure 19, shows the % adsorption decreasing from 60.5% to 56.1% as the concentration of the dye solution increased from 1.0x10^{-6} M to 1x 10^{-5} M at contact time of 30 minutes. At 60 minutes contact time, the percentage decrease was from 69.8% to 66.7% when the initial dye solution concentration changed from 1.0X10^{-6} M to 1X 10^{-5} M.

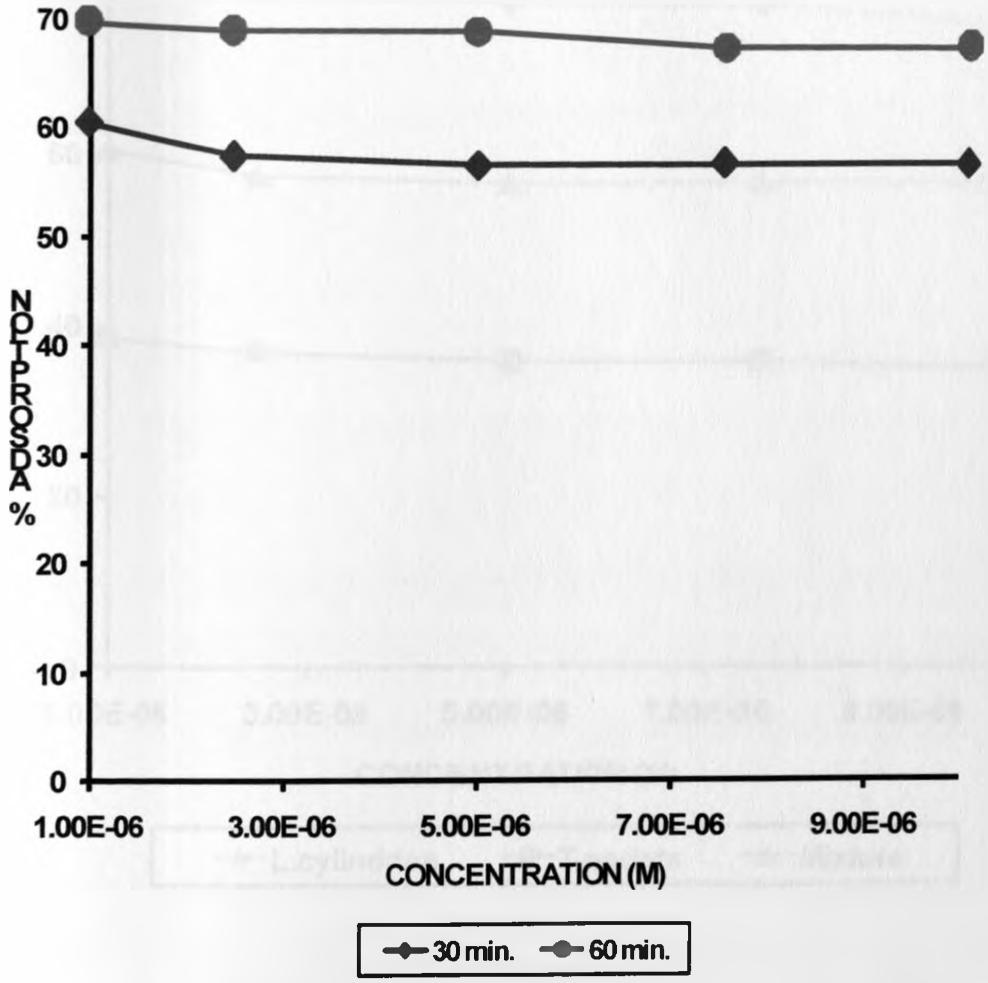


Figure 19: Plot of % adsorption of Congo red dye by the equal-weight mixture versus initial concentration of dye.

Figure 20 shows superimposed plots of % adsorptions of Congo red dye by *L.cylindrica*, *T.pedata* and their equal-weight mixtures for ease of comparison.

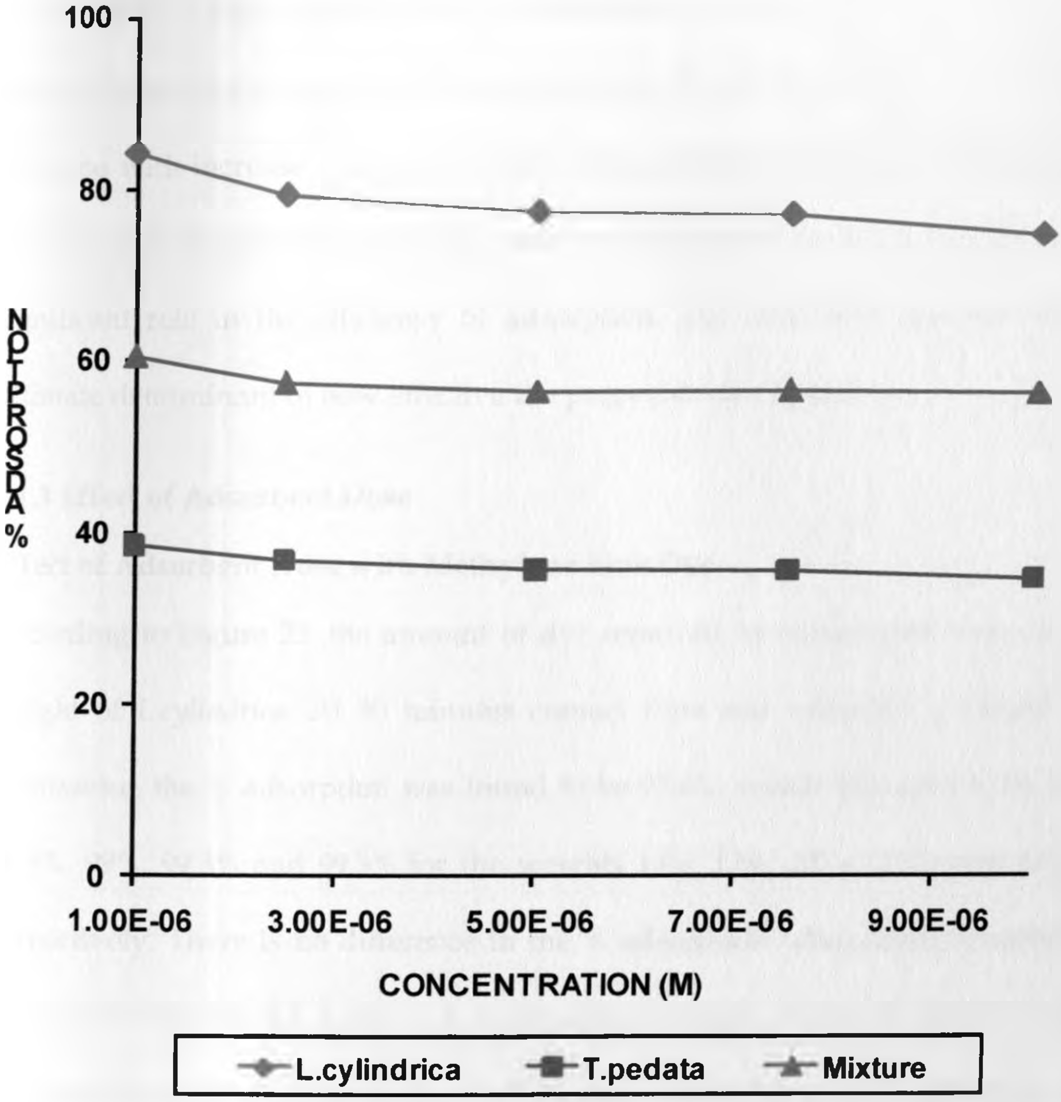


Figure 20: Superimposed plots of % adsorption of Congo red dye by *L.cylindrica*, *T.pedata* and their equal-weight mixture versus initial concentration of dye after 30 minutes contact time.

The trend in % adsorption for both the adsorbents and their mixture at the two contact times under study (i.e., 30 minutes and 60 minutes) show a near-linear decrease with increase in concentration of dye solution. The results lead to the conclusion that with Congo Red dye, the concentration of the dye does not play a significant role in the efficiency of adsorption. The adsorbent material is the ultimate determinant of how effective the process of dye uptake is.

4.1.3 Effect of Adsorbent Dose

Effect of Adsorbent Dose with Methylene blue Dye

According to Figure 21, the amount of dye removed increased with increase in weight of *L.cylindrica.* At 30 minutes contact time and using 0.5 g weight of *L.cylindrica*, the % adsorption was found to be 97.6%, which increased to 98.3%, 98.8%, 99%, 99.3% and 99.3% for the weights 1.0g, 1.5g, 2.0 g, 2.5 g and 3.0 g, respectively. There is no difference in the % adsorption when using adsorbent weight of between 2.5 g and 3 g, suggesting a region where all the dye was removed from solution. Similarly, at 60 minutes contact time, the % dye removal increased with the increase in adsorbent weight. The % adsorption recorded was 97.9% when 0.5 g weight of *L.cylindrica* was used. The % adsorption increased to the maximum of 100% when the weight used was increased to 3 g.

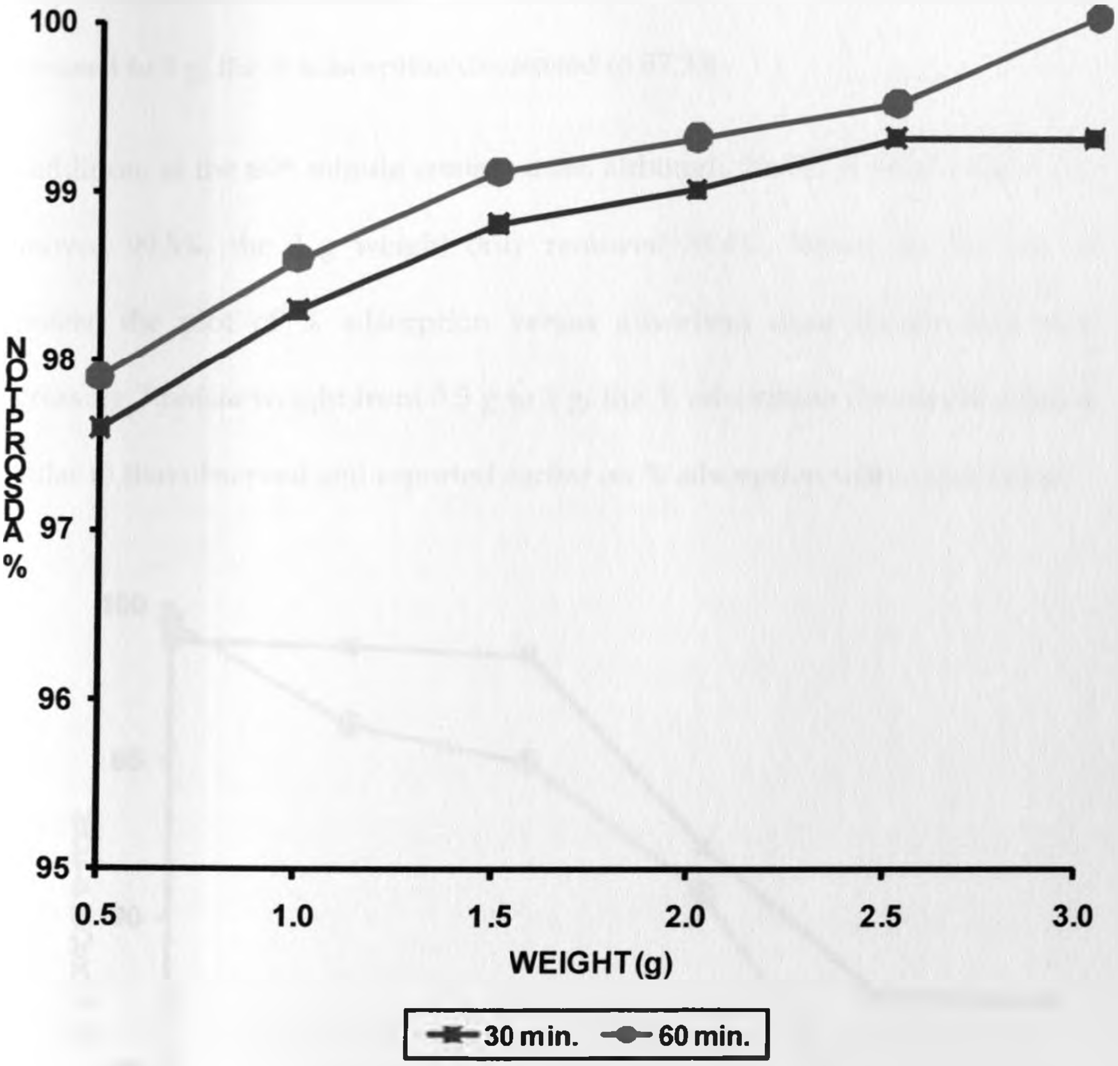


Figure 21: Plot of % adsorption of 1.0x10^{-5}M Methylene blue dye versus weight of *L.cylindrica*

Figure 22 shows that increase in weight of *T.pedata* resulted in decrease in % adsorption of the dye from the dye solution. At 30 minutes contact time, the 0.5 g weight was found to remove 98.9% of the dye. However, as the weight was increased to 3 g, the % adsorption decreased to 87.3%.

In addition, at the 60th minute contact time, although the 0.5 g weight efficiently removed 99.5%, the 3 g weight only removed 83.4%. Hence, in the case of *T.pedata*, the plot of % adsorption versus adsorbent dose reveals that with increasing *T.pedata* weight from 0.5 g to 3 g, the % adsorption decreased: a trend similar to that observed and reported earlier on % adsorption with contact time.

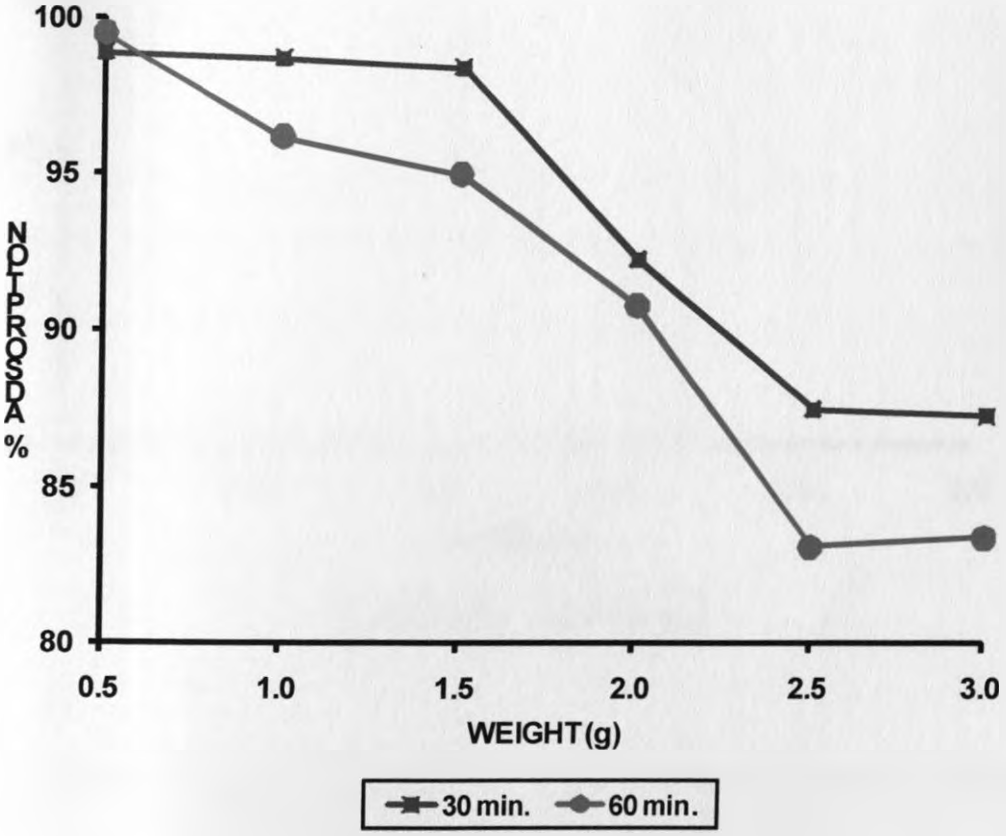


Figure 22: Plot of % adsorption of $1.0x10^{-5}$M Methylene blue dye versus weight of *T.pedata*

Figure 23 shows the results obtained with an equal weight mixture of the two adsorbents at the different combined weights shown. After 30 minutes contact time, the % adsorption by 0.5 g of the equal weight mixture was 99.8%.

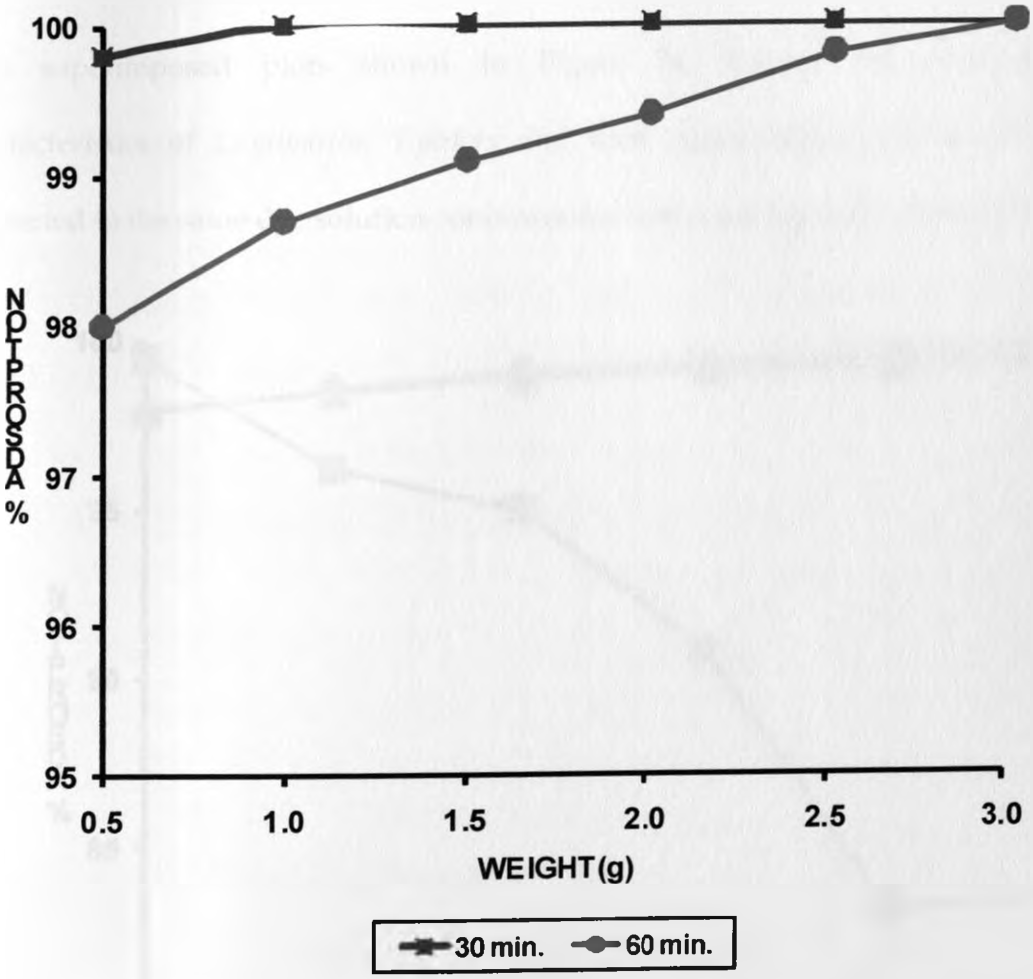


Figure 23: Plot of % adsorption of 1.0×10^{-5}M Methylene blue dye versus an equal-weight mixture of *L.cylindrica* and *T.pedata*

Observations made suggest an increase in % adsorption with an increase in adsorbent dose. At 60 minutes contact time, the % adsorption was 98% using an equimixture of 0.5 g each. With the 3 g combined weight, % adsorption was 100% at both 30 and 60 minutes contact time (*appendix* 2).

The superimposed plots shown in Figure 24, display the adsorption characteristics of *L.cylindrica, T.pedata* and their equal-weight mixture when subjected to the same dye solution concentration with varying sorbent weights.

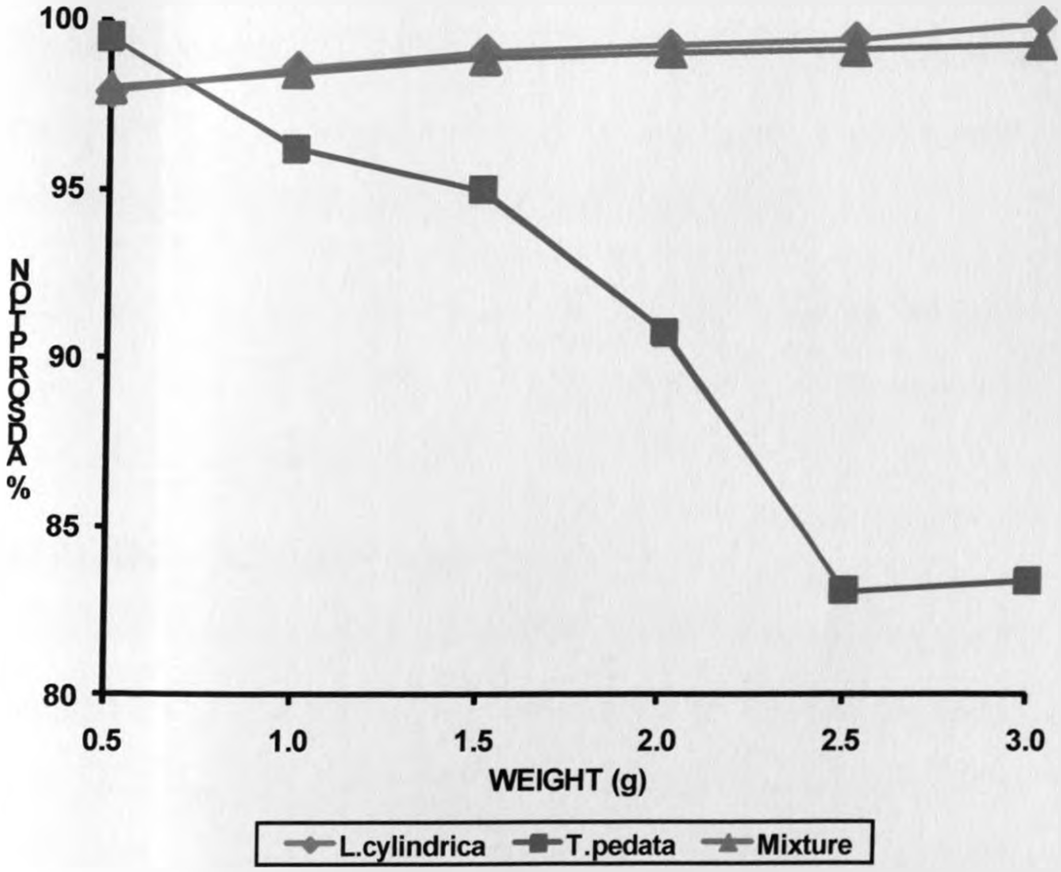


Figure 24: Superimposed plots of % adsorption of 1.0×10^{-5} M Methylene blue dye by *L.cylindrica, T.pedata* and their equal-weight mixture versus weight.

The % adsorption is above 80% in all the instances. *L.cylindrica* and the equal-weight mixture exhibited % increase in adsorption of dye from solution as the adsorbent dose increased. This is attributed to an increase in adsorption sites.

To the contrary, in the case of *T.pedata*, % adsorption decreased when adsorbent dose was increased. A possible factor explaining this characteristic as described by Han et.al (2006) {during their study of a material with a similar trend}, is that adsorption sites remain unsaturated during the adsorption process despite the number of sites available for adsorption increasing with higher adsorbent doses. According to these researchers, at higher weights, there is a very fast superficial adsorption onto the adsorbents' surface that produces a lower solute concentration in the solution than the adsorbent dose is lower.

This study brings out the cost effective aspect of the adsorbent materials. Regardless of whether the adsorbent dose is the least (0.5 g) or the most (3 g) used, the % adsorption is more than 80%.

Effect of Adsorbent Dose with Congo red Dye

Figure 25 shows that an increase in the weight of *L.cylindrica* led to an increase in the % adsorption of Congo red dye. At 30 minutes contact time and 0.5 g of the adsorbent, the % adsorption was found to be 43.5% which increased to 83% when the weight was raised to 3 g. At 60 minutes contact time, 0.5 g of the adsorbent adsorbed 57.4% of the dye and 3 g adsorbed 82.6%. It is evident from the % adsorption obtained that *L.cylindrica* has a weaker sorption affinity for Congo red dye than for Methylene blue dye.

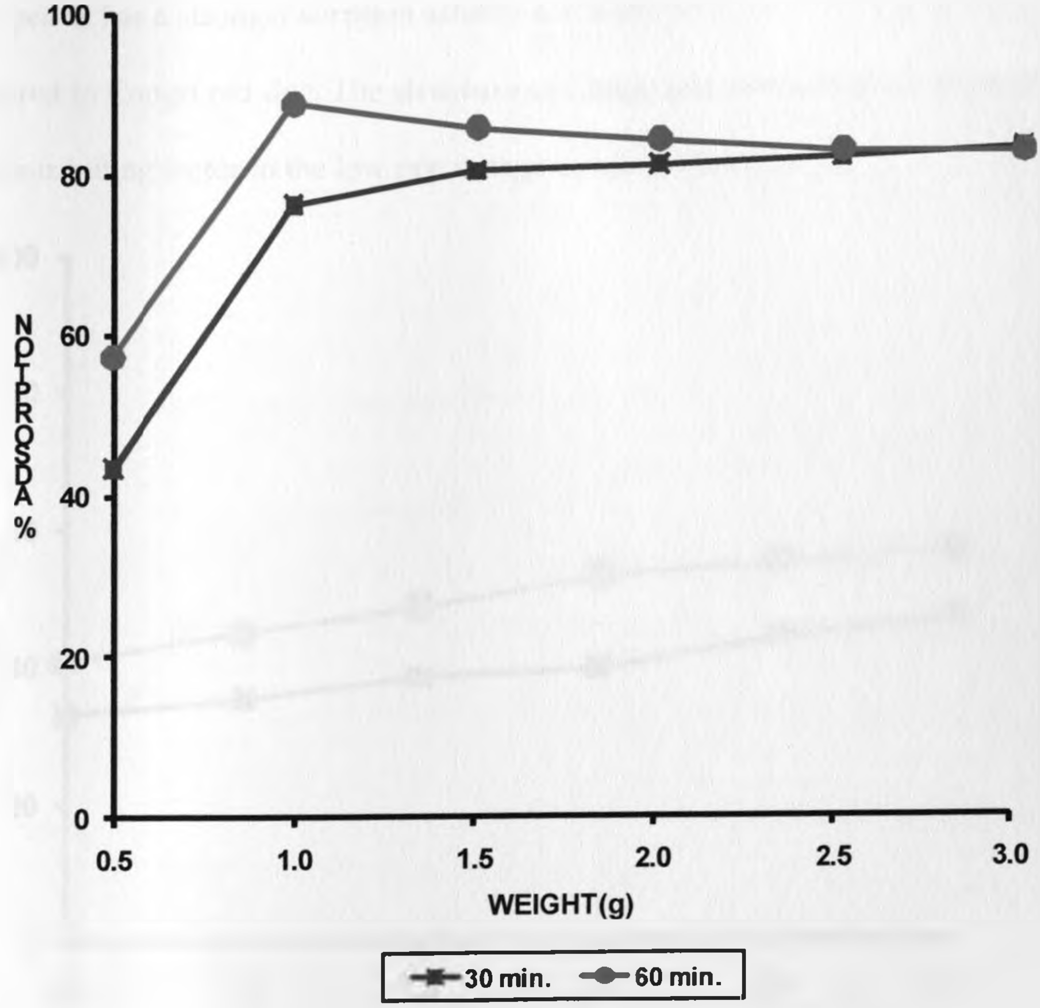


Figure 25: Plot of % adsorption of Congo red dye by *L.cylindrica* versus weight of *L.cylindrica*

Conversely, as the dosage of *T.pedata* increased, the % adsorption also increased. Figure 26 shows that at 30 minutes contact time, 33% of the dye had been adsorbed by 0.5 g of adsorbent. This increased steadily to 47.5% as the weight was increased to 3 g. At 60 minutes contact time, % adsorption was found to be 40.9% and 57.2% at 0.5 g and 3 g, respectively. It is clear from the % adsorption that *T.pedata* has a stronger sorption affinity for Methylene blue dye (*Figure* 22) as compared to Congo red dye. The structure of Congo red dye (see *figure* 2) could be a contributing factor to the low percentage uptake of the dye.

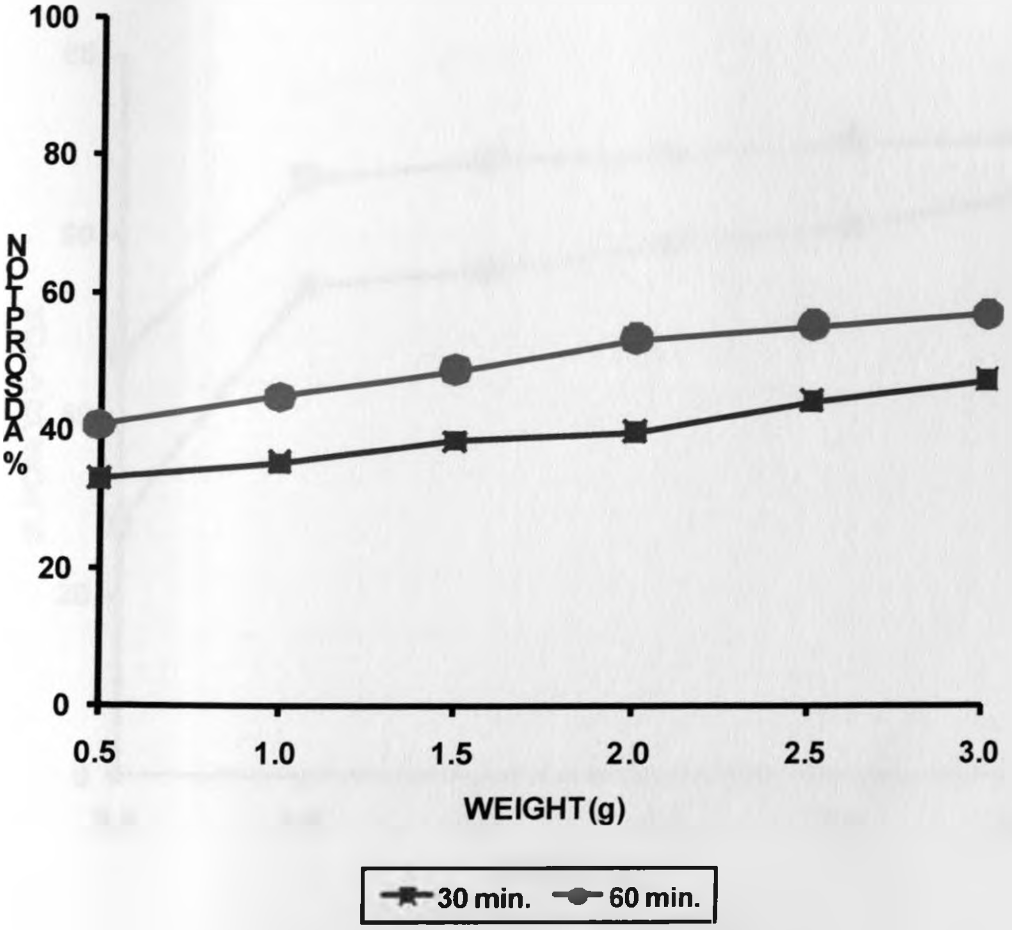


Figure 26: Plot of % adsorption of Congo red dye by *T.pedata* versus weight of *T.pedata*

The influence of increasing weight of adsorbent when *L.cylindrica* and *T.pedata* are mixed in equal proportions is presented in Figure 27. At contact time of 30 minutes, the % adsorption is 27.7% for a total mixture weight of 0.5 g. At contact time of 60 minutes, this percentage increased to 46.6%. Using a total weight of 3 g the% adsorption was found to be 64.8% after 30 minutes contact time and 70.9% after 60 minutes contact time.

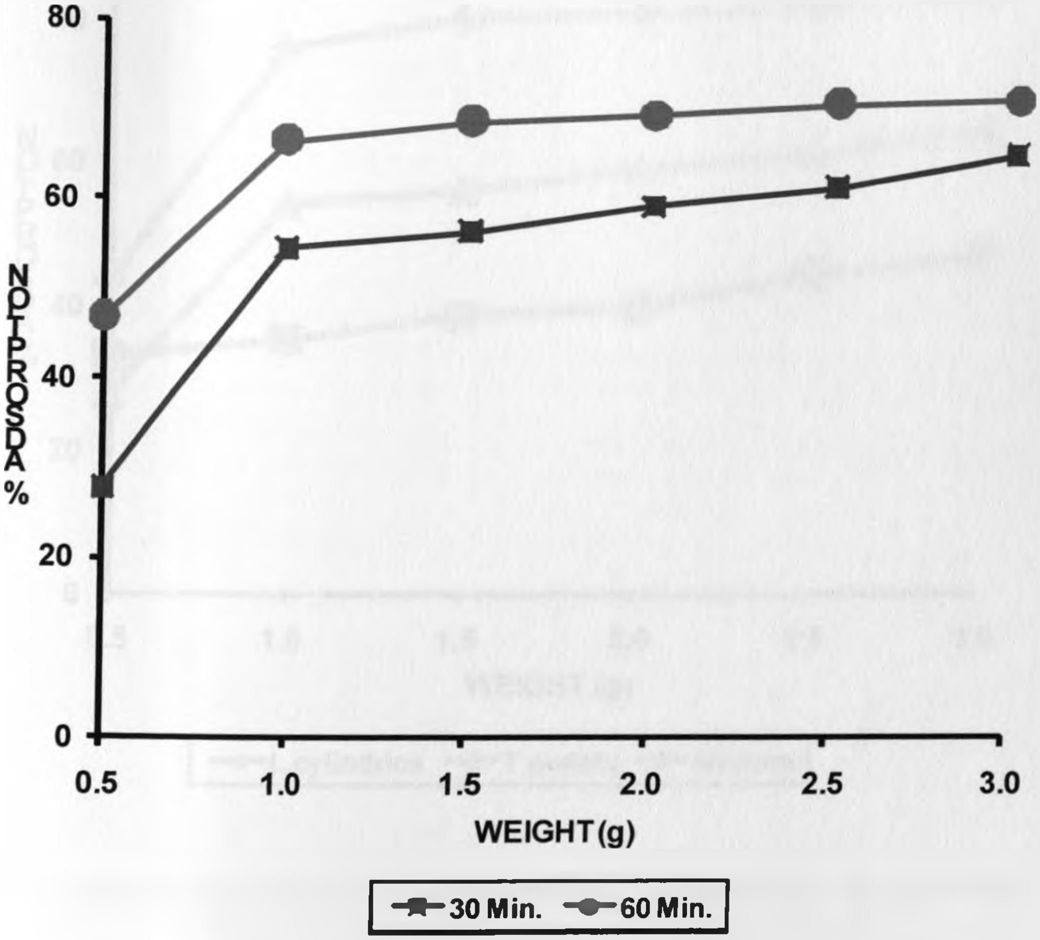


Figure 27: Plot of % adsorption of Congo red dye by the equal-weight mixture of *L.cylindrica* and *T.pedata* versus weight of the mixture

Superimposed plots for the three adsorbent types (i.e. *L.cylindrica, T.pedata* and their equal-weight mixture); clearly compares their adsorption efficiencies for Congo red dye. This is shown in Figure 28, for 30 minutes contact time.

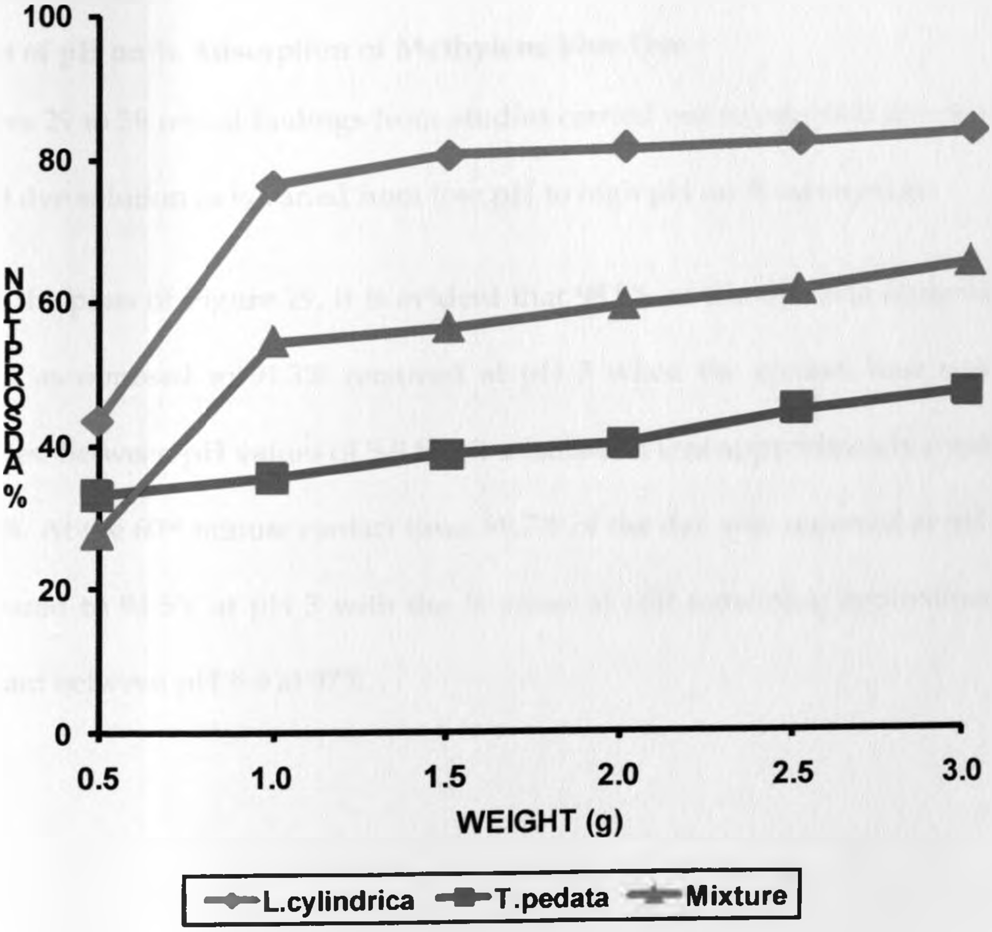


Figure 28: Superimposed plot of % adsorption of Congo red dye by *L.cylindrica, T.pedata* and their equal-weight mixture versus weights

In contrast to results found when studying Methylene blue dye, these results show that with Congo red dye, the highest % adsorption rates are achieved by increasing the adsorbent dose, so that , the higher the adsorbent dose, the higher the adsorption efficiency.

4.1.4 Effect of pH

Effect of pH on % Adsorption of Methylene blue Dye

Figures 29 to 39 reveal findings from studies carried out to establish the effect of pH of dye solution as is varied from low pH to high pH on % adsorption.

From the plots of Figure 29, it is evident that 98.5% of the dye was removed at pH 10 as opposed to 91.3% removed at pH 3 when the contact time was 30 minutes. Between pH values of 5-9 the % adsorption was approximately constant at 97%. At the 60th minute contact time, 99.7% of the dye was removed at pH 10, compared to 94.5% at pH 3 with the % removal still remaining approximately constant between pH 5-9 at 97%.

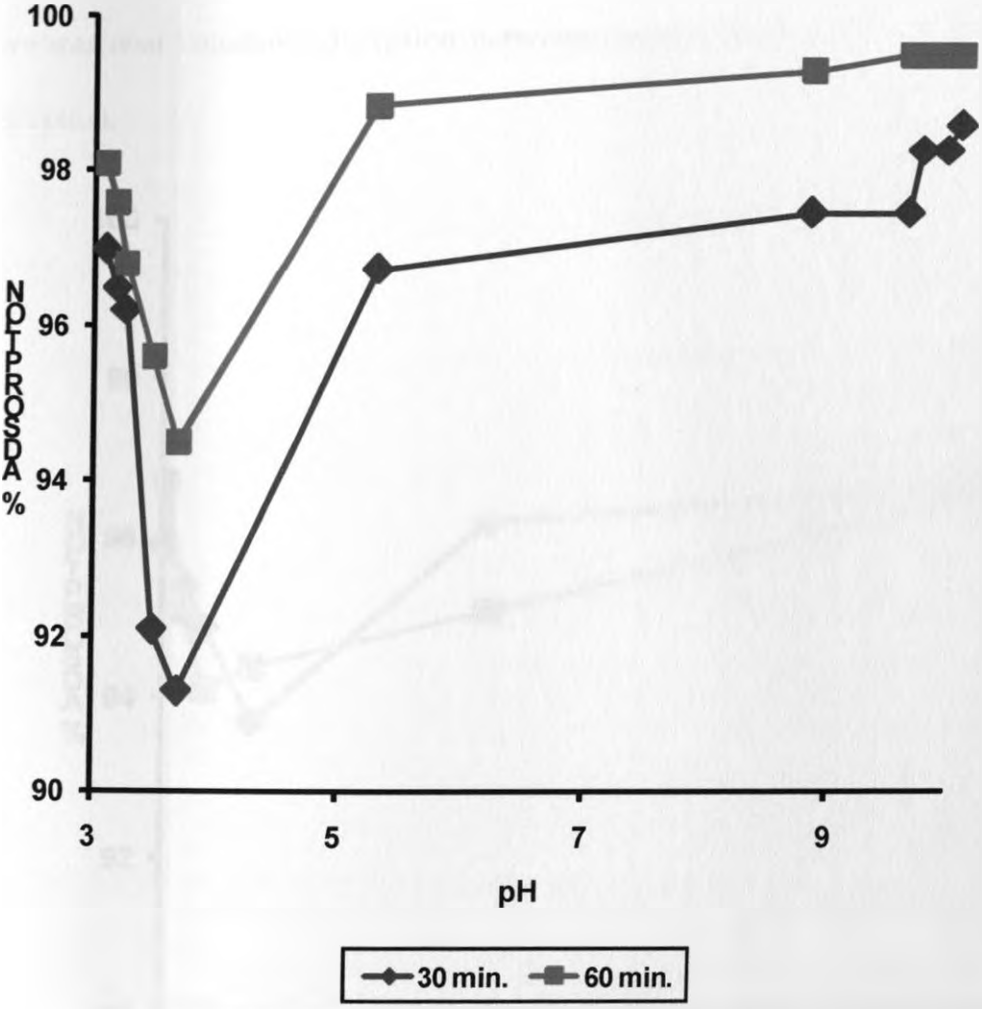


Figure 29: Plot of % adsorption of Methylene blue dye by *L.cylindrica* versus pH of the dye.

Similarly, according to Figure 30, *T.pedata* at contact time of 30 minutes recorded % adsorption of 98.3% at pH 10 and a reduced % adsorption of 93.7% at pH 3. Between pH 5-9, the % adsorption remained approximately constant. A similar trend in % adsorption was observed at the 60th minute contact time. The % adsorption was 99.3% and 94.1% at pH values of 10 and 3, respectively. Again, there was near constant adsorption between the pH values of 5-9 of about 97% adsorption.

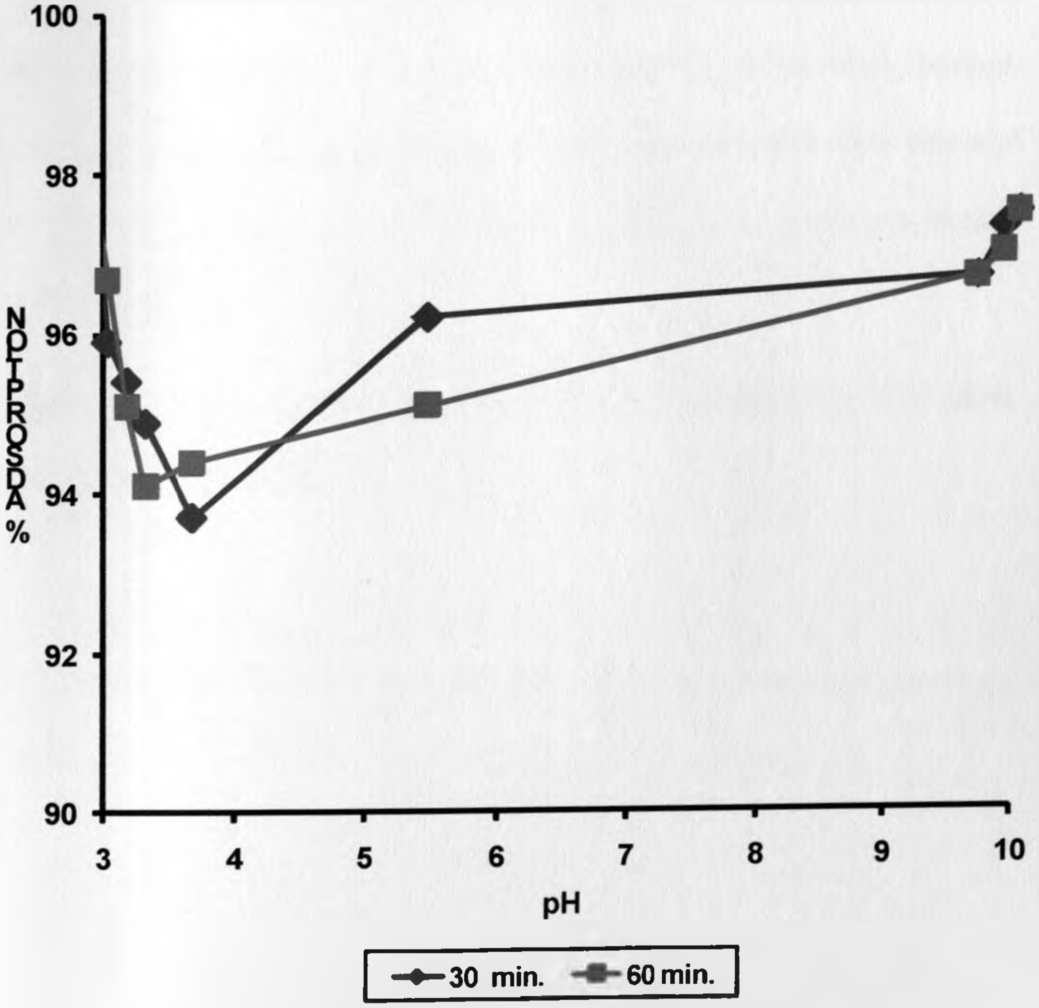


Figure 30: Plot of % adsorption of Methylene blue dye by *T.pedata* versus pH of the dye

Both *T.pedata* and *L.cylindrica* increased their respective % adsorptions with increase in contact time. This is an indication that both adsorbents have a strong sorption affinity for the dye solution due to their cellulosic nature. Dissolved Methylene blue ions are positively charged and will undergo attraction on approaching the anionic structure of the materials. At lower pH values, the surface of the adsorbents would be surrounded by hydroxonium ions (H^+ ions) which compete with Methylene blue ions binding the sites of the adsorbent. At higher pH values, the surface of the adsorbents becomes negatively charged, which enhances the positively charged dye cations through electrostatic forces of attraction (Waranusantigul et al, 2003; Han et al, 2006). This explains the higher % adsorption at higher pH values.

As per Figure 31, the % adsorption was 99.1% at pH 10 and 94.8% at pH 3 when the contact time was 30 minutes.

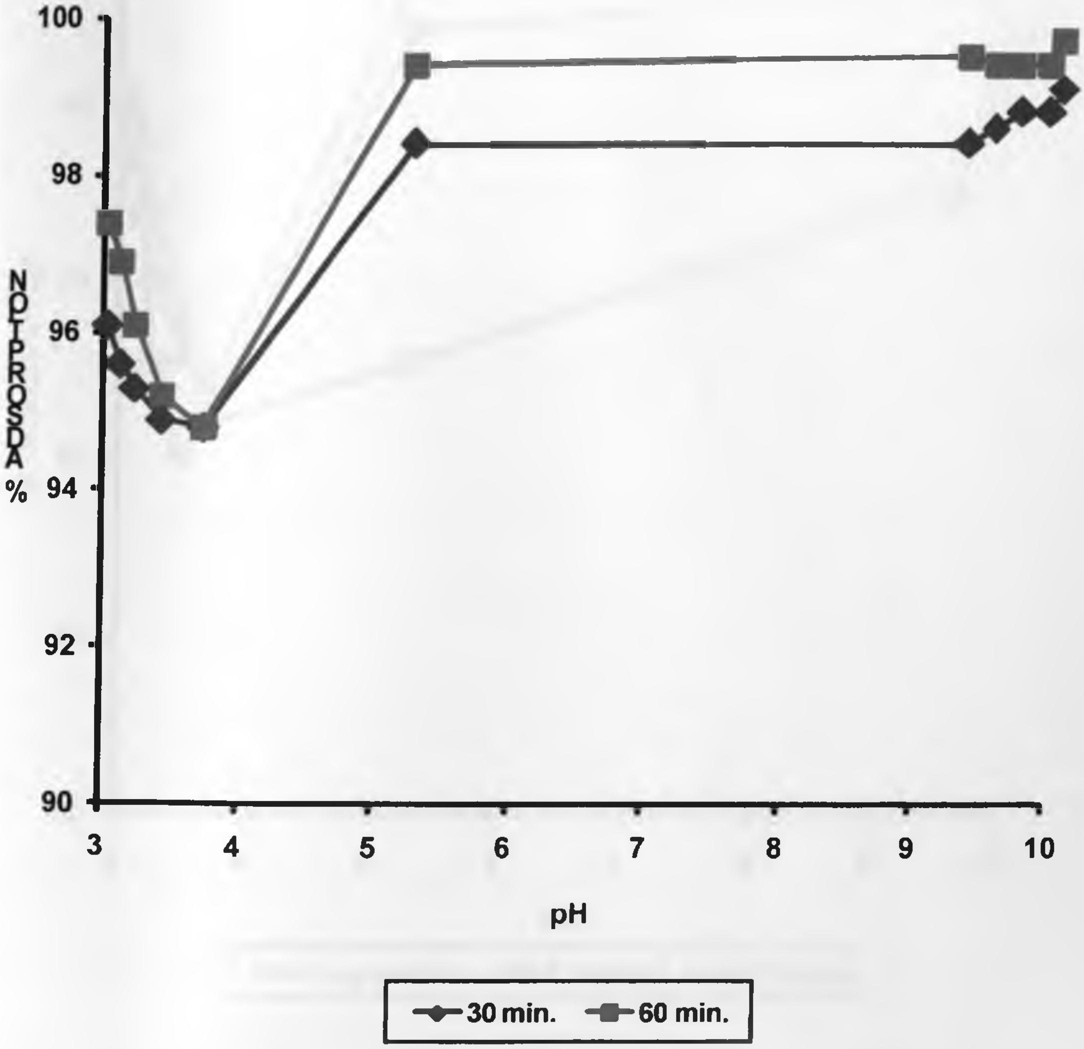


Figure 31: Plot of % adsorption of Methylene blue dye by the equal-weight mixture versus pH of the dye

In the same way, the % adsorption was 99.7% at pH 10 and 95.2% at pH 3 when the contact time was 60 minutes.

A comparison of the three studies is featured in Figure 32.

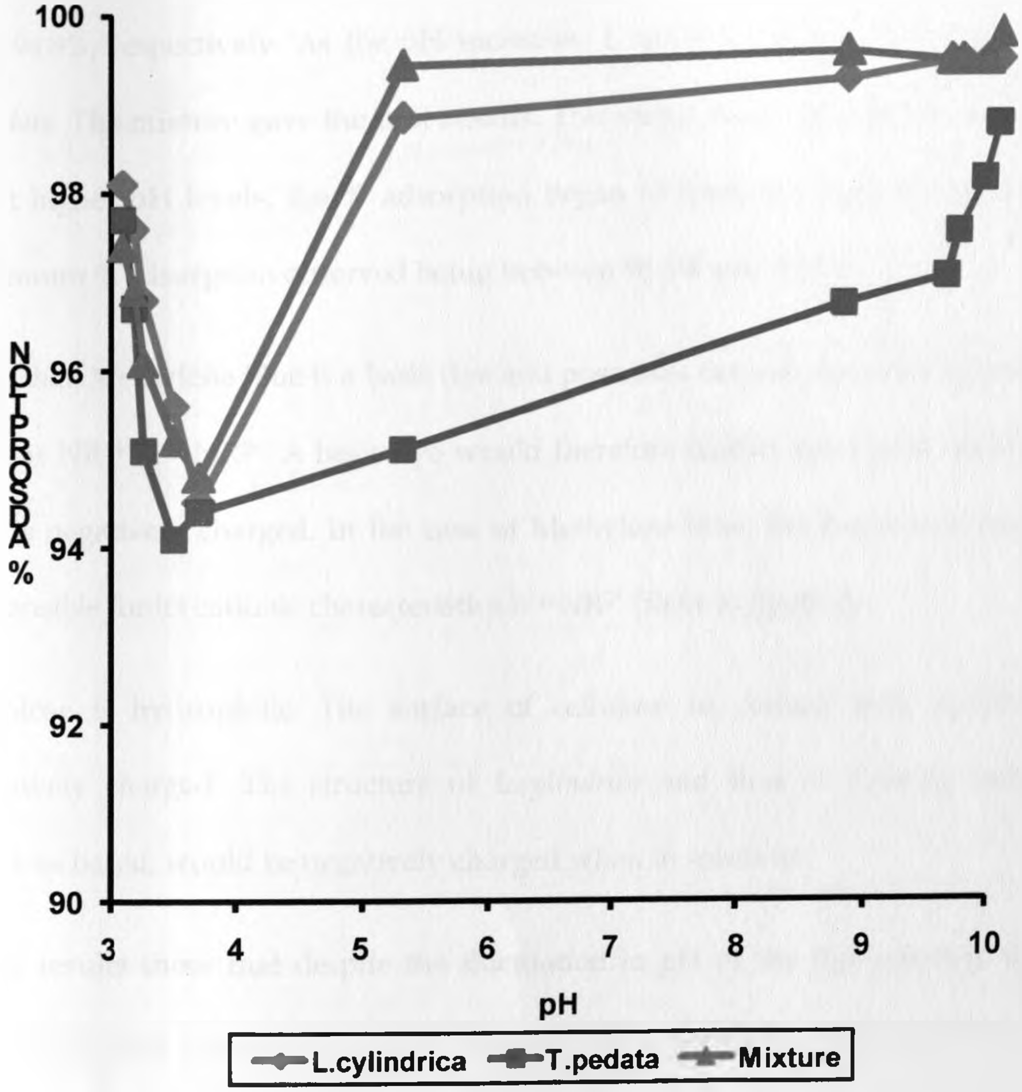


Figure 32: Superimposed plots of % adsorption of Methylene blue dye by *L.cylindrica, T.pedata* and their equal-weight mixture against pH of the dye

From the figure, the following observations were made:

At contact time of 30 minutes and low pH values, there was a distinct reduction in % adsorption between pH 3 and pH 5. *L.cylindrica* recorded the lowest % adsorption, followed by *T.pedata* and the equal-weight mixture at 91.3%, 93.7%

and 94.8%, respectively. As the pH increases, *L.cylindrica* adsorbed better than *T.pedata.* The mixture gave the best results. This status was maintained until pH 9. At higher pH levels, the % adsorption began to level out until pH 10 with maximum % adsorption observed being between 98.3% and 99.1%.

Note that, Methylene blue is a basic dye and possesses cationic functional groups such as NR^{3+} or $=NR^{2+}$. A basic dye would therefore readily react with material that is negatively charged. In the case of Methylene blue, the functional group responsible for its cationic characteristics is $=NR^{2+}$ (*Refer to figure 1*).

Cellulose is hydrophilic. The surface of cellulose in contact with water is negatively charged. The structure of *L.cylindrica* and that of *T.pedata,* being cellulose based, would be negatively charged when in solution.

These results show that despite the fluctuation in pH of the dye solution, the percent adsorption using the adsorbents under study yielded a minimum of 94%.

% adsorption is significant regardless of the change in pH, leading to the conclusion that the material is useful for any composition of dye wastewater.

Effect of pH on % Adsorption of Congo red Dye

Figure 33 reveals that *L.cylindrica* adsorbs most dye over the weakly acidic pH range of between 5.8 and 6.9. For both contact times (i.e. 30 and 60 minutes), the least % adsorption was seen in the alkaline pH range of between 9.2 and 10.2.

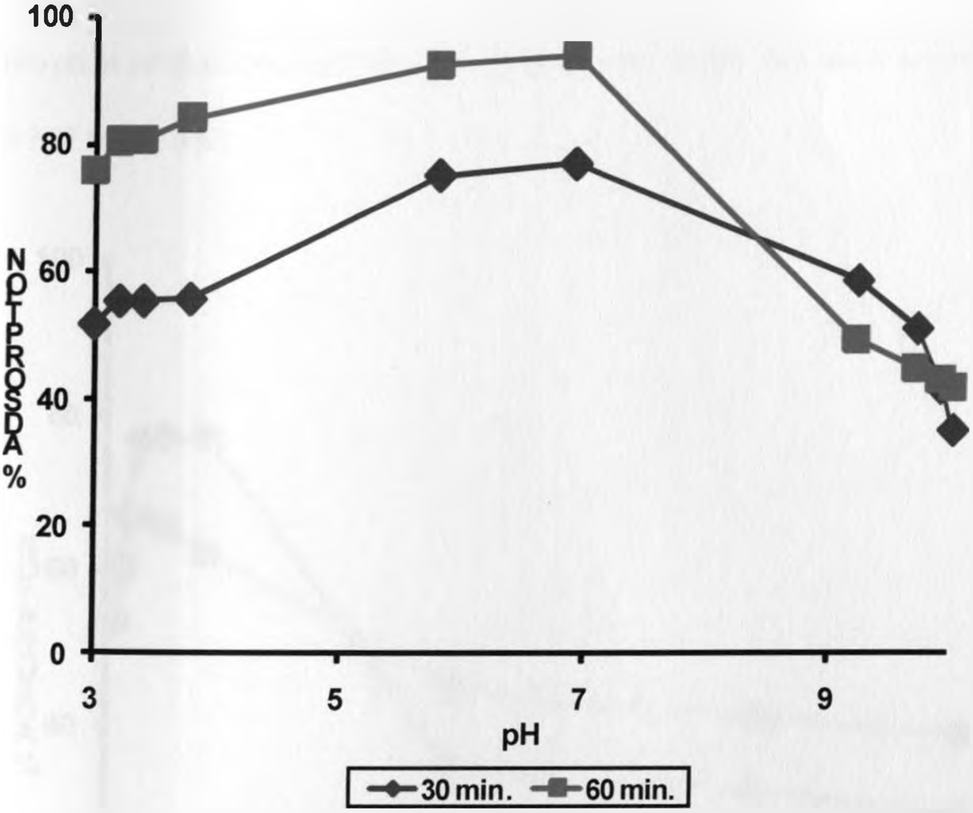


Figure 33: Plot of % adsorption of Congo red dye by *L.cylindrica* versus

pH of the dye.

These observations could be explained considering the fact that Congo red is an acidic dye. Acid dyes usually have a sulphonyl or amino group on the molecule making them soluble in water. Congo red is the sodium salt of benzidinediazo-bis-1-naphtylamine-4-sulfonic acid (see *figure* 2), hence the functional group responsible for its acidity is the sulphonyl group.

Figure 34 shows the observations made when *T.pedata* was studied under similar conditions as those for Figure 33. At lower pH values, the %

adsorption of dye was seen to increase gradually as the pH was increased from pH 3.07 to pH 3.82.

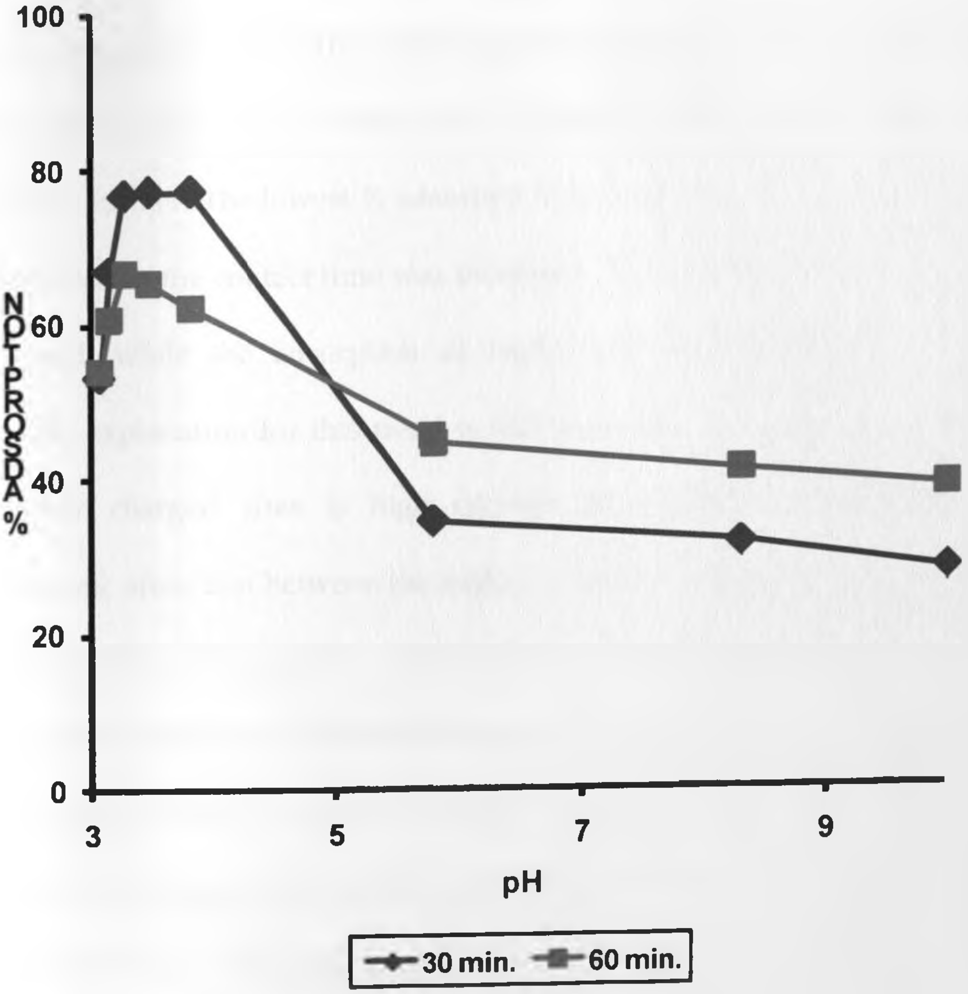


Figure 34: Plot of % adsorption of Congo red dye by *T.pedata* versus pH of the dye

At about pH 3.82, maximum % adsorption was recorded at 77.2%. Thereafter, the % adsorption decreased as pH approached neutral. There was a further decrease in % adsorption when higher pH values were employed. The lowest % adsorption of dye adsorbed was observed at pH 10.3, calculated to be 23.8%. With a higher contact time of 60 minutes, the maximum % adsorption recorded was 66.7% at pH 3.27. As the system approached neutral pH, the % adsorption decreased as well. This decrease in % adsorption continued as the pH was increased further. The lowest % adsorbed in this case was 31.6% at pH 10.3. This implies that as the contact time was increased, % adsorption at lower pH values decreased; while the adsorption at higher pH values increased. The most plausible explanation for this trend is that at certain pH values, the number of positively charged sites is high enough to facilitate a significantly high electrostatic attraction between the surface of the adsorbent and the anionic dye. For *L.cylindrica,* the number of positively charged sites increased as one approached neutral pH values whereas for *T.pedata,* the increase of positively charged sites reached a maximum at the pH range of between 3 and 4. Lower adsorption of Congo red under alkaline pH conditions can be attributed to the presence of excess OH^- ions competing with the dye anions for the adsorption sites (Namasivayam and Kavitha, 2002).

From the previous pH studies with both *L.cylindrica* and *T.pedata,* one would expect interplay between the two pH-dependent adsorption effects when a mixture of the two adsorbents is employed in equal proportion. This is depicted in Figure 35.

From the figure, it is evident that at lower pH values the % adsorption by the equal-weight mixture decreased between pH 3 and 4 for both plots. Between pH 4 and pH 5, % adsorption increased from 43.2% to 56.8% for the contact time of 30 minutes. The % adsorption for the dye remained relatively constant through neutral pH but started to decrease in the higher pH values. At pH values beyond neutral, the OH^- ions in solution compete with the dye molecules and hence the reduction in % adsorption. On the other hand, under highly acidic conditions, the dye molecules are predominantly negatively charged hence limited interaction with the adsorbent surface.

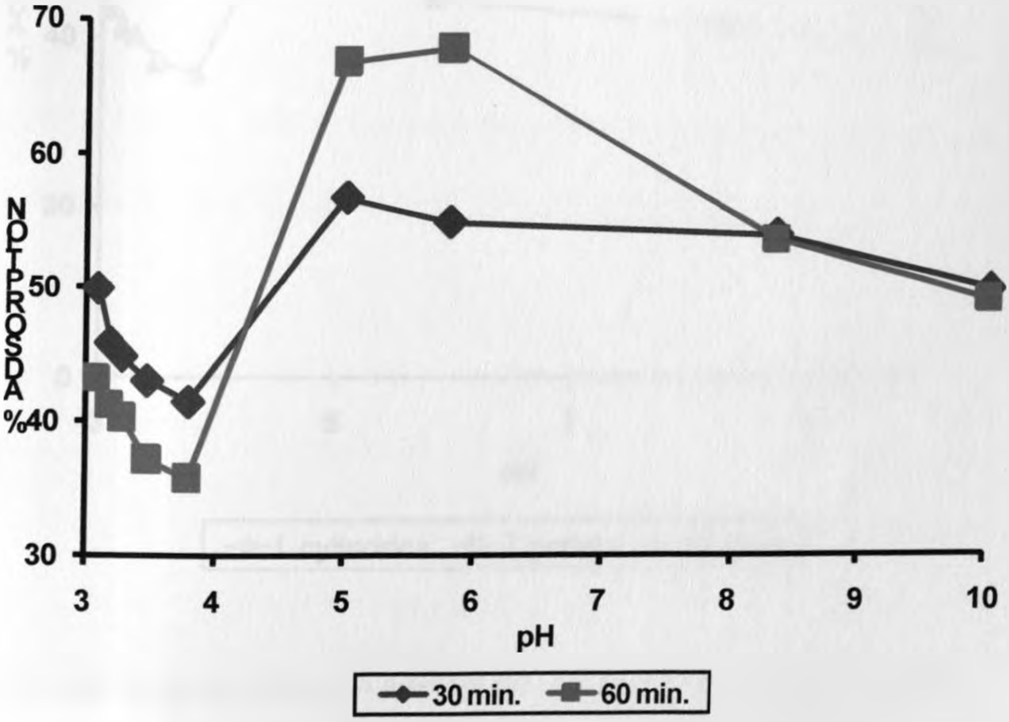


Figure 35: Plot of % adsorption of Congo red dye by the equal-weight mixture of *L.cylindrica* and *T.pedata* versus pH of the solution

Figure 36 gives a summary of the results for the two adsorbents and their equal-weight mixture.

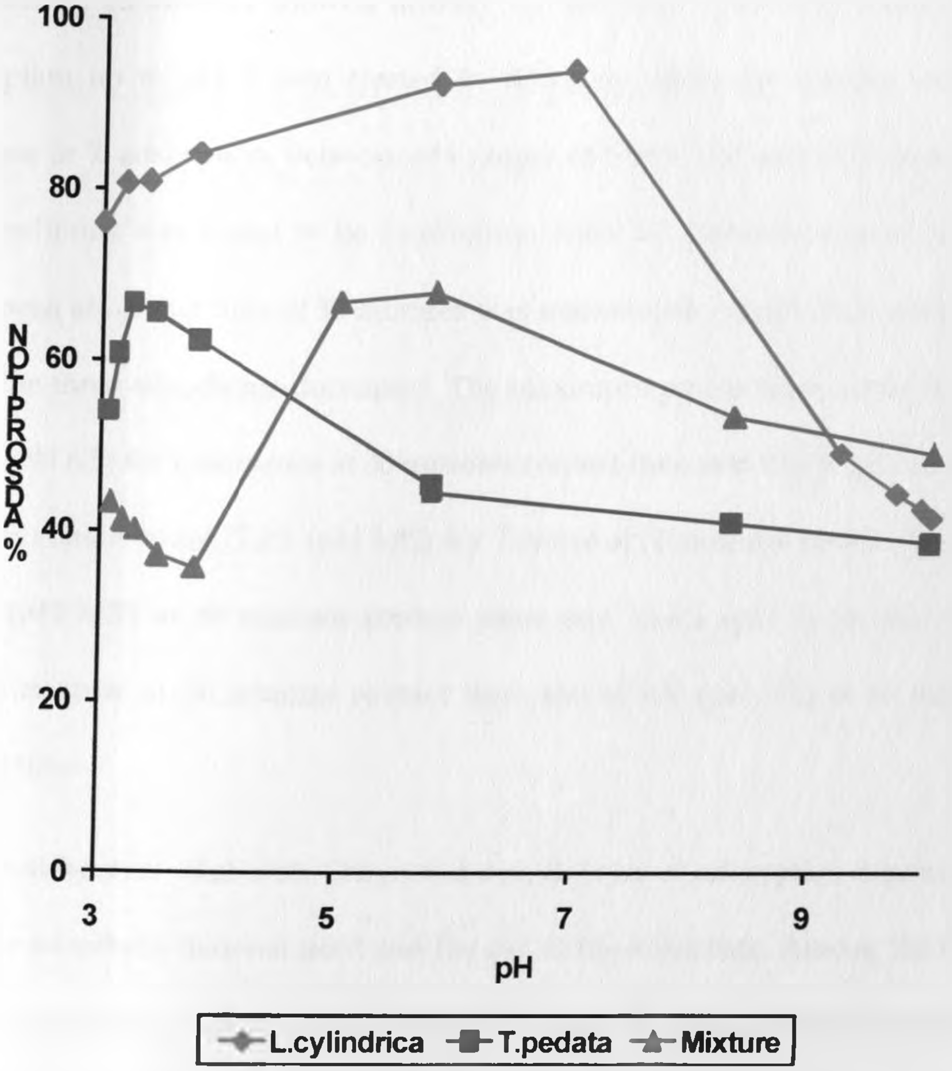


Figure 36: Superimposed plot of % adsorption of Congo red dye by *L.cylindrica*, *T.pedata* and their equal-weight mixture versus pH of the dye

From the figure, it is clear that at low pH of between 3 and 5, *L.cylindrica* and *T.pedata* showed a general increase in % adsorption while their equal-weight mixture showed a decreased % adsorption. As the contact time was increased to 60 minutes, *L.cylindrica* showed affinity for the dye; *T.pedata* increased the % adsorption up to pH 3 then started to decrease; while the mixture exhibited decrease in % adsorption. Between pH ranges of 5 to 9, the best adsorbent under the conditions was found to be *L.cylindrica.* After 60 minutes contact time, the trend seen at contact time of 30 minutes was maintained. At pH 10, % adsorption of all the three adsorbents decreased. The maximum percentages achieved were 76.9% (pH 6.9) for *L.cylindrica* at 30 minutes contact time and 93.7% (pH 6.9) at 60 minutes contact time; 77.2% (pH 3.82) for *T.pedata* at 30 minutes contact time and 66.7% (pH 3.27) at 60 minutes contact time; and 56.8% (pH 5) for the equal-weight mixture at 30 minutes contact time and 67.9% (pH 5.8) at 60 minutes contact time.

These results show that with Congo red dye, the rate of adsorption depends on both the adsorbent material used and the pH of the adsorbate. Among the three materials studied, *L.cylindrica* was observed to give the best % adsorption over a wider range of pH- especially between strong acidic pH to neutral pH of pH 3 to pH 7- than the either *T.pedata* or the mixture.

The results show that the adsorption process is dependant on ionic interaction of the dye solution and plant material.

4.1.5 Effect of Temperature

Effect of Temperature on % Adsorption of Methylene blue Dye

Preliminary studies in this thesis showed *L.cylindrica* to be effective in the removal of Methylene blue dye solution at room temperature. In temperatures close to room temperature such as 20 ⁰C and 30 ⁰C, the % adsorption was shown to be high. According to Figure 37, the % adsorption is 97% at 20 ⁰C and 94.6% at 30 ⁰C. A further increase in temperature led to a decrease in % adsorption to 90.9%, 90.4% and 88.9% for 40 ⁰C, 50 ⁰C and 60 ⁰C, respectively. A similar trend was observed when the contact time was 60 minutes. That is, a general decrease in % adsorption with increase in temperature.

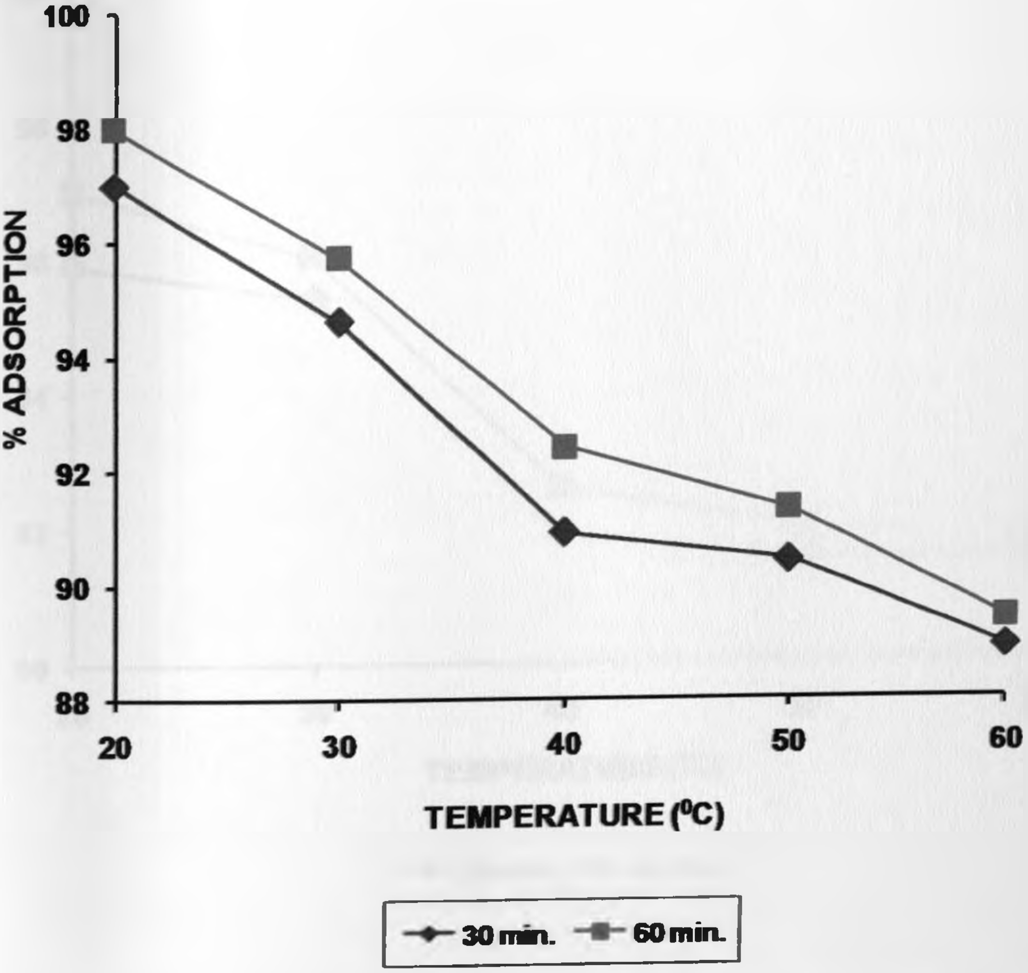


Figure 37: Plot of % adsorption of Methylene blue dye by *L.cylindrica* versus temperature of the solution

Figure 38 shows similar observations made with *T.pedata*. Here too, % adsorption appears to decrease with increase in temperature, for both the two contact times investigated.

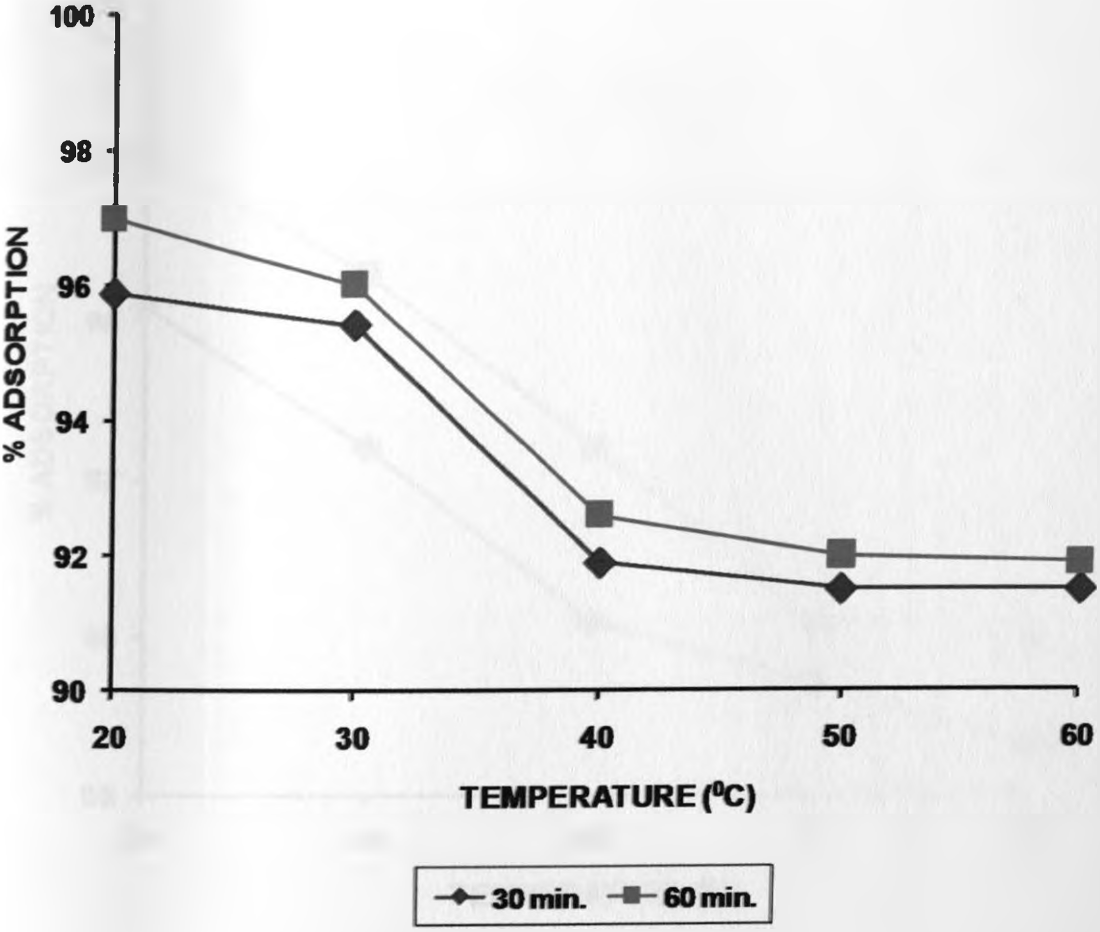


Figure 38: Plot of % adsorption of Methylene blue dye by T.*pedata* versus temperature.

Figure 39 reveals a similar influence of temperature on % adsorption of Methylene blue dye by an equal-weight mixture of *L.cylindrica* and *T.pedata*. From the figure, it can be seen that the increase of temperature resulted in decrease of % adsorption both after 30 and 60 minutes of contact time.

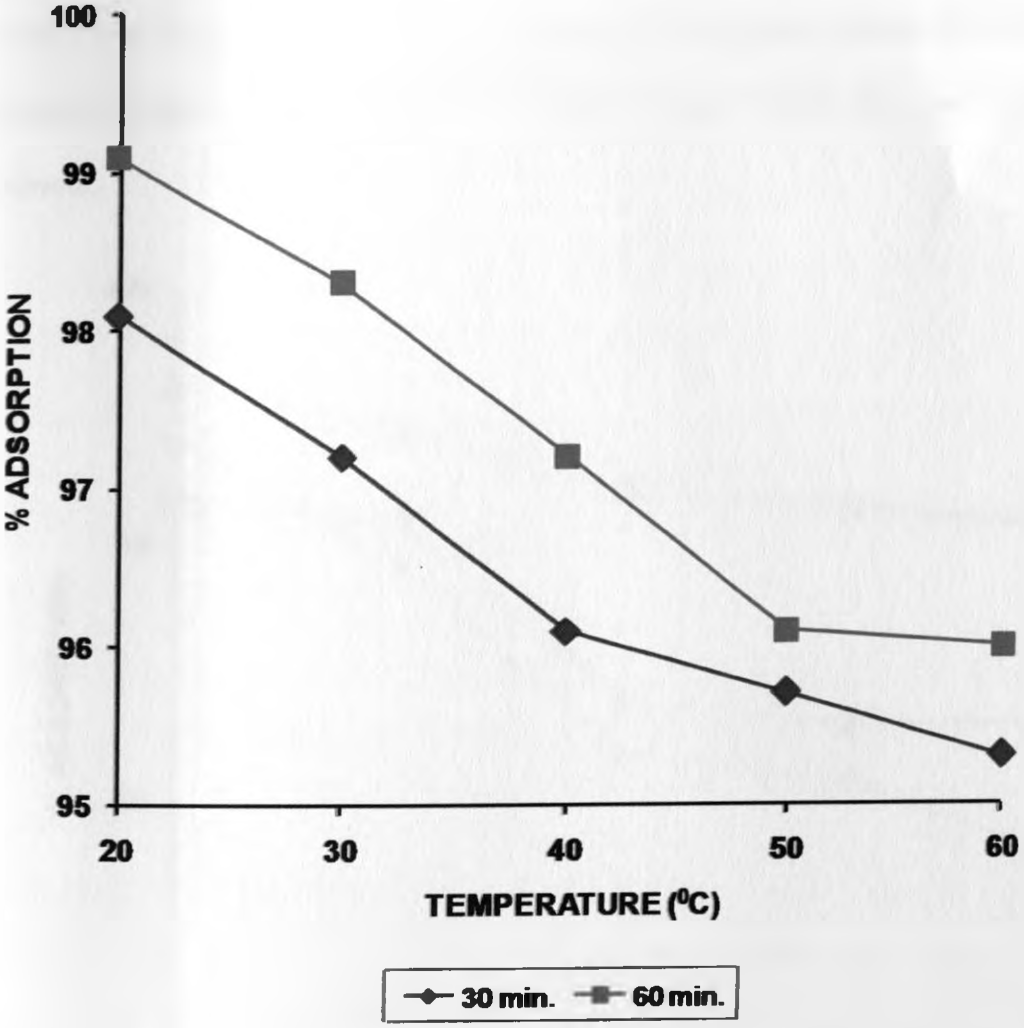


Figure 39: Plot of % adsorption of Methylene blue dye by equal-weight mixture of 0.5g *L.cylindrica* and 0.5g *T.pedata* versus temperature

Figure 40 shows superimposed plots of % adsorption of Methylene blue dye versus temperature for the three adsorbents. It is evident from the figure that there was a general decrease in % adsorption of the Methylene blue dye by the three adsorbent types with increased temperature; with the equal-weight mixture adsorbent type showing much higher % adsorption values followed by *T.pedata*. Similar trends were evident when contact time was raised to 60 minutes.

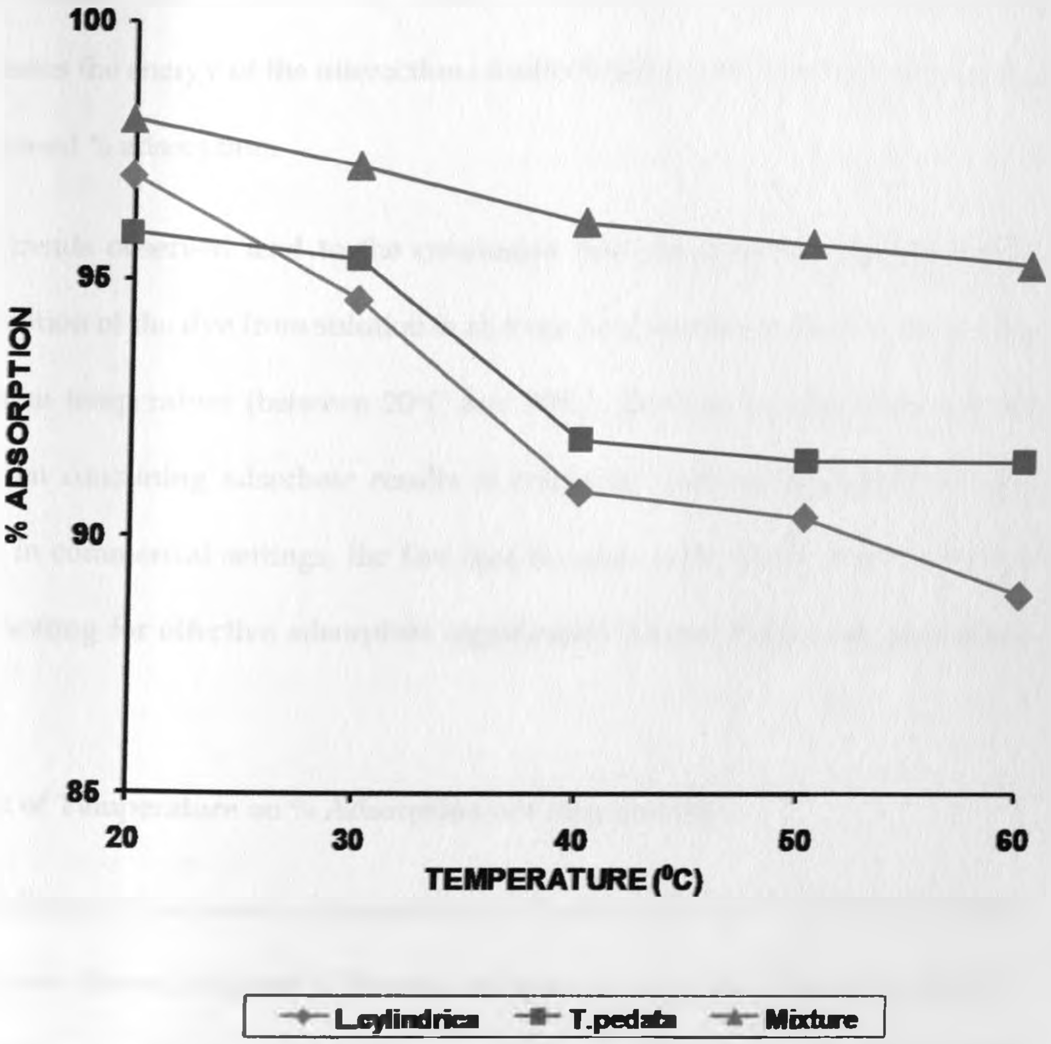


Figure 40: Superimposed plots of % adsorption of Methylene blue dye by *L.cylindrica, T.pedata* and their equal-weight mixture versus temperature for a contact time of 30 minutes

The decrease of the equilibrium adsorption with increasing temperature indicated that the adsorption of Methylene blue ions onto either of the adsorbents or their mixture was exothermic in nature (Han et.al, 2006, Vadivelan and Kumar, 2005; Otero et.al, 2003). In addition, increase in temperature increases the energy of the interaction of adsorbents in solution leading to overall decreased % adsorption.

The trends observed lead to the conclusion that the optimal temperatures for adsorption of the dye from solution is at room temperature or temperatures close to room temperature (between 20°C and 30°C). Increase in temperature of the solution containing adsorbate results in minimum percent adsorption of over 85%. In commercial settings, the fact that the dye waste water will not require any heating for effective adsorption significantly lowers the overall production cost.

Effect of Temperature on % Adsorption of Congo red Dye

The influence of increase in temperature on % adsorption of Congo red dye from solution is shown in Figure 41 through to Figure 43. Figure 41 shows the effect of temperature on % adsorption of Congo red dye by *L.cylindrica*. Here too, increase in temperature led to a decrease in % adsorption both at 30 and 60 minutes contact time: An observation similar to that with Methylene blue dye.

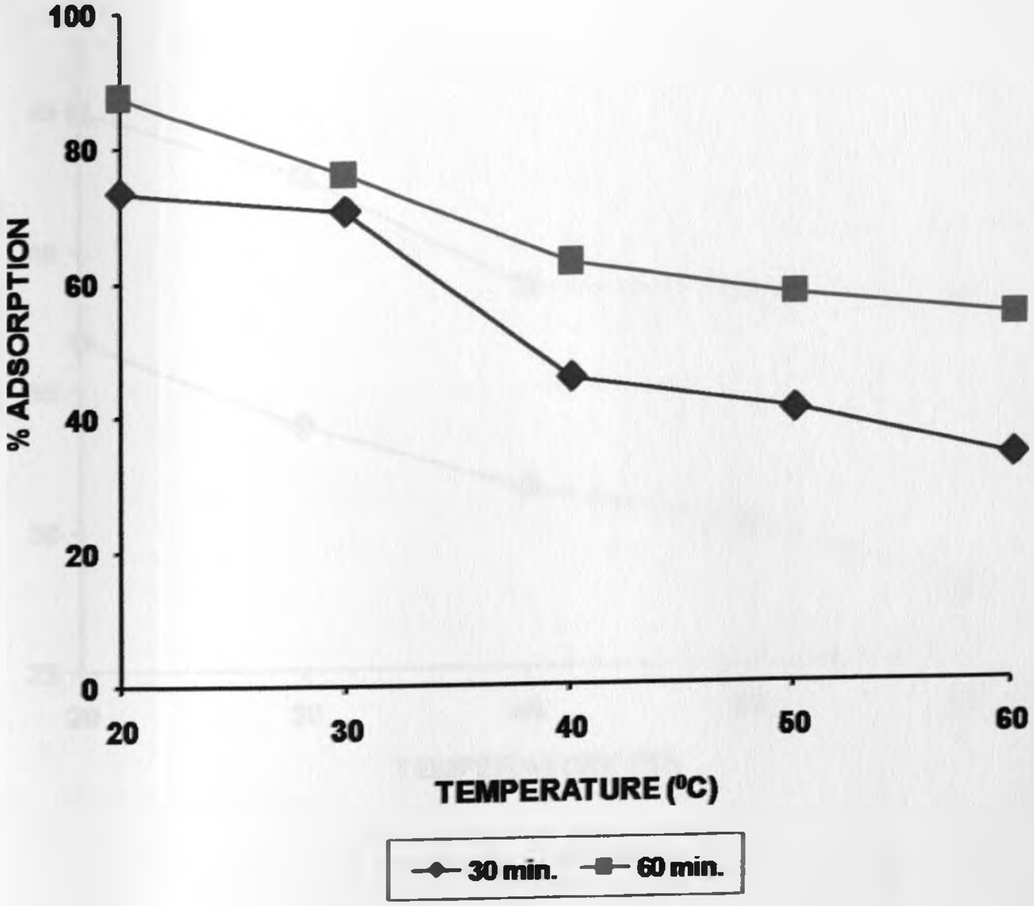


Figure 41: Plot of % adsorption of Congo red dye by *L.cylindrica* versus temperature of solution

Figure 42 also shows the effect of temperature on % adsorption of Congo red on *T.pedata.* The highest % adsorption was seen at near room temperature conditions (i.e. 36.8% at 20⁰C). At contact time of 60 minutes, this capacity had increased to 44.9%. *T.pedata* also showed a decrease in % adsorption as the temperature was increased.

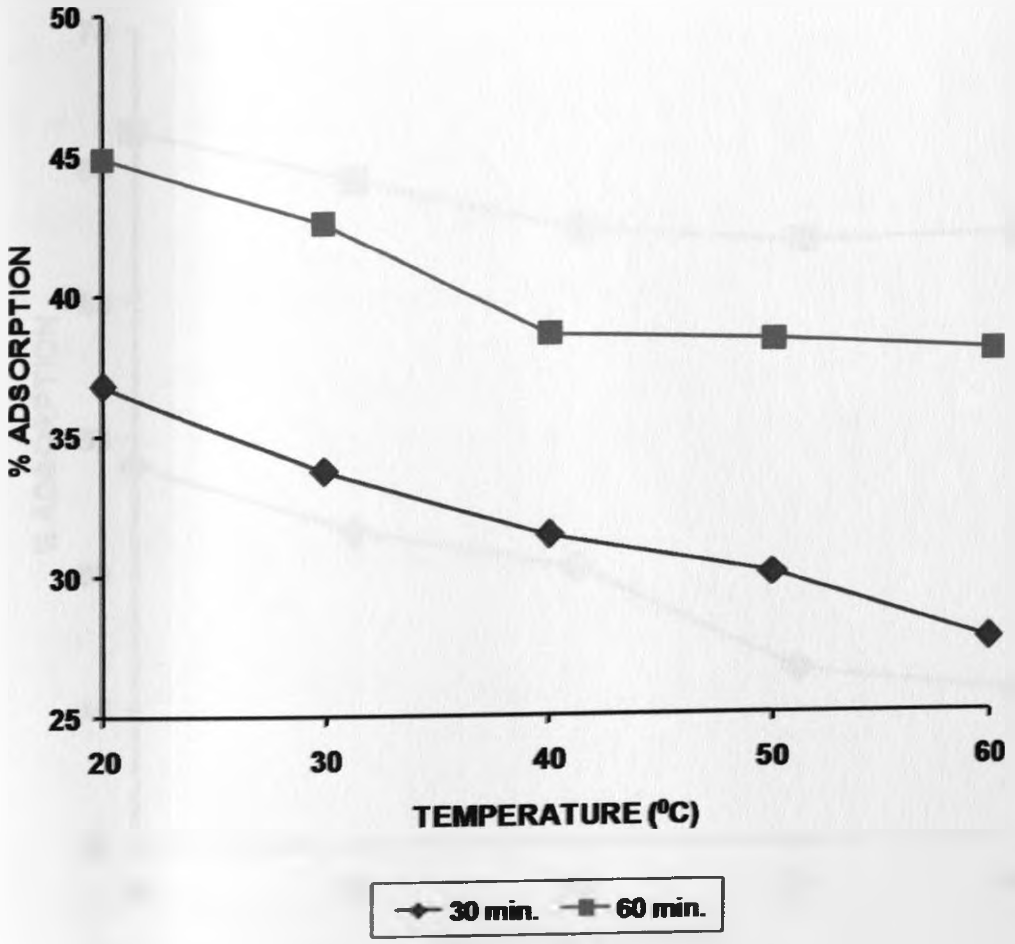


Figure 42: Plot of % adsorption of Congo red dye by *T.pedata* versus temperature of solution

Results of further studies carried out using the equal-weight mixture of *L.cylindrica* and *T.pedata* as adsorbent for Congo red is given in Figure 43 below. According to the figure, the highest % adsorption was at temperatures close to room temperature with % adsorptions showing continuous decrease with increase in temperature.

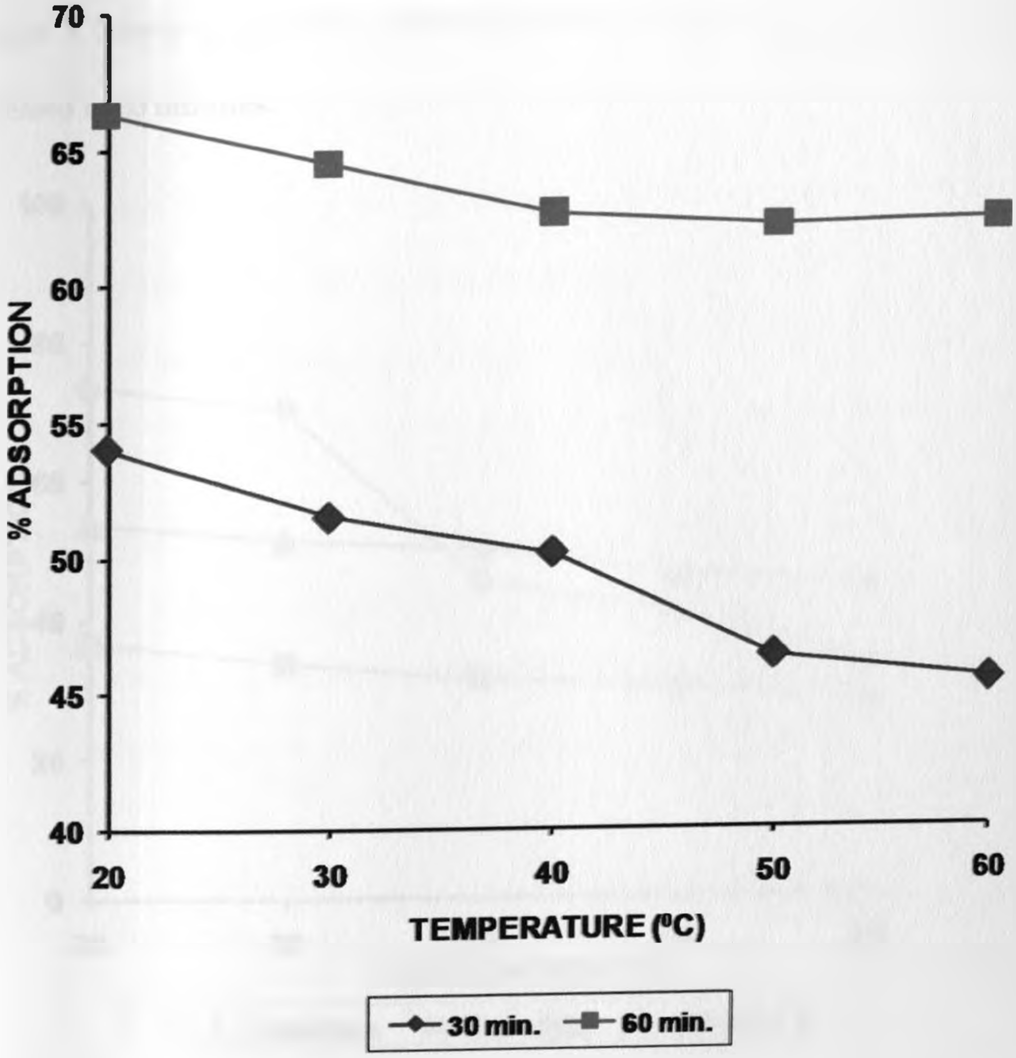


Figure 43: Plot of % adsorption of Congo red dye by the mixture versus temperature of solution

Figure 44 compares *L.cylindrica*, *T.pedata* and their equal weight mixture.

Comparing the three adsorbents, *L.cylindrica* exhibited the highest % adsorption between 20 ⁰C and 30 ⁰C. At 40 ⁰C onwards, the equal-weight mixture shows the highest % adsorption. Similar observations were made when contact time was increased to 60 minutes.

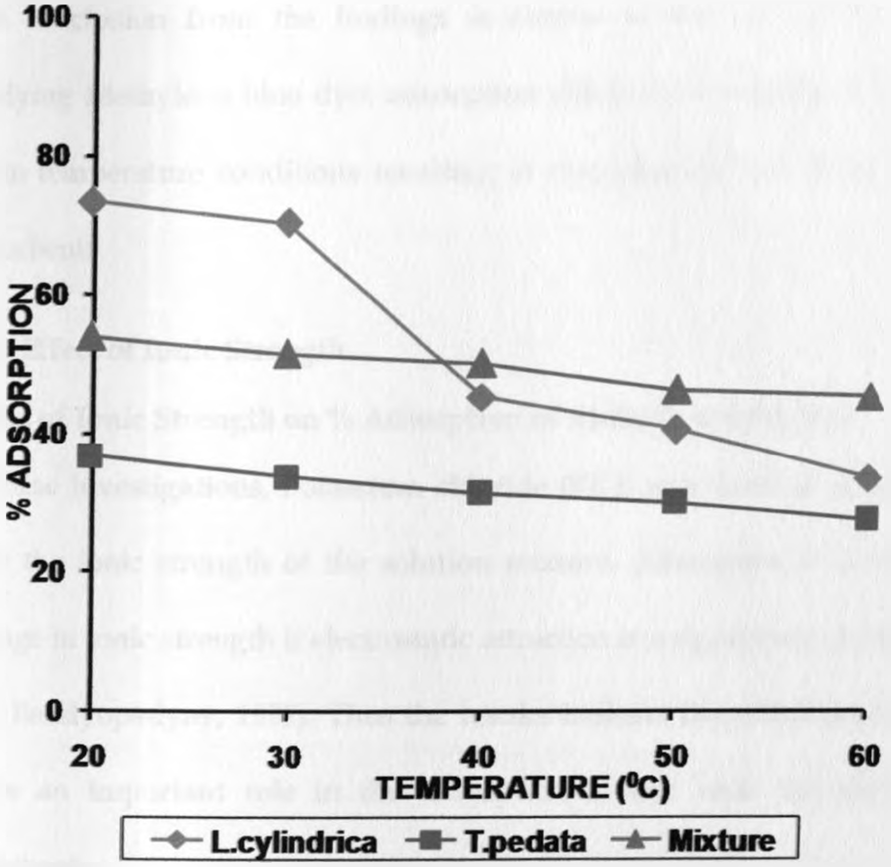


Figure 44: Superimposed plots of % adsorption of Congo red dye by *L.cylindrica T.pedata* and their equal-weight mixture versus temperature

It can therefore be concluded that this was an indication that the adsorption of Congo red ions onto *L.cylindrica, T.pedata* and their equal-weight mixture was exothermic in nature. In addition, for both Methylene blue and Congo red dyes, it is a physical process. If sorption is governed only by physical phenomena, an increase in temperature will generally be followed by a decrease in sorption capacity. Adsorption favored by a decrease in temperature is characteristic of physical adsorption (Benguella and Benaissa, 2002; Chegrouche and Bensmaili, 2002).

The conclusion from the findings is similar to the one encountered while studying Methylene blue dye: adsorption efficiency is highest at room or near room temperature conditions resulting in cost effective use of the materials as adsorbents.

4.1.6 Effect of Ionic Strength

Effect of Ionic Strength on % Adsorption of Methylene blue Dye

In these investigations, Potassium chloride (KCl) was used as a neutral salt to alter the ionic strength of the solution mixture. Adsorption is sensitive to the change in ionic strength if electrostatic attraction is a significant mechanism (Das and Bandyopadyay, 1991). Thus the results indicate that electrostatic attraction plays an important role in the adsorption of dye onto the three types of adsorbents.

According to Figure 45, at 30 minutes contact time, *L.cylindrica* showed a decrease in % adsorption from 97.1% to 87.6% with an increase in concentration of KCl from 0 M to 4.0×10^{-3} M. At contact time of 60 minutes, the % adsorption decreased from 98% to 85.8%, when the solution had no KCl to when the solution had maximum KCl concentration, respectively (*Appendix* 2).

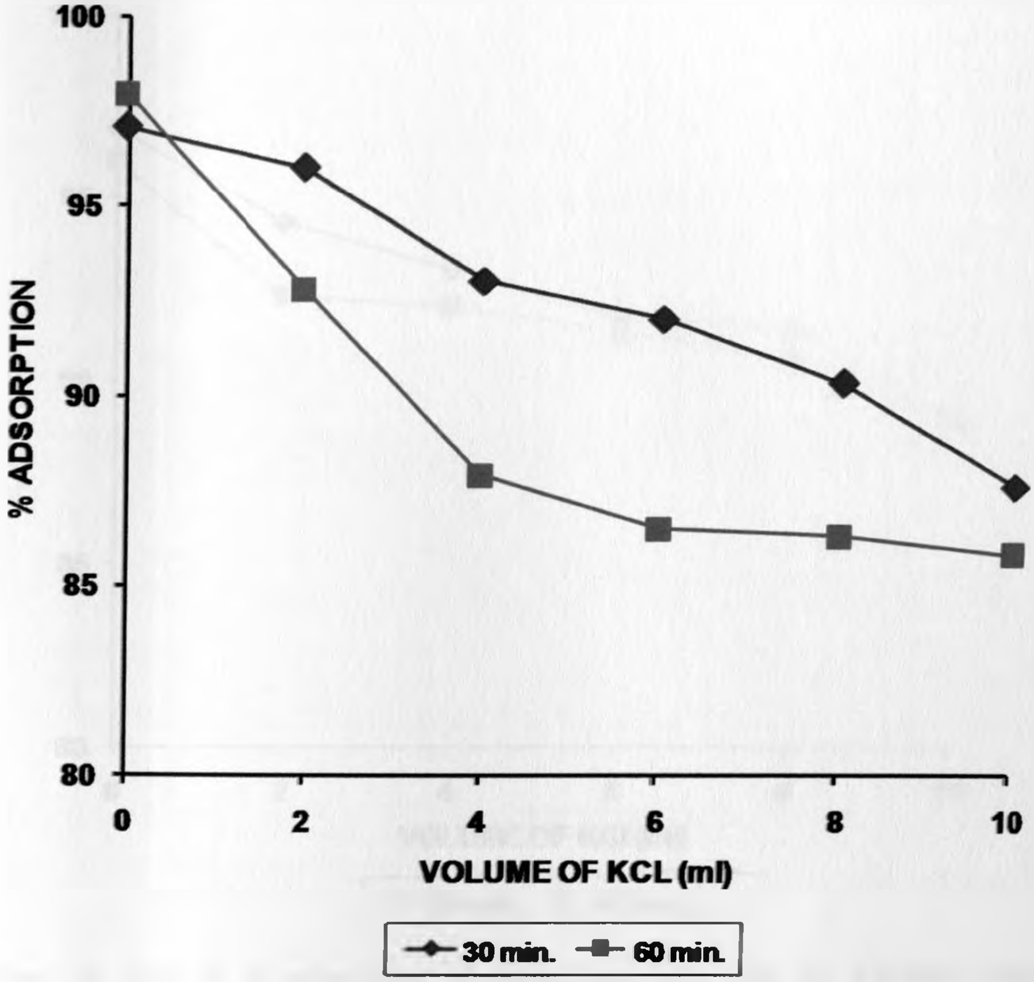


Figure 45: Plot of % adsorption of Methylene blue dye by *L.cylindrica* versus volume of KCl

Similar experiments with *T.pedata* yielded the results illustrated in Figure 46. The plots show that there was a general decrease in % adsorption with increase in the amount of KCl in solution.

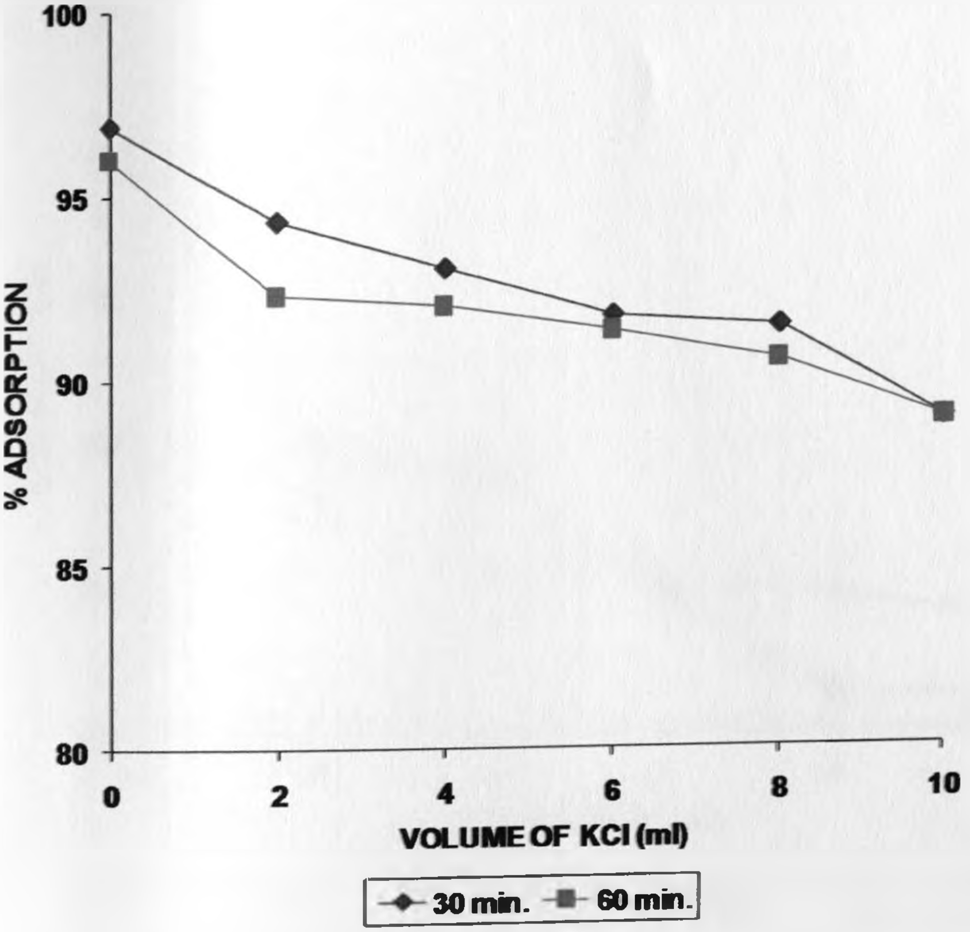


Figure 46: Plot of % adsorption of Methylene blue dye by *T.pedata* versus volume of KCl

Figure 47 also shows that combining *L.cylindrica* and *T.pedata* in equal proportions results in a decrease in the % adsorption with increase in ionic strength of the solution.

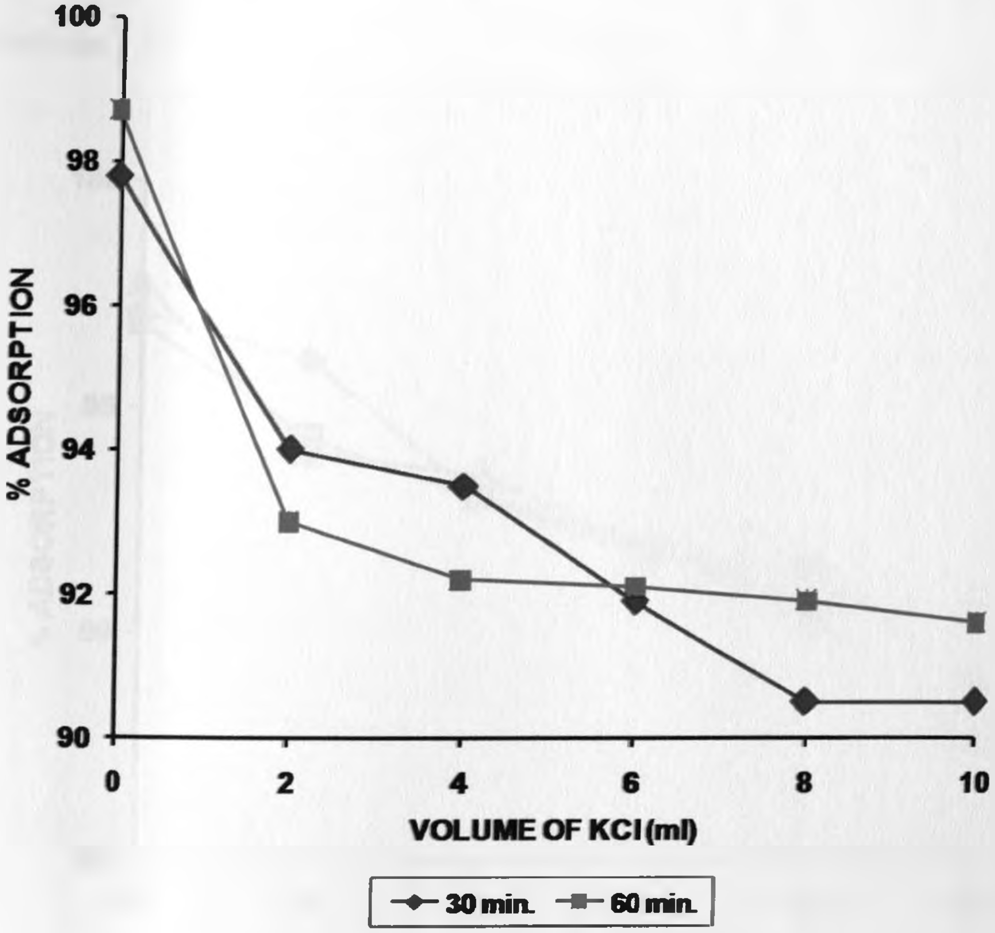


Figure 47: Plot of % adsorption of Methylene blue dye by the equal-weight mixture of *L.cylindrica* and *T.pedata* versus volume of KCl

Superimposed plots on the effect of concentration of KCl on % adsorption of Methylene Blue dye on *L.cylindrica, T.pedata* and their equal-weight mixture is given in Figure 48 for comparison. Figure 48 shows that there was a decrease in

% adsorption with an increase in the concentration of KCl with all the three adsorbents.

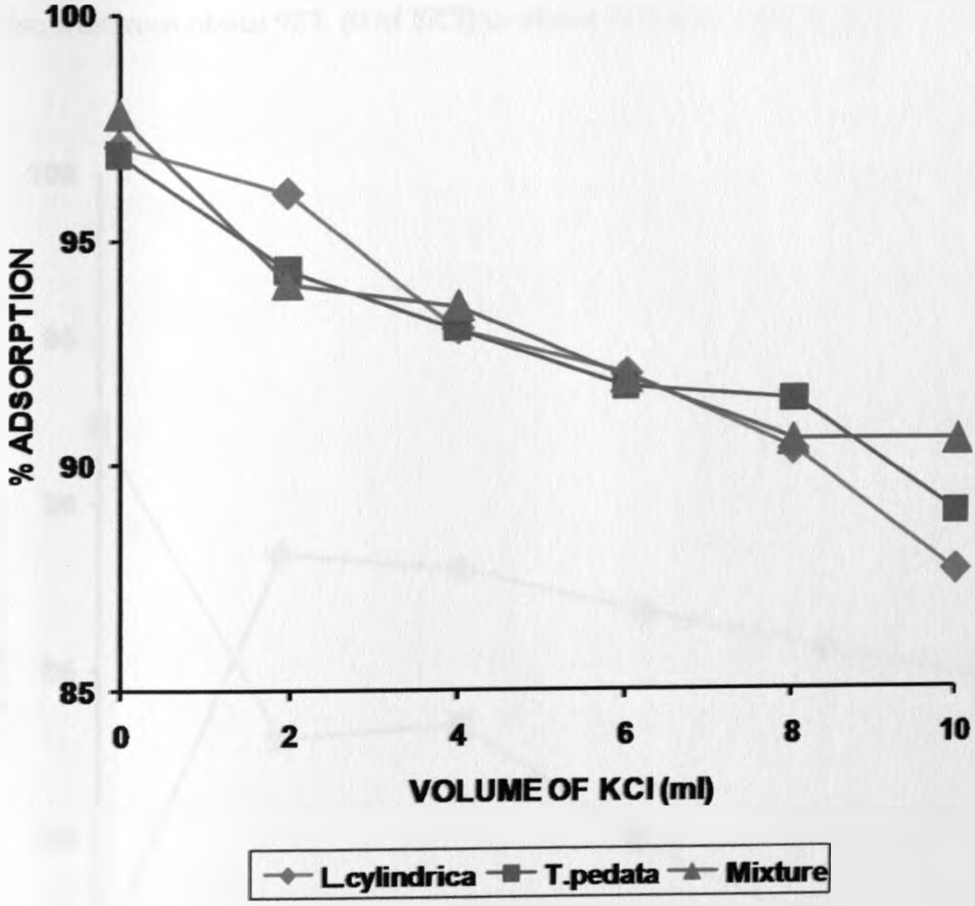


Figure 48: Superimposed plots of % adsorption of Methylene blue dye by *L.cylindrica, T.pedata* and their equal-weight mixture versus volume of KCl at t=30 minutes.

Effect of Ionic Strength on % Adsorption of Congo red Dye

Figure 49 shows that with *L.cylindrica,* % adsorption decreases very minimally with increase in KCl concentration for the 60 minutes contact time. In fact, the % decrease was from about 92% (0 M KCl) to about 74% (4.0 X10^{-3} M KCl).

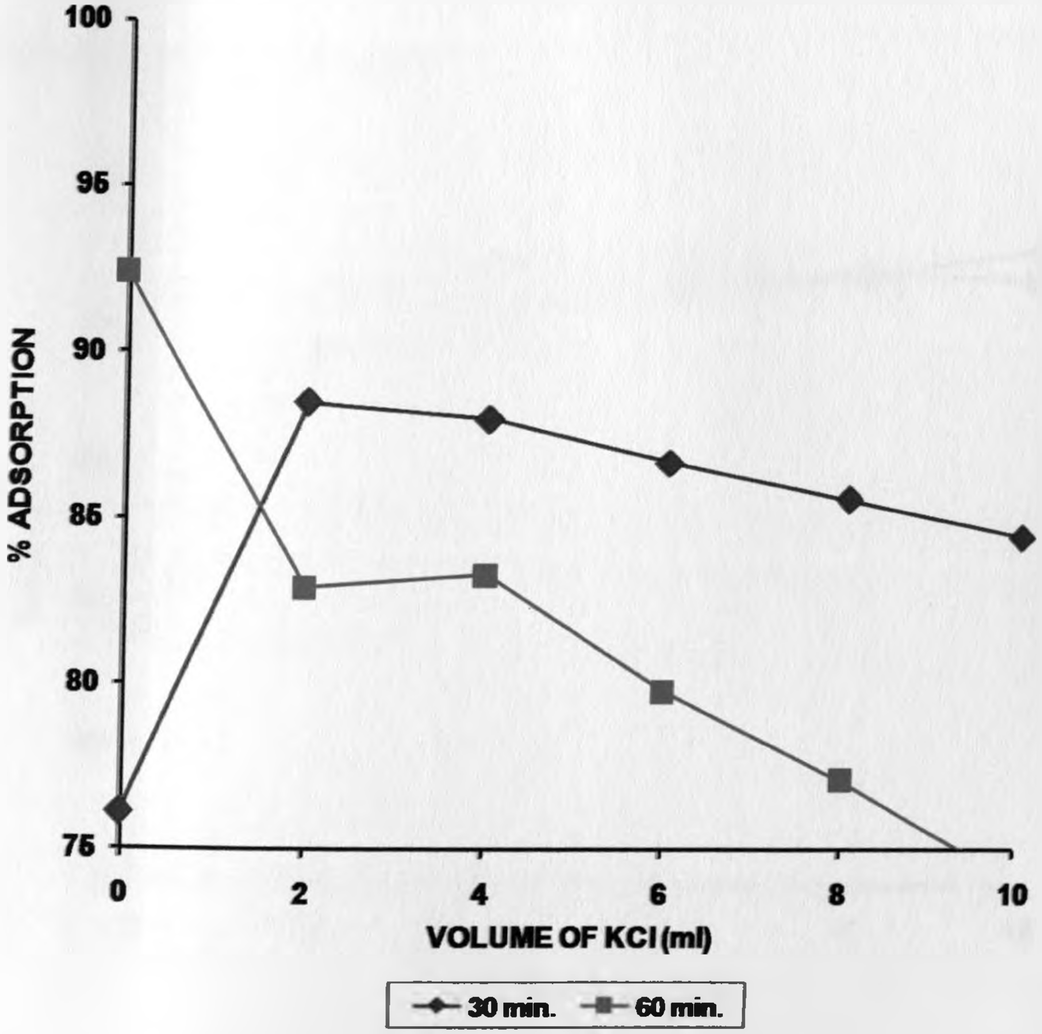


Figure 49: Plot of % adsorption of Congo red dye by *L.cylindrica* versus volume of KCl

For 30 minutes contact time, there was an initial increase in % adsorption which subsequently decreased as the ionic strength was further increased. From this, it can be concluded that Ionic strength does not seem to influence % adsorption of Congo red by *L.cylindrica*.

In contrast, as per Figure 50, *T.pedata* exhibited an increase in % adsorption as the concentration of KCl was increased.

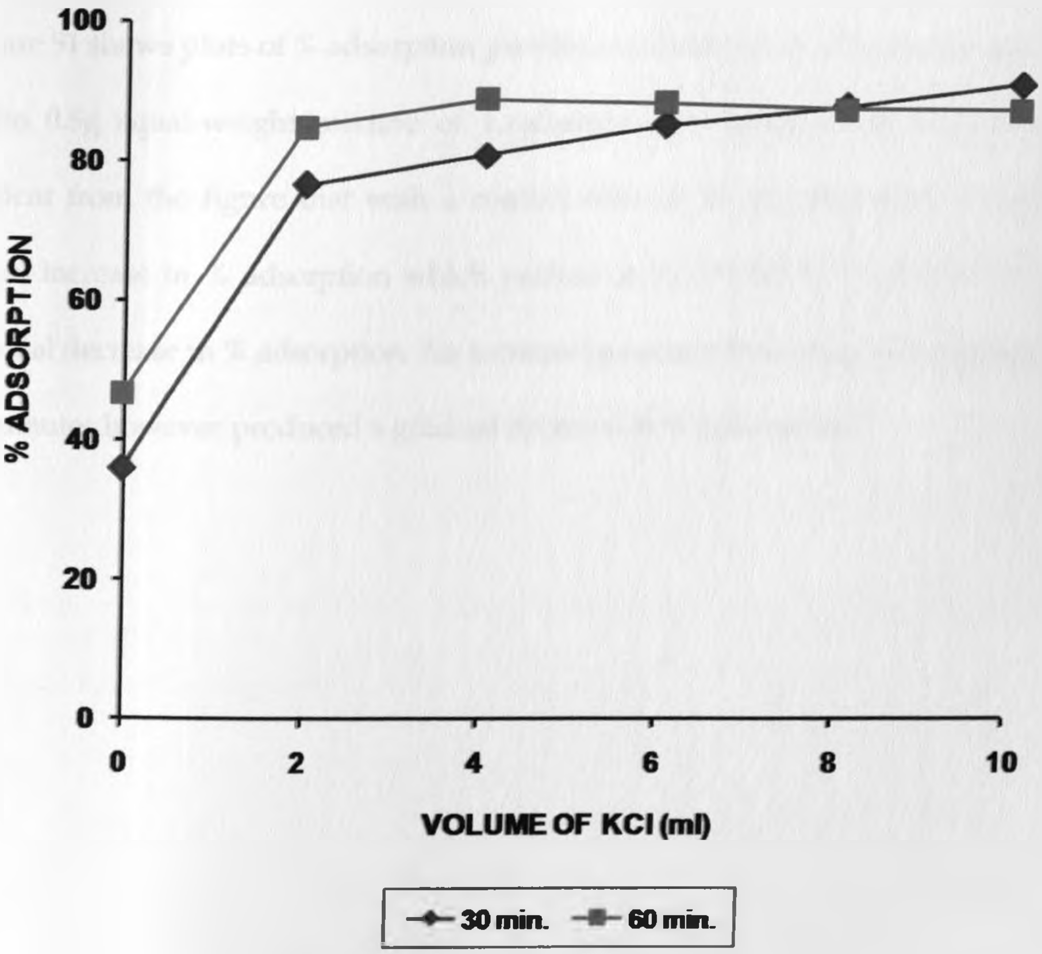


Figure 50: Plot of % adsorption of Congo red dye by *T.pedata* versus volume of KCl

The assumption made was that the overall charge of the molecules on *T.pedata* surface (i.e. the adsorbent) "reversed" in orientation upon addition of the salt. The orientation theory (Ware, 1936) accounts for a possible change in charge when the conditions are varied as, for instance, the addition of a salt. A positively charged surface can become negatively charged on account of the rotation to a certain degree of the adsorbed molecules, in essence, the reversal of oriented molecules by a change in conditions.

Figure 51 shows plots of % adsorption profiles as a function of KCl concentration when 0.5g equal-weight mixture of *L.cylindrica* and *T.pedata* was used. It is evident from the figure that with a contact time of 30 minutes, there was an initial increase in % adsorption which peaked at 9.5×10^{-4}M KCl followed by a gradual decrease in % adsorption. An increase in contact time from 30 minutes to 60 minutes however produced a gradual decrease in % adsorption.

The assumption made was that the overall charge of the molecules on *T.pedata* surface (i.e. the adsorbent) "reversed" in orientation upon addition of the salt. The orientation theory (Ware, 1936) accounts for a possible change in charge when the conditions are varied as, for instance, the addition of a salt. A positively charged surface can become negatively charged on account of the rotation to a certain degree of the adsorbed molecules, in essence, the reversal of oriented molecules by a change in conditions.

Figure 51 shows plots of % adsorption profiles as a function of KCl concentration when 0.5g equal-weight mixture of *L.cylindrica* and *T.pedata* was used. It is evident from the figure that with a contact time of 30 minutes, there was an initial increase in % adsorption which peaked at 9.5×10^{-4}M KCl followed by a gradual decrease in % adsorption. An increase in contact time from 30 minutes to 60 minutes however produced a gradual decrease in % adsorption.

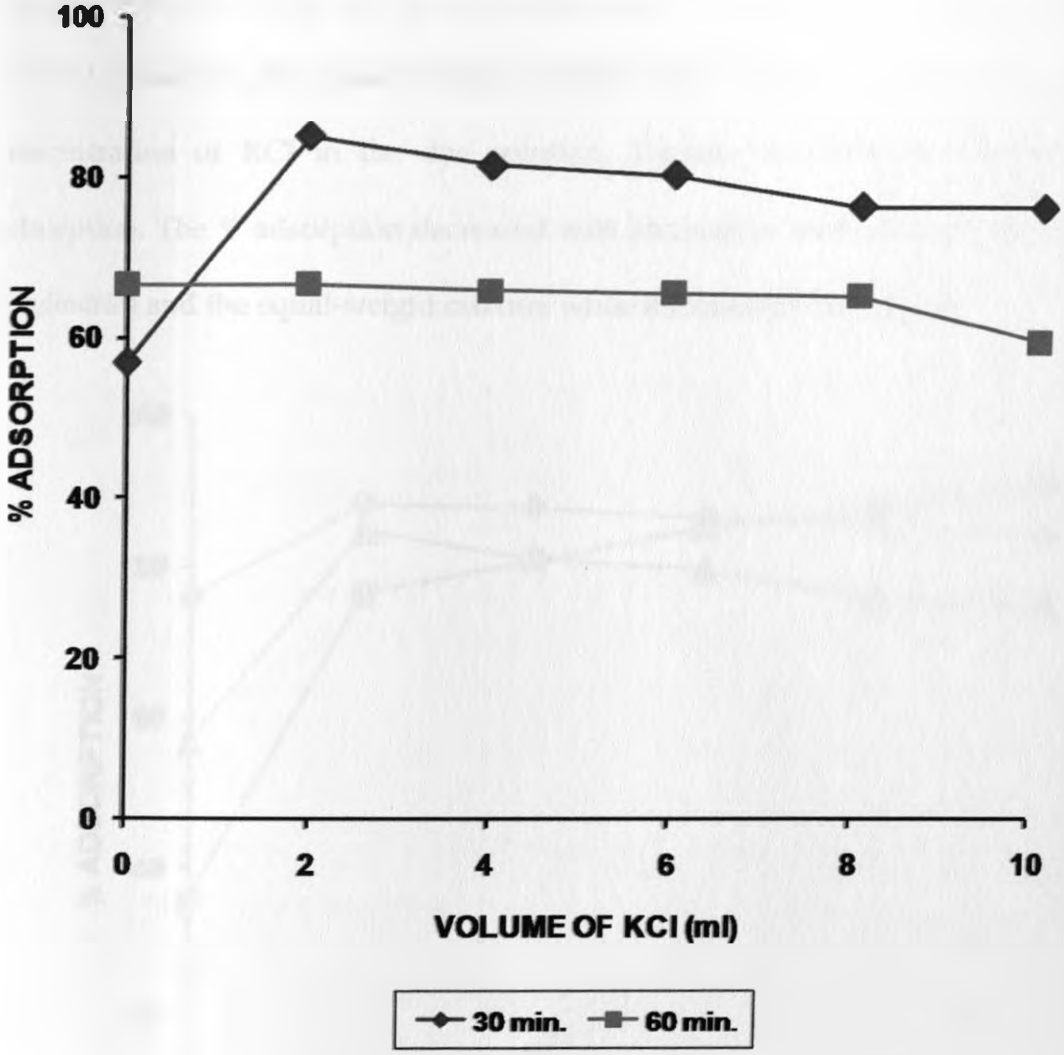


Figure 51: Plot of % adsorption of Congo red dye by the equal-weight mixture of *L.cylindrica* and *T.pedata* versus volume of KCl

Superimposed plots for *L.cylindrica, T.pedata,* and their equal-weight mixture as shown in Figure 52, clearly shows influence of KCl concentration on % adsorption when the three adsorbent types are employed. Generally, when the solution was free of any salt, the adsorbents had the highest % adsorption in the order *L.cylindrica,* the equal-weight mixture and *T.pedata*. At the maximum concentration of KCl in the dye solution, *T.pedata* recorded the highest % adsorption. The % adsorption decreased with increase in ionic strength for both *L.cylindrica* and the equal-weight mixture while it increased for *T.pedata.*

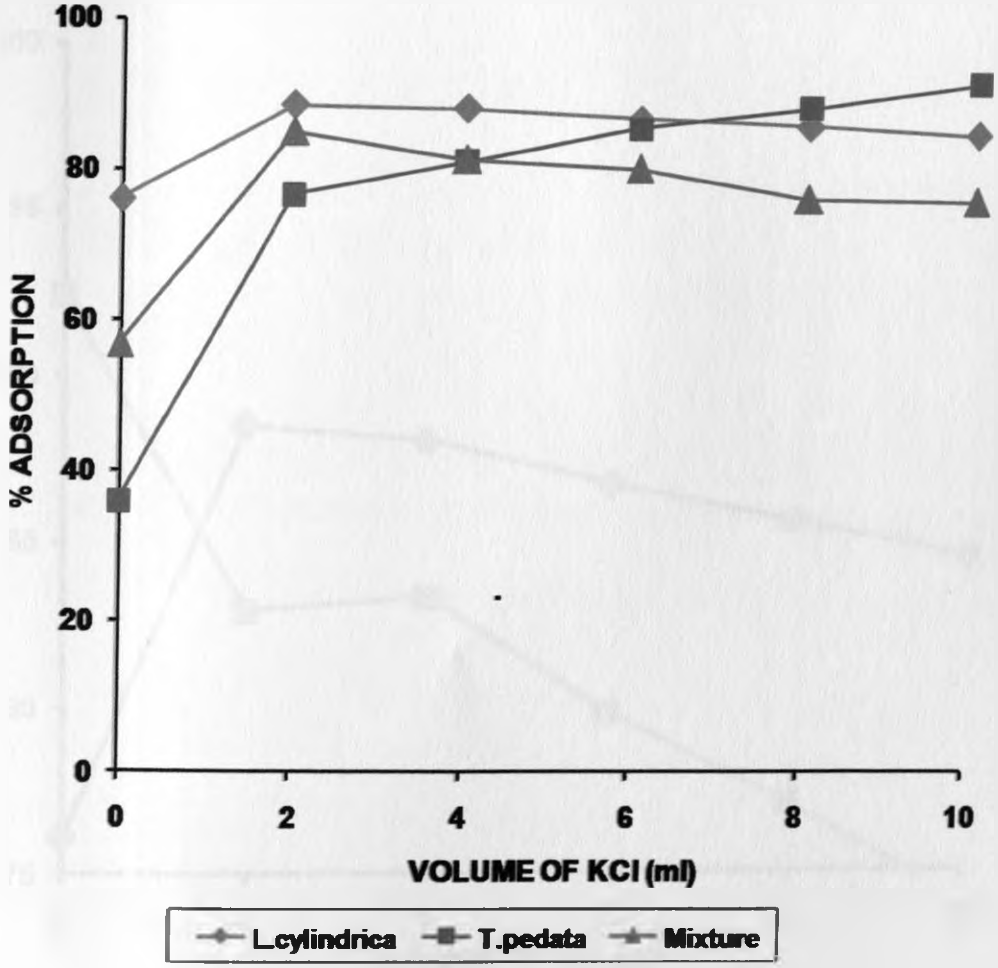


Figure 52: Superimposed plot of % adsorption of Congo red dye by *L.cylindrica, T.pedata* and their equal-weight mixture versus volume of KCl for a contact time of 30 minutes.

Effect of Ionic Strength on % Adsorption of Congo red Dye

Figure 49 shows that with *L.cylindrica,* % adsorption decreases very minimally with increase in KCl concentration for the 60 minutes contact time. In fact, the % decrease was from about 92% (0 M KCl) to about 74% (4.0 X10^{-3} M KCl).

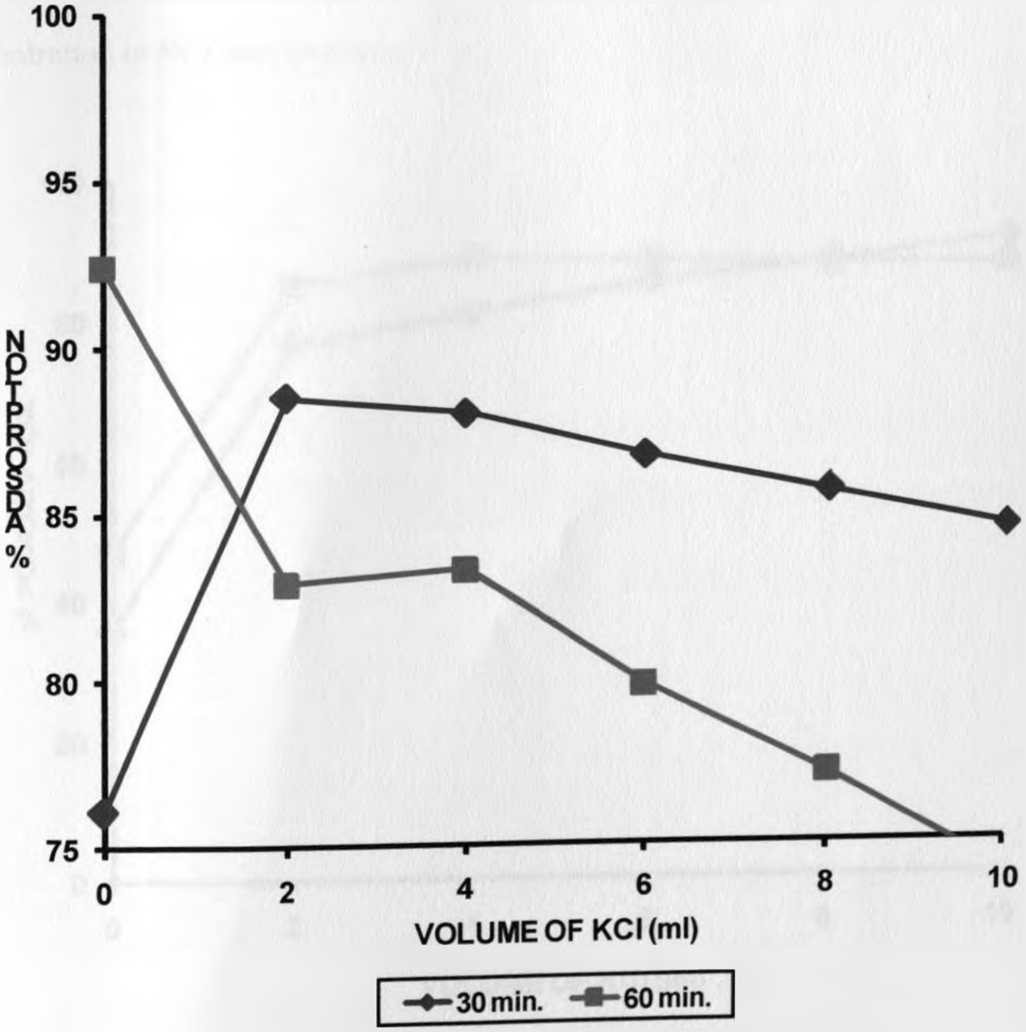


Figure 49: Plot of % adsorption of Congo red dye by *L.cylindrica* versus volume of KCl

For 30 minutes contact time, there was an initial increase in % adsorption which subsequently decreased as the ionic strength was further increased. From this, it can be concluded that Ionic strength does not seem to influence % adsorption of Congo red by *L.cylindrica.*

In contrast, as per Figure 50, *T.pedata* exhibited an increase in % adsorption as the concentration of KCl was increased.

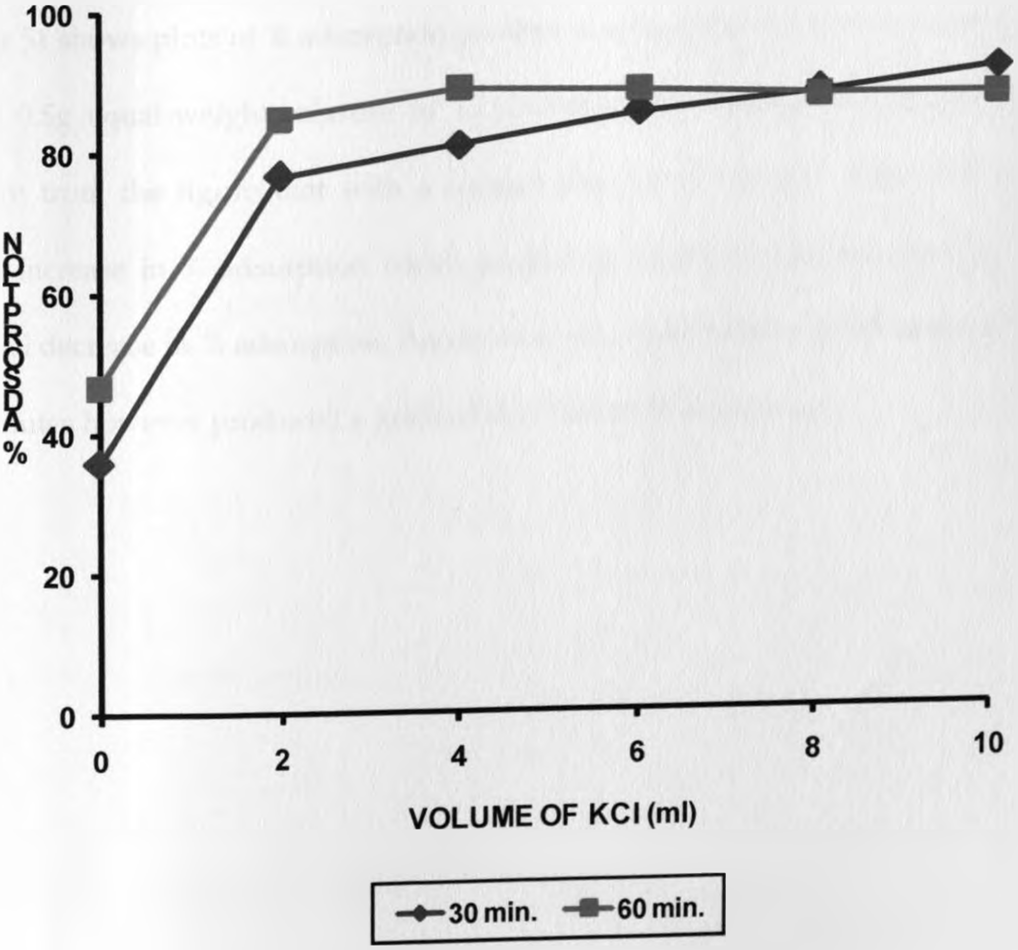


Figure 50: Plot of % adsorption of Congo red dye by *T.pedata* versus volume of KCl

The assumption made was that the overall charge of the molecules on *T.pedata* surface (i.e. the adsorbent) "reversed" in orientation upon addition of the salt. The orientation theory (Ware, 1936) accounts for a possible change in charge when the conditions are varied as, for instance, the addition of a salt. A positively charged surface can become negatively charged on account of the rotation to a certain degree of the adsorbed molecules, in essence, the reversal of oriented molecules by a change in conditions.

Figure 51 shows plots of % adsorption profiles as a function of KCl concentration when 0.5g equal-weight mixture of *L.cylindrica* and *T.pedata* was used. It is evident from the figure that with a contact time of 30 minutes, there was an initial increase in % adsorption which peaked at $9.5x10^{-4}$M KCl followed by a gradual decrease in % adsorption. An increase in contact time from 30 minutes to 60 minutes however produced a gradual decrease in % adsorption.

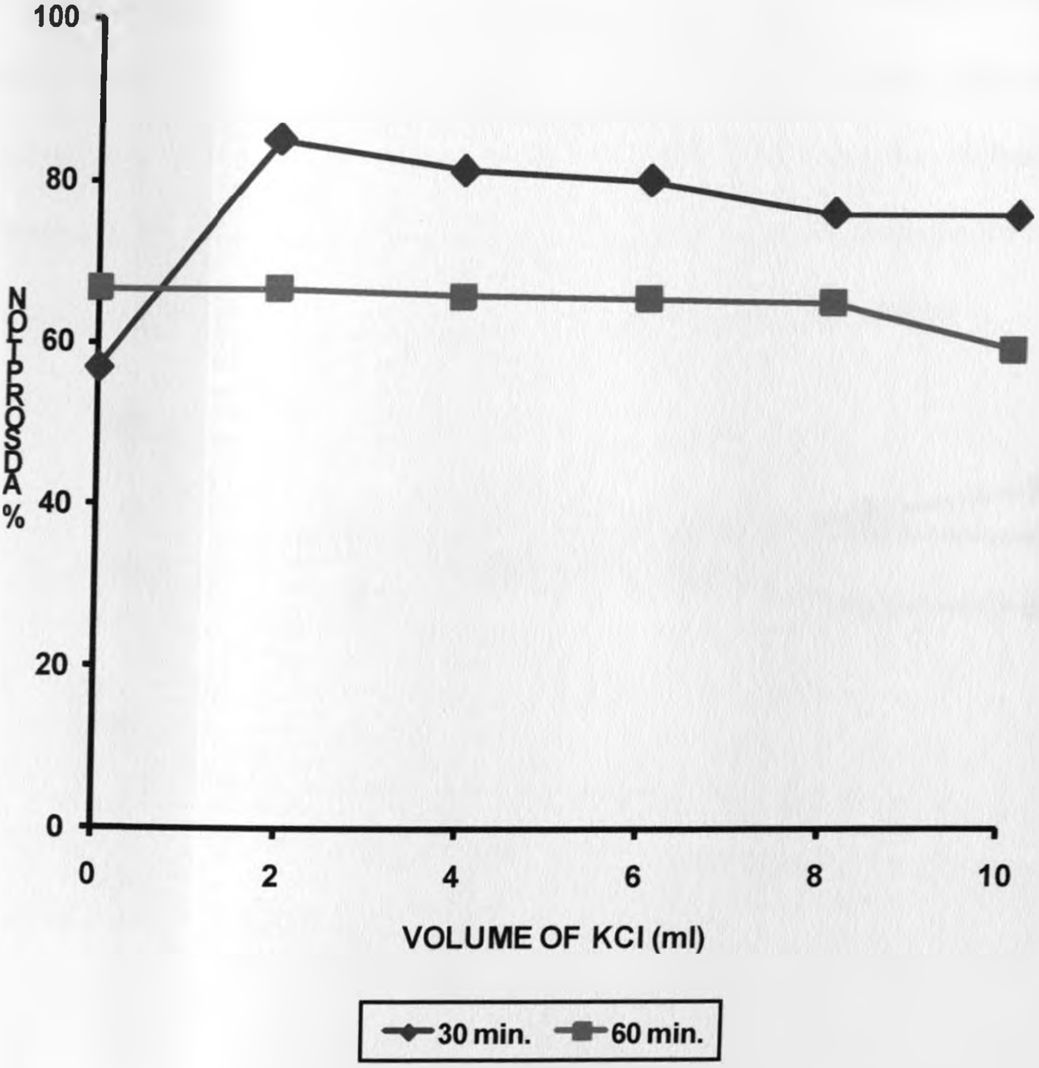


Figure 51: Plot of % adsorption of Congo red dye by the equal-weight mixture of *L.cylindrica* and *T.pedata* versus volume of KCl

Superimposed plots for *L.cylindrica, T.pedata,* and their equal-weight mixture as shown in Figure 52, clearly shows influence of KCl concentration on % adsorption when the three adsorbent types are employed. Generally, when the solution was free of any salt, the adsorbents had the highest % adsorption in the order *L.cylindrica,* the equal-weight mixture and *T.pedata.* At the maximum concentration of KCl in the dye solution, *T.pedata* recorded the highest % adsorption. The % adsorption decreased with increase in ionic strength for both *L.cylindrica* and the equal-weight mixture while it increased for *T.pedata.*

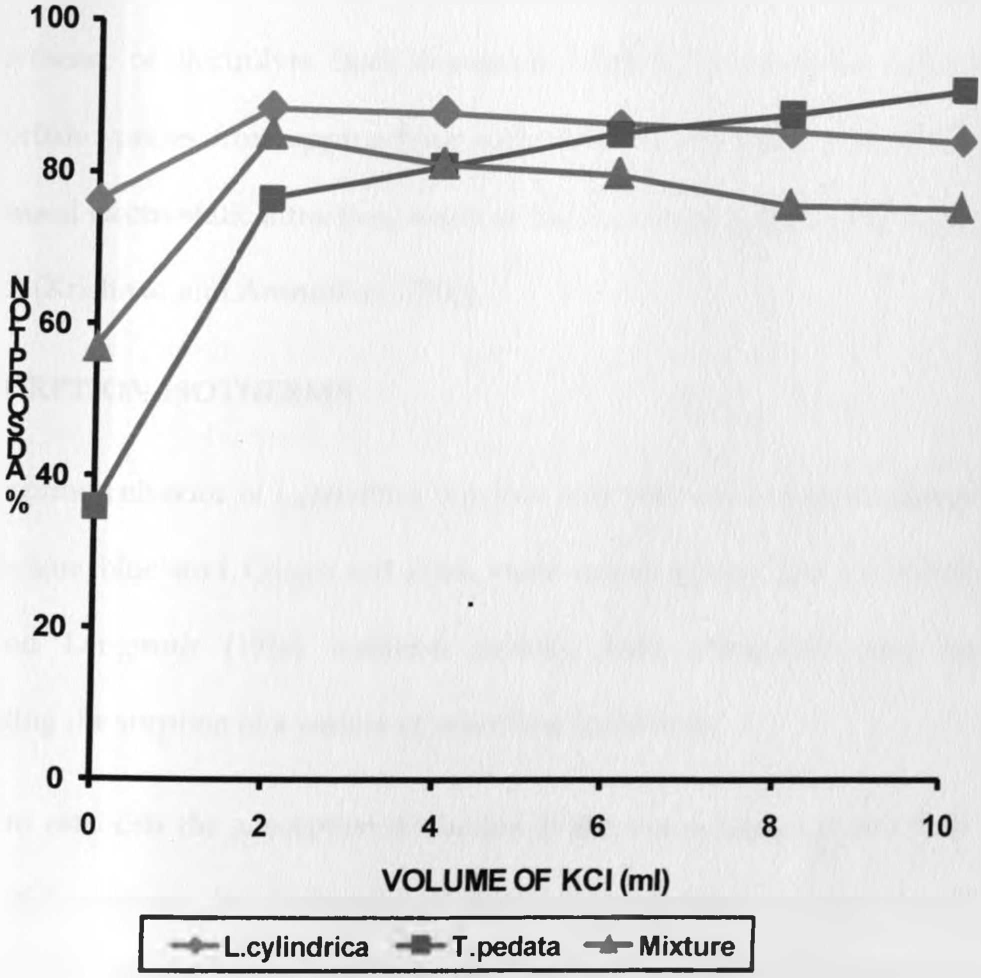


Figure 52: Superimposed plot of % adsorption of Congo red dye by *L.cylindrica, T.pedata* and their equal-weight mixture versus volume of KCl for a contact time of 30 minutes.

At highest ionic strengths, the increased amount of KCl can help to swamp the surface of the adsorbent, which decreases the respective dyes' access to the adsorbents' surface for adsorption. According to the Surface Chemistry Theory developed by Guoy and Chapman- Osipow, 1972-, when solid adsorbent is in contact with sorbate species in solution, they are bound to be surrounded by an electrical diffused double layer, the thickness of which is significantly expanded by the presence of electrolyte. Such expansion inhibits the adsorbent particles and adsorbate species from approaching each other more closely and, through the decreased electrostatic attraction, leads to the decreased uptake of adsorbate molecules (Krishnan and Anirudhan, 2003).

4.2 ADSORPTION ISOTHERMS

The adsorption behavior of *L.cylindrica, T.pedata* and their equal-weight mixture for Methylene blue and Congo red dyes were tested against the Freundlich (1906) and Langmuir (1916) isotherm models, both commonly used for investigating the sorption of a variety of adsorbate molecules.

In order to establish the adsorption isotherms of the two adsorbents and their equal-weight mixture, the influence of initial concentration of dye on % adsorption was studied. The results have been previously presented in *Figure 16* and *Figure 20* for Methylene blue and Congo red dyes, respectively. The results showed that with the increase of the initial concentration of dye, more adsorption sites of the adsorbent get occupied. Therefore, the adsorption of more adsorbate becomes increasingly difficult leading to a decrease in % adsorption.

This confirms that the saturation of the adsorption sites of the adsorbent is dependent on the initial adsorbate concentration, hence proof that the ratio of the adsorbent weight to the initial adsorbate concentration plays a significant role in influencing the adsorption process.

Sorption equilibrium is established when the concentration of the solute in the bulk solution (C_e) is in dynamic balance with that of the interface (q_e). There are several forms of presenting isotherms, each one supplying important information on the adsorption mechanism. The linear adsorption isotherm passes through the origin and the amount of solute adsorbed is proportional to the concentration of the solute in the fluid (Petruzzelli et.al., 1985). The amount of adsorbate adsorbed at equilibrium (q_e) per g of the adsorbent is calculated using the equation:

$$q_e = \frac{V(C_o - C_e)}{M_s}$$

where, C_o (mol/L) is the initial concentration, C_e (mol/L) is the final or equilibrium concentration, V (Litres) is the volume of the solution in the flask and M_s (g) is the mass of the adsorbent.

Figure 53 shows a plot of adsorption capacity, defined as the maximum amount of adsorbate sorbed by 1.0 g of adsorbent, versus equilibrium concentration of Methylene blue dye for its adsorption onto the adsorbate (s) under study.

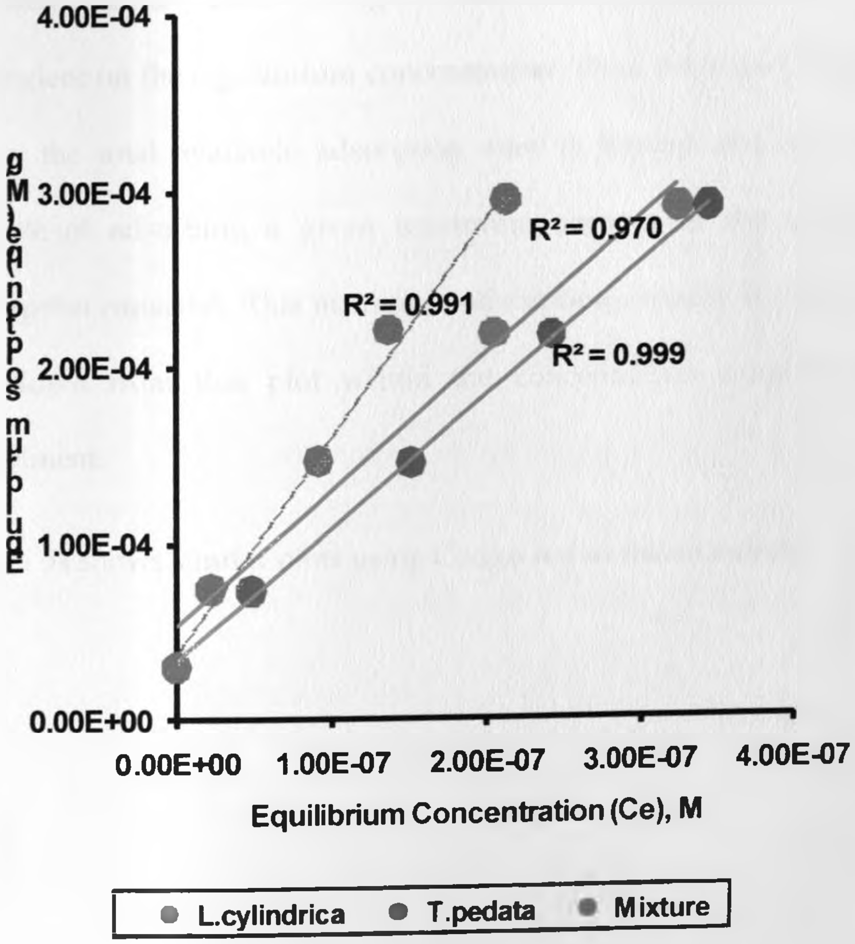


Figure 53: Plot of sorption equilibrium (q_e) versus equilibrium concentration (C_e) for the adsorption of Methylene blue onto the adsorbents.

From Figure 53, it is evident that an increase in the equilibrium dye concentration causes an increase in the amount of dye ions uptake per unit mass of the adsorbent (mol/Litre/g). This is because, at higher initial concentrations of the adsorbate, the ratio of initial number of moles of this adsorbate to the available surface area is high; hence the fractional adsorption becomes dependent on the equilibrium concentration. Thus, for a fixed adsorbent dose of 1.0 g, the total available adsorption sites is limited and fixed, thereby only capable of adsorbing a given maximum amount of the sorbate (maximum adsorption capacity). This maximum adsorption capacity is yet to be reached as is evident from this plot within the concentration ranges studied in this experiment.

Figure 54 shows similar plots using Congo red as the adsorbate.

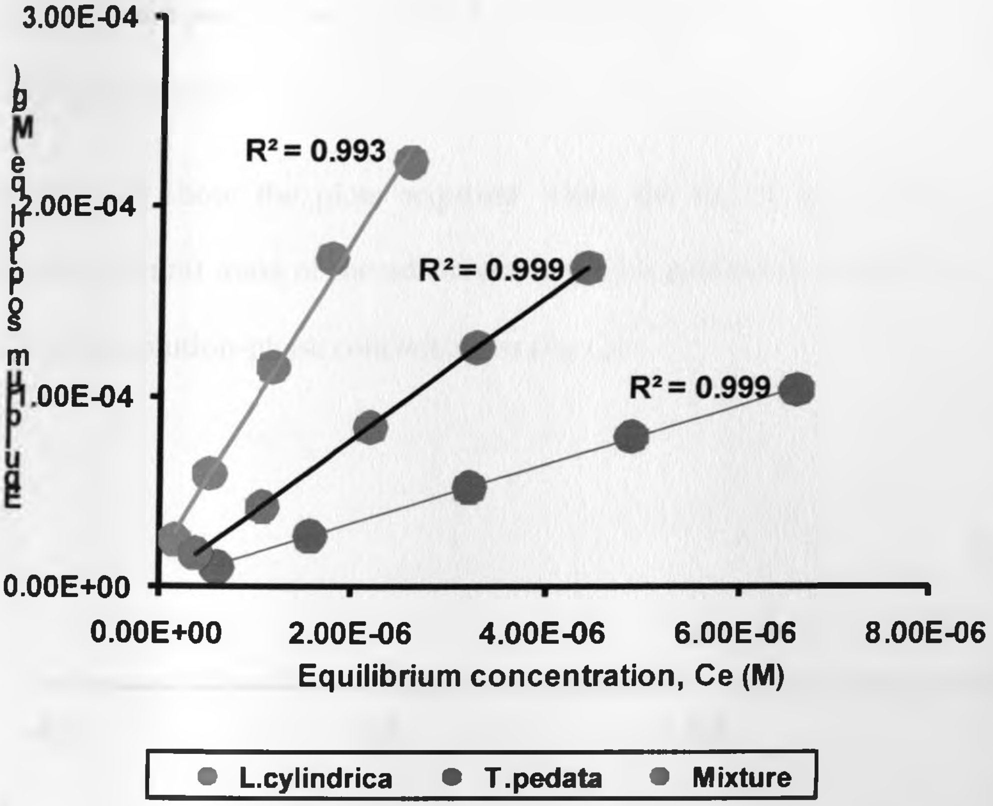


Figure 54: Plot of sorption equilibrium (q_e) versus equilibrium concentration (C_e) for the adsorption of Congo red onto the adsorbents.

4.2.1 THE FREUNDLICH PARAMETERS OF ADSORPTION ISOTHERMS

The Freundlich Isotherm model assumes neither homogeneous site energies nor limited levels of sorption and can result to several Langmuir-type (*see section 4.2.2*) sorption phenomena occurring at different sites of complex sorbents. It is an empirical model and is expressed by the logarithmic *equation 2.8* of page 35 in this thesis. The Freundlich constants were estimated by linear regression analysis from the experimental data obtained at room temperature for Methylene blue and Congo red dyes.

Figures 63-65 show the plots acquired when the log of the amount of dye adsorbed per unit mass of the adsorbent (*log q_e*) is plotted against the log of the equilibrium solution-phase concentration (*log C_e*).

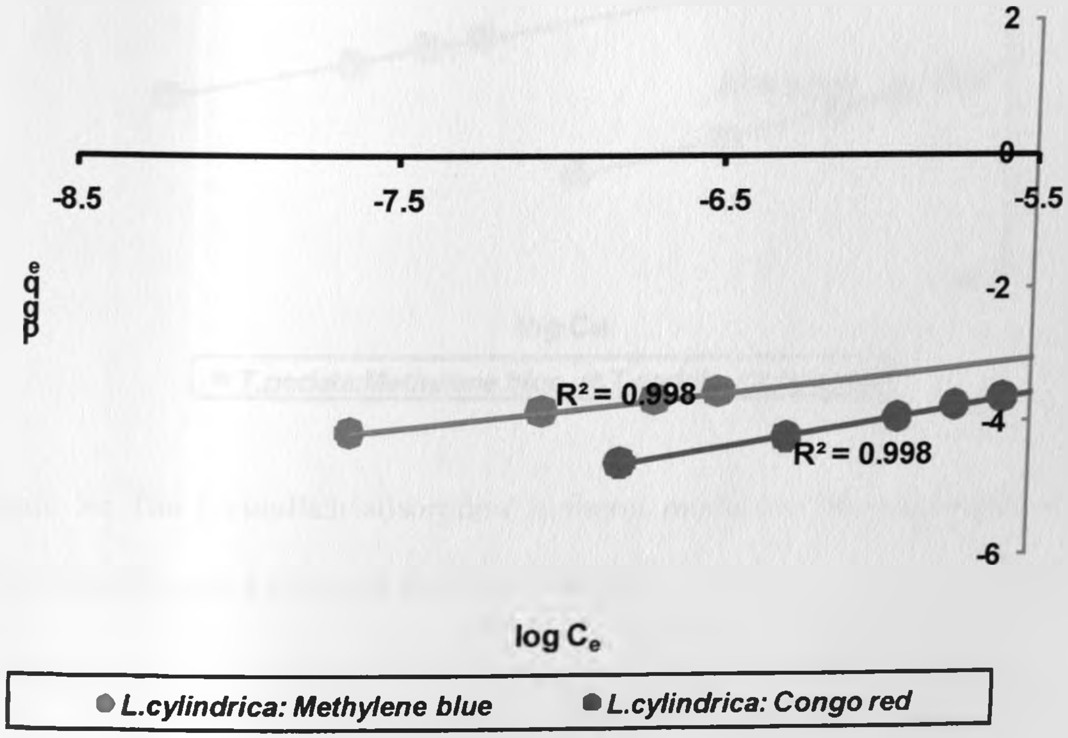


Figure 55: The Freundlich adsorption isotherm model for the adsorption of Methylene blue and Congo red dyes onto *L.cylindrica*.

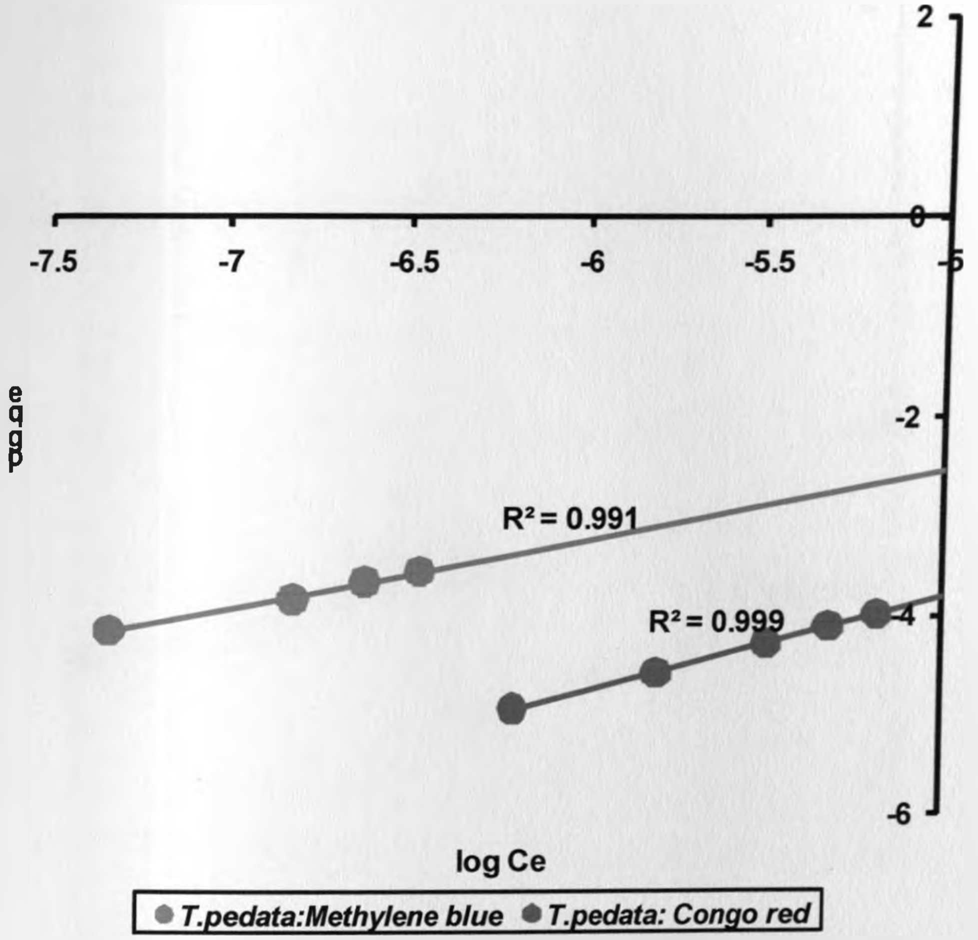


Figure 56: The Freundlich adsorption isotherm model for the adsorption of Methylene blue and Congo red dyes onto *T.pedata.*

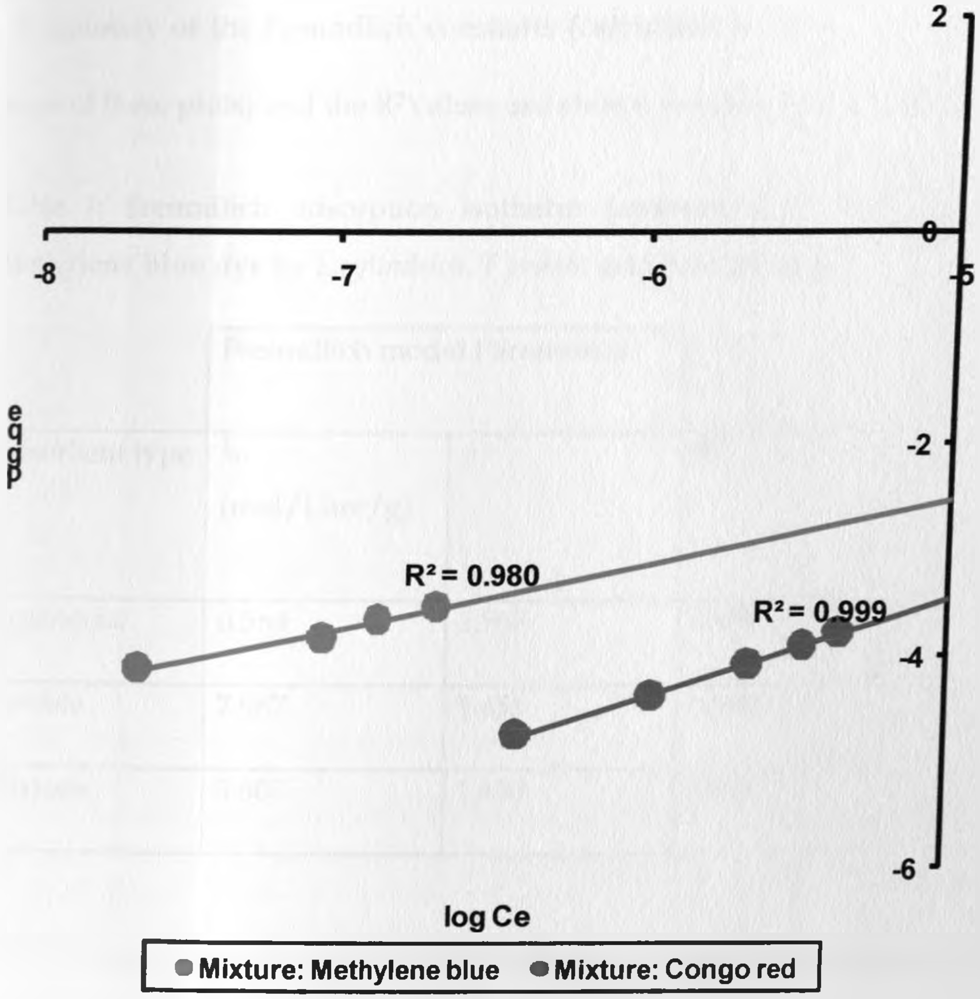


Figure 57: The Freundlich adsorption isotherm model for the adsorption of Methylene blue and Congo red dyes onto *the equal-weight mixture of L.cylindrica* and *T.pedata.*

A summary of the Freundlich constants (calculated from the intercept and the slope of these plots) and the R^2 values are shown in tables 1 and 2 below.

Table 1: Freundlich adsorption isotherm parameters for the adsorption of **Methylene blue dye** by *L.cylindrica*, *T.pedata* and their mixture.

	Freundlich model Parameters		
Adsorbent type	k_f (mol/Litre/g)	n	R^2
L.cylindrica	0.564	1.968	0.999
T.pedata	7.987	1.451	0.992
Mixture	3.507	1.630	0.981

Table 2: Freundlich adsorption isotherm parameters for the adsorption of **Congo red dye** by *L.cylindrica*, *T.pedata* and their mixture.

	Freundlich model Parameters		
Adsorbent type	k_f (mol/Litre/g)	n	R^2
L.cylindrica	6.000	1.262	1.000
T.pedata	6.900	1.075	1.000
Mixture	14.438	1.083	1.000

The value of n obtained for the Freundlich adsorption model is an indication of favorable adsorption of both Methylene Blue and Congo red dyes onto the adsorbents. Values of n greater than 1 show favorable Freundlich adsorption (McKay *et al.*, 1982). In both instances, *L.cylindrica* has higher n values as compared to either the equal-weight mixture or *T.pedata* (Tables 1 and 2). This indicates that *L.cylindrica* has higher affinity for the dyes as compared to the other two adsorbents. The corresponding correlation index (R^2 values) obtained is also an indication of the applicability of the experimental data to the Freundlich adsorption isotherm model.

From Tables 1 and 2, it is evident that k_f values vary. The higher the k_f value the greater the affinity of the adsorbent for the adsorbate. The equal-weight mixture has the highest k_f value of 14.438 when the adsorbate is Congo red dye followed by *T.pedata* (6.900) then *L.cylindrica* (6.000). Conversely, *T.pedata* has the highest value of 7.987 when the adsorbate used was Methylene Blue followed by the mixture and *L.cylindrica* with the values of [illegible] and [illegible] respectively. Hence depending on the type of adsorbate, the affinity of the adsorbent for the adsorbate shifts. This is attributed to the chemical structure of both the adsorbate and adsorbent; to the kinetics of the solution while interacting with the adsorbents and equilibrium sorption dynamics of dye removal from aqueous solution by the adsorbents.

4.2.2 THE LANGMUIR PARAMETERS OF ADSORPTION ISOTHERMS

The Langmuir (1916) isotherm equation is based on the following "pseudo-monolayer" adsorption model:

$$\frac{1}{q}=\frac{1}{q_m}+\frac{1}{k_a q_m C}$$

where k_a is the Langmuir constant related to the energy of adsorption (litre/g) and q_m the amount of dye adsorbed (mol/litre/g) when saturation is attained. If the isotherm experimental data approximates the Langmuir equation, the parameters k_a and q_m can be obtained by plotting $1/q$ *vs.* $1/C$. These values were determined from the intercept and the slope, respectively, of the linear plots of $1/q$ *vs.* $1/C$ at room temperature (25 ± 0.5°C). The plots are presented in figures 58, 59 and 60 for *L.cylindrica, T.pedata* and their equal-weight mixture, respectively.

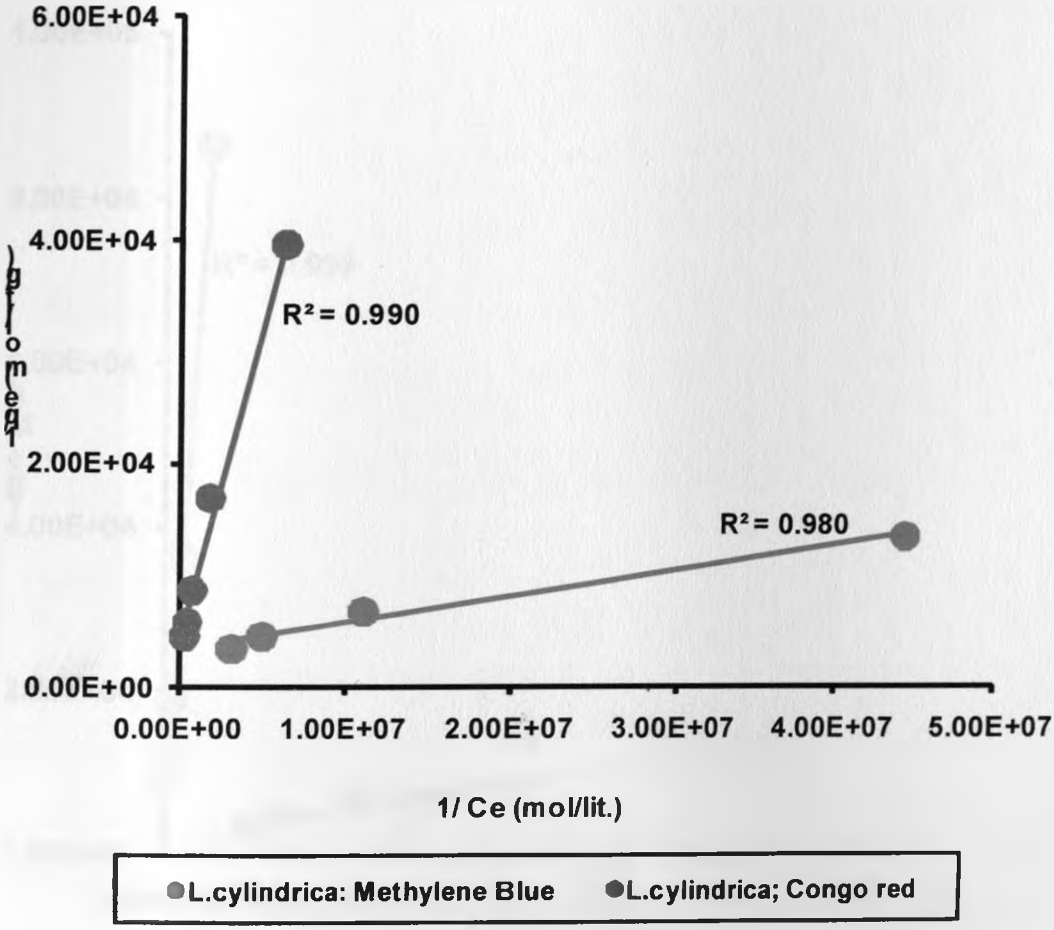


Figure 58: The Langmuir adsorption isotherm model for the adsorption of Methylene blue and Congo red dyes onto *L.cylindrica.*

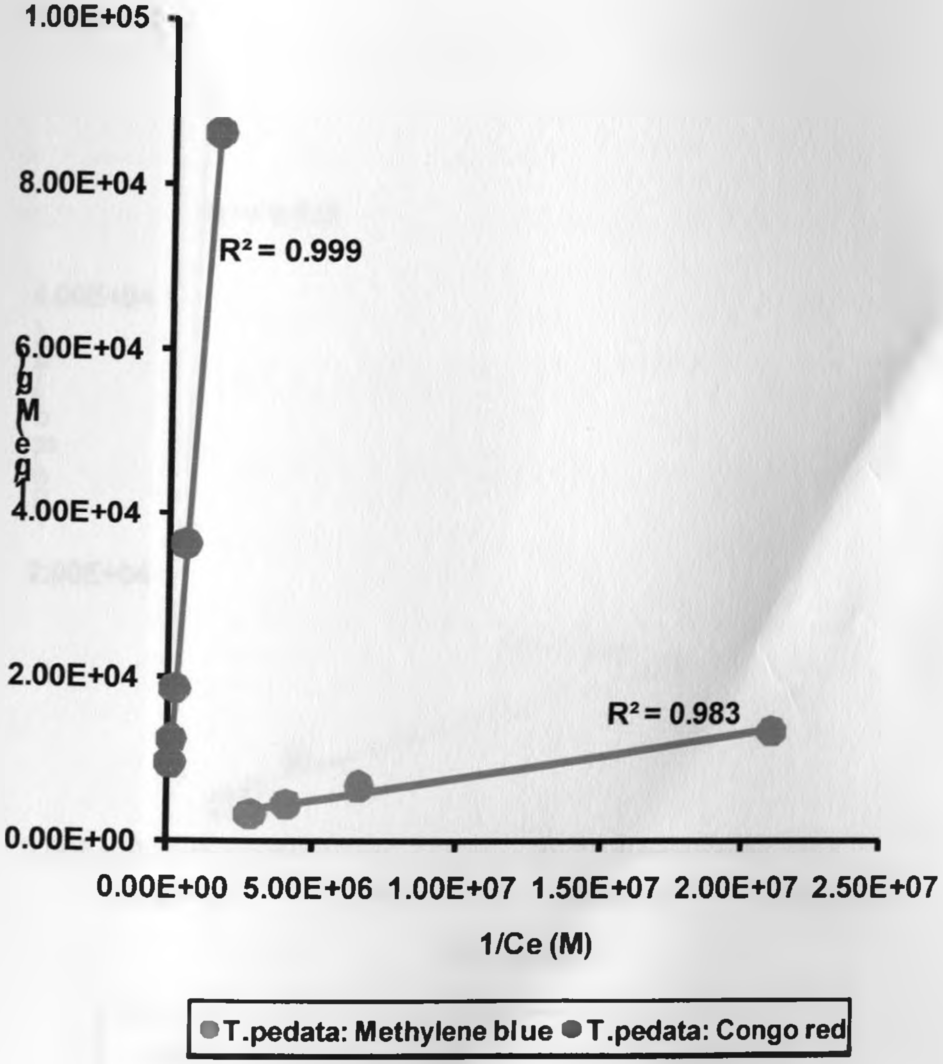


Figure 59: The Langmuir adsorption isotherm model for the adsorption of Methylene blue and Congo red dyes onto *T.pedata.*

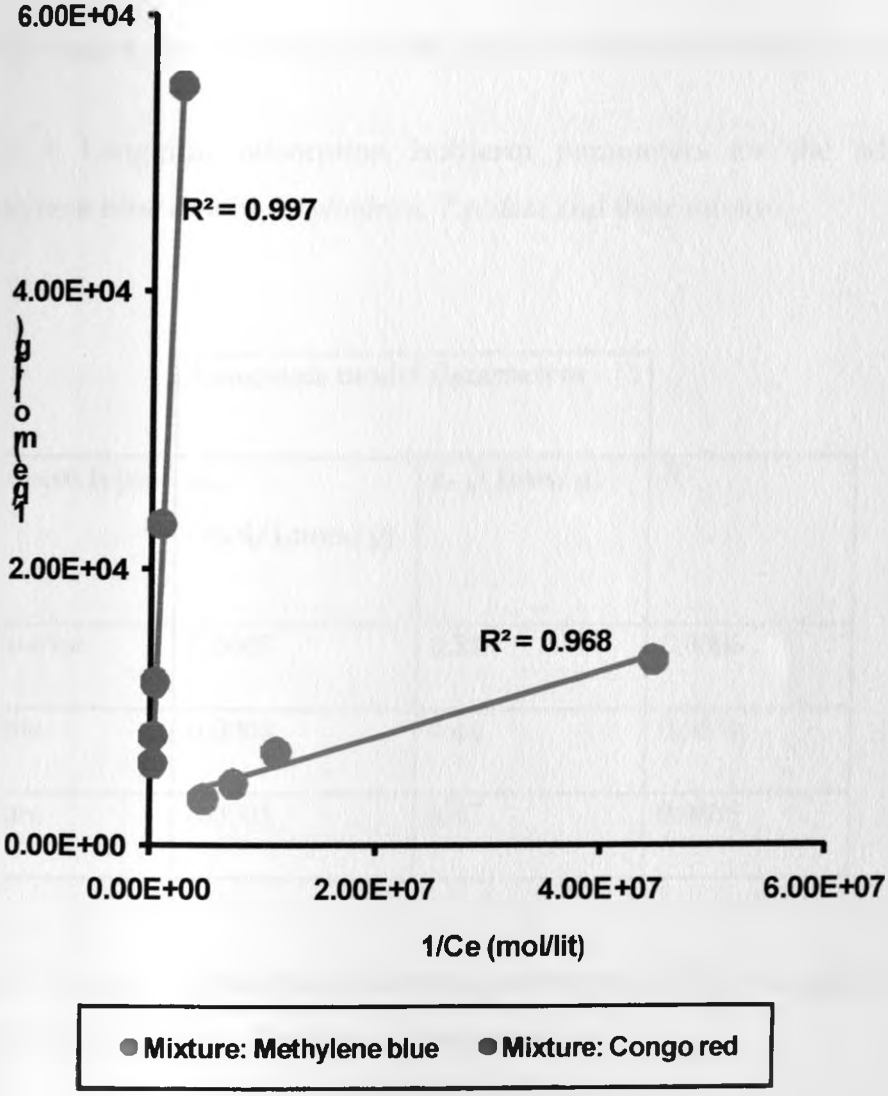


Figure 60: The Langmuir adsorption isotherm model for the adsorption of Methylene blue and Congo red dyes onto the equal-weight mixture of *L.cylindrica* and *T.pedata*.

Tables 3 and 4 give a summary of the Langmuir adsorption isotherm parameters.

Table 3: Langmuir adsorption isotherm parameters for the adsorption of **Methylene blue dye** by *L.cylindrica, T.pedata* and their mixture.

	Langmuir model Parameters		
Adsorbent types	q_m (mol/Litres/g)	k_a (Litres/g)	R^2
L.cylindrica	0.0003	0.51	0.9806
T.pedata	0.0004	0.44	0.9831
Mixture	0.0003	0.67	0.9685

Table 4: Langmuir adsorption isotherm parameters for the adsorption of **Congo red dye** by *L.cylindrica, T.pedata* and their mixture.

	Langmuir model Parameters		
Adsorbent types	q_m (mol/Litres/g)	k_a (Litres/g)	R^2
L.cylindrica	0.0003	0.034	0.9908
T.pedata	0.0004	0.007	0.9995
Mixture	5.06E-4	0.020	0.9978

The correlation index values (R^2) obtained throughout for the Langmuir adsorption isotherm model were close to unity. This indicates the applicability of the Langmuir model to describe the adsorption of both adsorbates by the adsorbents.

This suggests that the adsorption of Methylene blue dye and that of Congo red dyes could be occurring through the formation of monolayer coverage. However, the adsorption capacity obtained using the Langmuir model was lower compared to what was obtained with the Freundlich model. This signifies that the sorption process resulted from the overlapping of several Langmuir-type sorption phenomenon occurring at different sites on complex sorbents as suggested by the definition of the Freundlich model. This model, as mentioned earlier, assumes neither homogeneous site energies nor limited levels of sorption.

CHAPTER 5

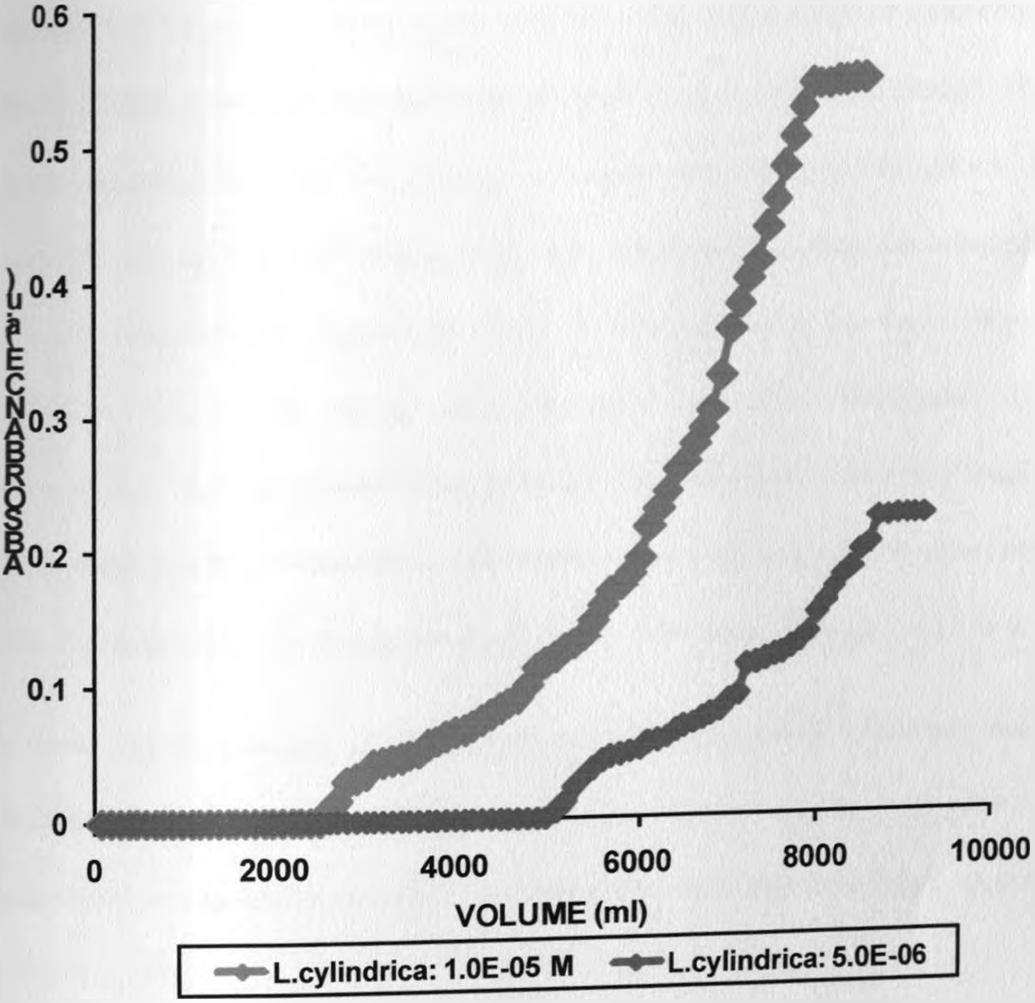
FIXED-BED STUDIES

5.1 Effect of Influent Concentration of Methylene blue Dye on Breakthrough Point

In order to determine the efficacy of *L.cylindrica, T.pedata* and their equal-weight mixture in adsorbing Methylene blue dye in a column, the effect of the initial concentration of the dye was investigated.

Breakthrough point is used to establish the adsorption capacity of an adsorbent. It is the point when the first trace of color is observed in a solution collected from a column. This is ascertained by measuring the absorbance of the solution at regular time intervals.

Figure 61 represents results from a fixed-bed study conducted using *L.cylindrica* as adsorbent.



igure 61: Effect of influent dye concentration at a flow rate of 20 ml/min in a ixed-bed column containing *L.cylindrica* in removal of Methylene Blue dye

he breakthrough points for the 1x10^{-5}M and 5.0x10^{-6}M Methylene blue dye oncentrations using *L.cylindrica* was evident after about 2 hours and 4 hours, orresponding to 2400 mls and 5000 mls of dye solution, respectively. The plots how that the breakthrough time decreased with the increase of influent dye concentration. At a lower influent dye concentration, the volume of clear column effluent is higher compared to when the influent dye concentration is high. These results demonstrate that the change of concentration gradient affects the saturation rate and breakthrough point. The implication is that the adsorption process is concentration dependent. This can be explained in the fact that more adsorption sites were being covered with increased Methylene blue concentration. As the influent concentration was increased, adsorbate loading rate increases leading to saturation of the adsorbent sites much earlier (Goel et al, 2005). The faster the rate of saturation, the sooner the breakthrough point occurs.

The curve usually takes an "*S*" shape and is ideally symmetrical. However, many breakthrough curves, like the one shown by Figure 61, are not perfectly symmetrical owing to the nature of the adsorption system under study (Batzias and Sidiras, 2007).

Figure 62 illustrates the outcome when *T.pedata* was used as the adsorbent.

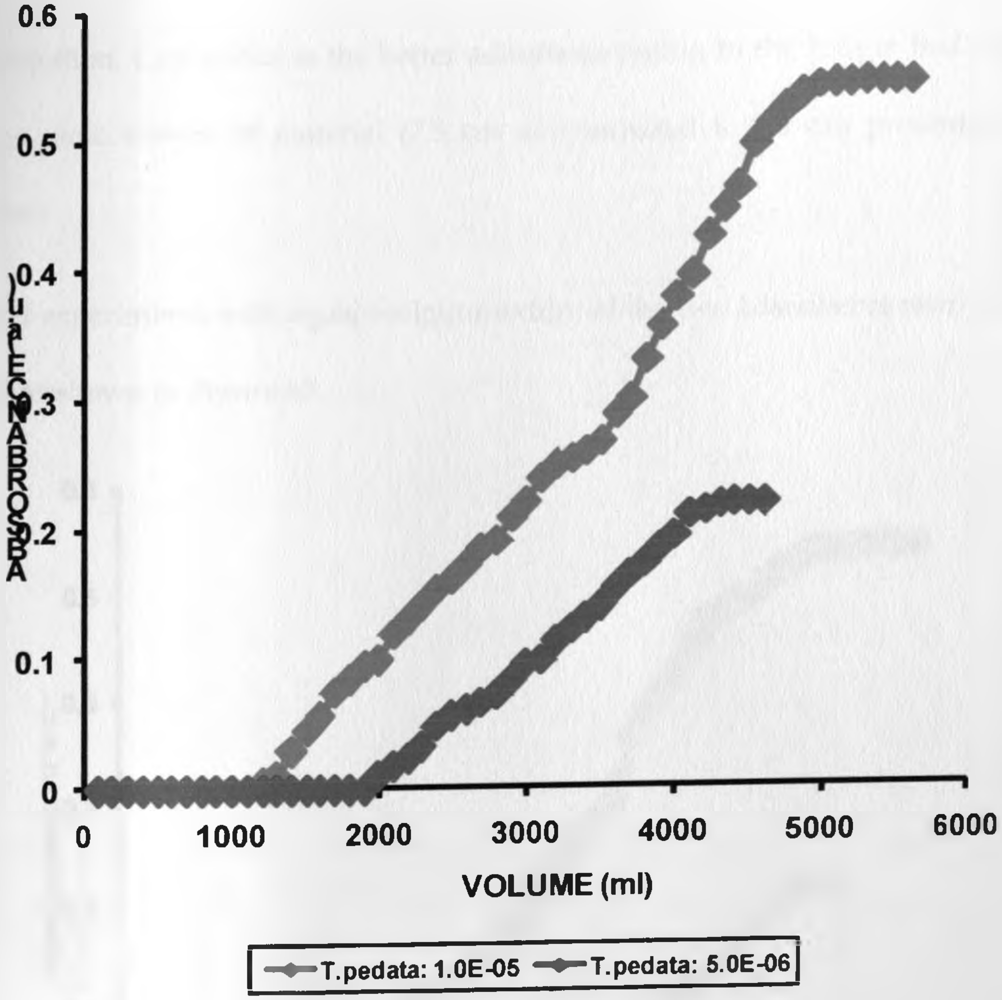


Figure 62: Effect of influent dye concentration at a flow rate of 20 ml/min in a fixed-bed column containing *T.pedata* in removal of Methylene Blue dye

The breakthrough point was observed after an hour with dye concentration of 1X10^{-5}M and after one and a half hours when the dye concentration was reduced to 5.0X10^{-6}M. For the same amount of adsorbent, *T.pedata* results in a shorter bed depth and hence provides the breakthrough point after a shorter time as compared to *L.cylindrica*. This implies that irrespective of the influent dye concentration, *L.cylindrica* is the better adsorbent owing to the longer bed depth for the same weight of material (7.5 cm as compared to 2.9 cm presented by *T.pedata*).

Further experiments with equal-weight mixture of the two adsorbents resulted in the plots shown in Figure 63.

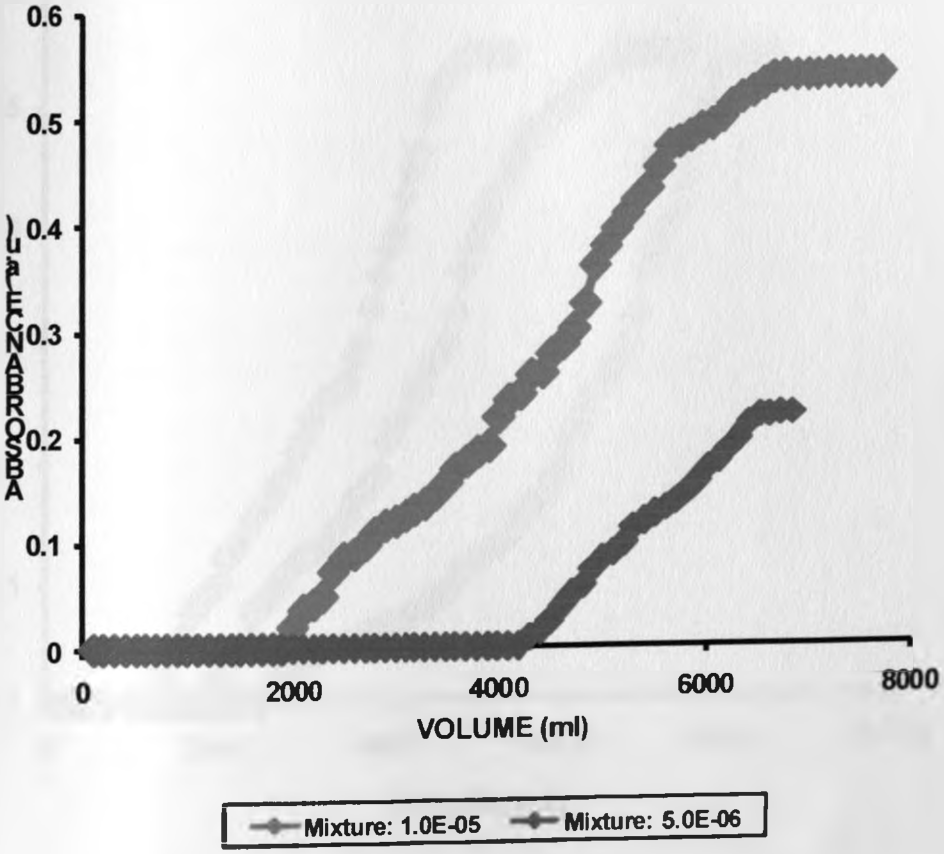


Figure 63: Effect of influent dye concentration at a flow rate of 20 ml/min in a fixed-bed column containing an equal-weight mixture of *L.cylindrica* and *T.pedata* in removal of Methylene Blue dye

The breakthrough points are at about 1900ml, after 1hour 40 minutes, and at around 4200ml after about 3 hours.

The superimposed % adsorption curves of the two adsorbents and their equal-weight mixture is shown in Figure 64.

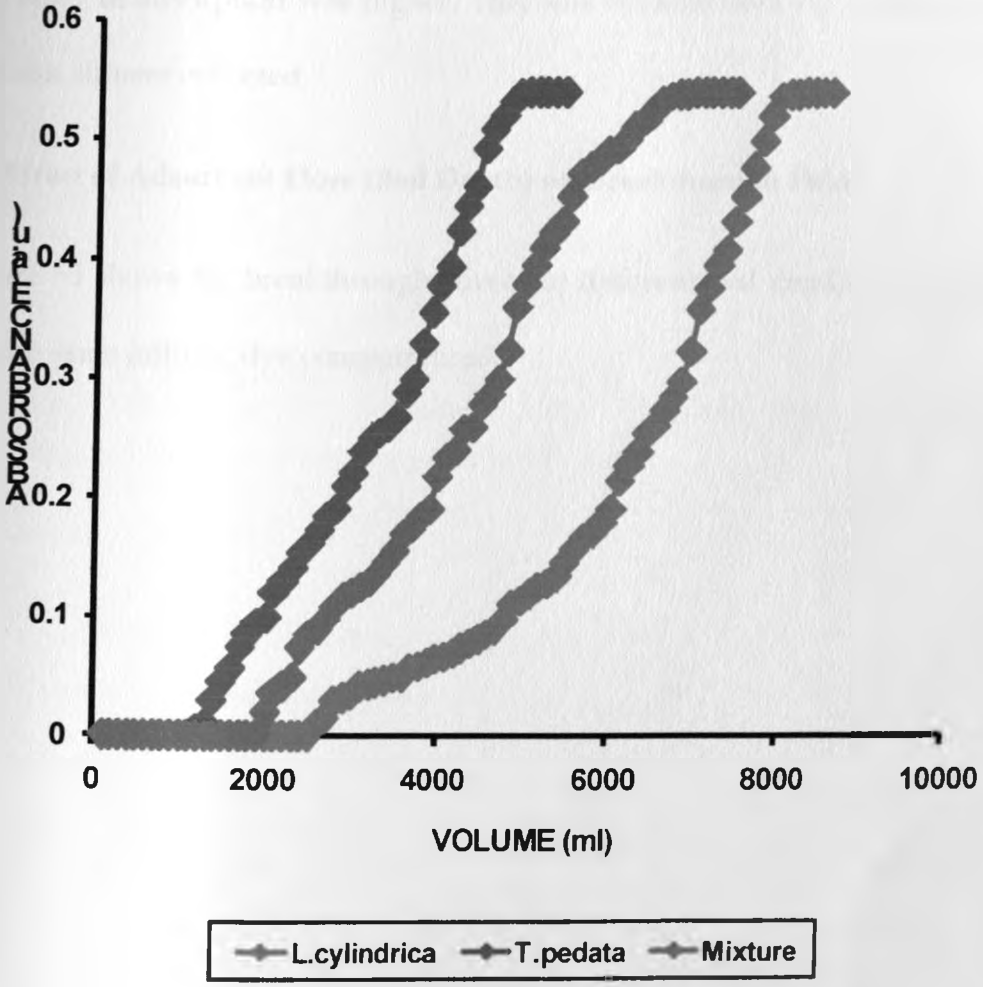


Figure 64: Effect of influent dye concentration at a flow rate of 20 ml/min in fixed-bed columns containing *L.cylindrica, T.pedata* and their equal-weight mixture separately, in removal of Methylene Blue dye

These results are from experiments with influent dye concentration of $1X10^{-5}$M. A shift of the adsorption curve from left to right indicates that more dye is removed (Han et.al, 2006). Consequently, according to the figure, *L.cylindrica* was found to remove the dye most effectively when subjected to the column technique. The adsorbent spent more time to reach saturation, and therefore the efficiency of adsorption was higher. This was evident from the volume of clear column effluent collected.

5.2 Effect of Adsorbent Dose (Bed Depth) on Breakthrough Point

Figure 65 shows the breakthrough curves at different bed depths of *L.cylindrica* for the same influent dye concentration.

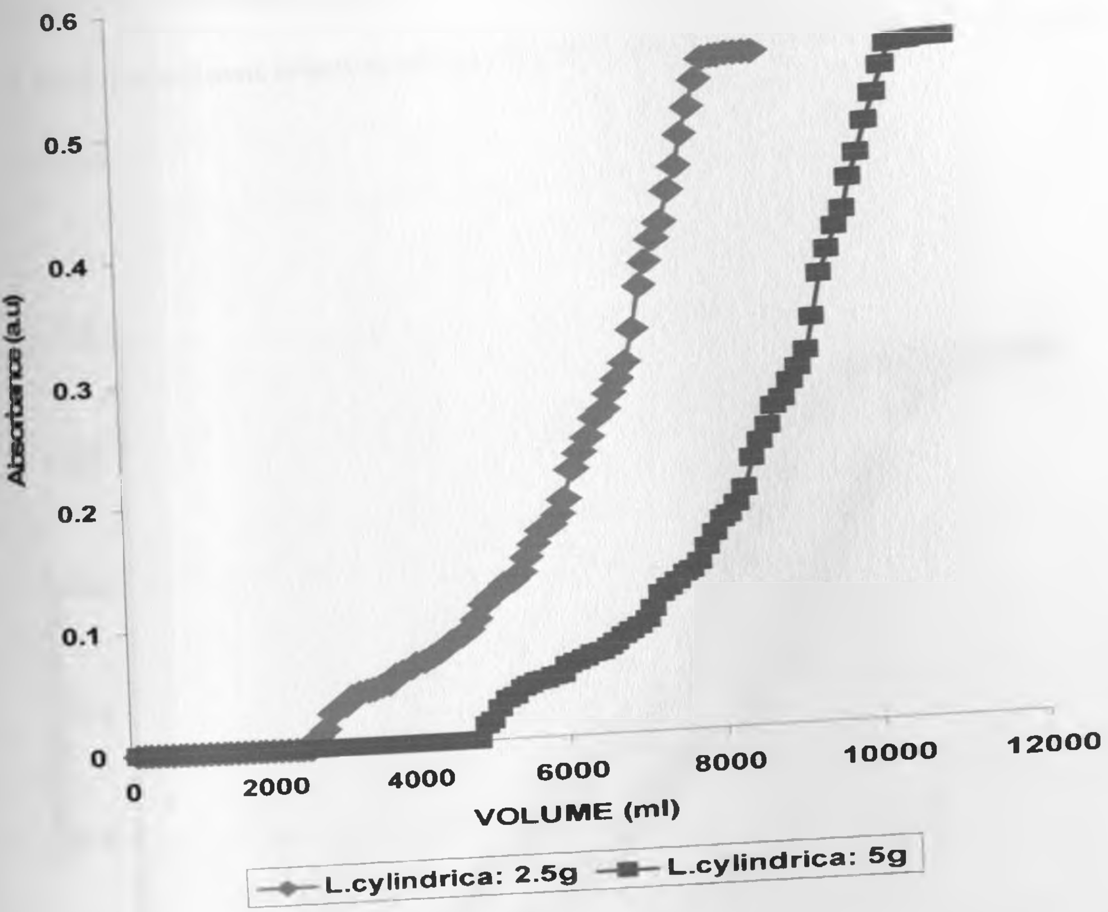


Figure 65: Effect of bed depth at a flow rate of 19 ml/min in a fixed-bed column containing *L.cylindrica* in removal of Methylene Blue dye

From Figure 65, it is evident that as the bed depth was increased from 7.5cm to about 15.0cm, a higher volume of clear solution was collected from the column. Therefore, a larger volume of dye solution was decolorised. There was longer contact time for dye adsorption in the column containing 5g of adsorbent. High uptake was observed at the longer bed depth due to an increase in surface area of bioadsorbent, which provided more binding sites for the sorption process.

From Figure 66, it can be deduced that the potential of removal of larger volumes of dye from the influent solution using *T.pedata* also increases with the increase n bed depth.

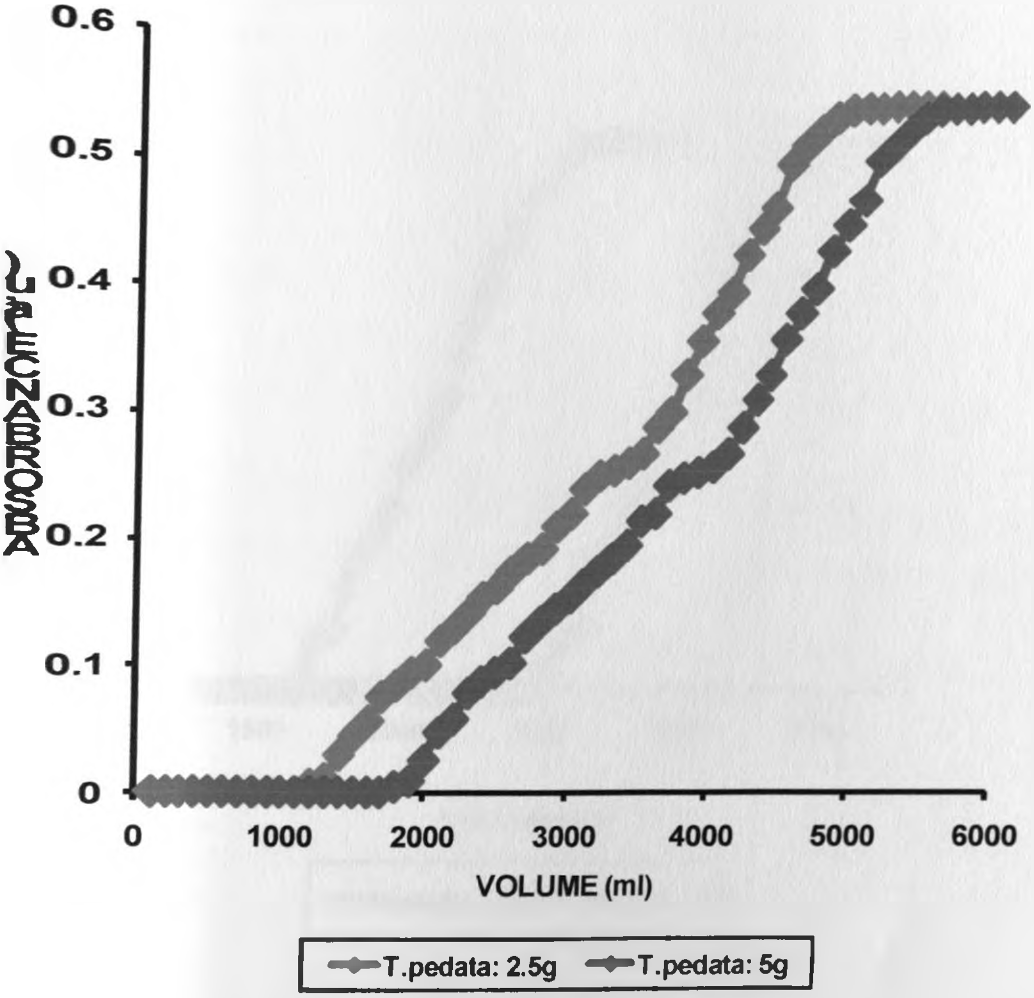


Figure 66: Effect of bed depth at a flow rate of 18 ml/min in a fixed-bed column containing *T.pedata* in removal of Methylene Blue dye

Figure 67 shows that an increase in bed depth results in a corresponding increase in the volume of clear column effluent. As discussed earlier, a higher bed depth affords more adsorbate contact time with the adsorbent.

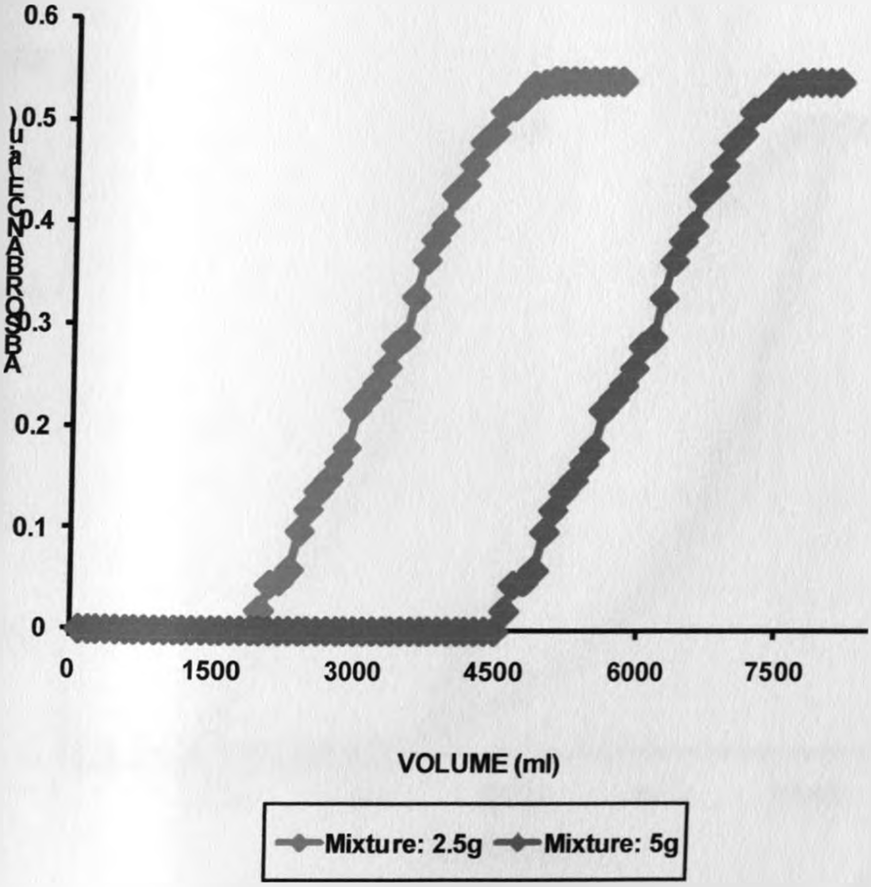


Figure 67: Effect of bed depth at a flow rate of 18 ml/min in fixed-bed columns containing equal-weight mixtures of *L.cylindrica and T.pedata* in removal of Methylene Blue dye

Figure 68 gives a comparison of the two adsorbents and their equal-weight mixture. The breakthrough point is at almost the same position for the equal-weight mixture and *L.cylindrica.* However, the mixture exhibits a smoother curve which translates to a more homogeneous flow of influent through the column.

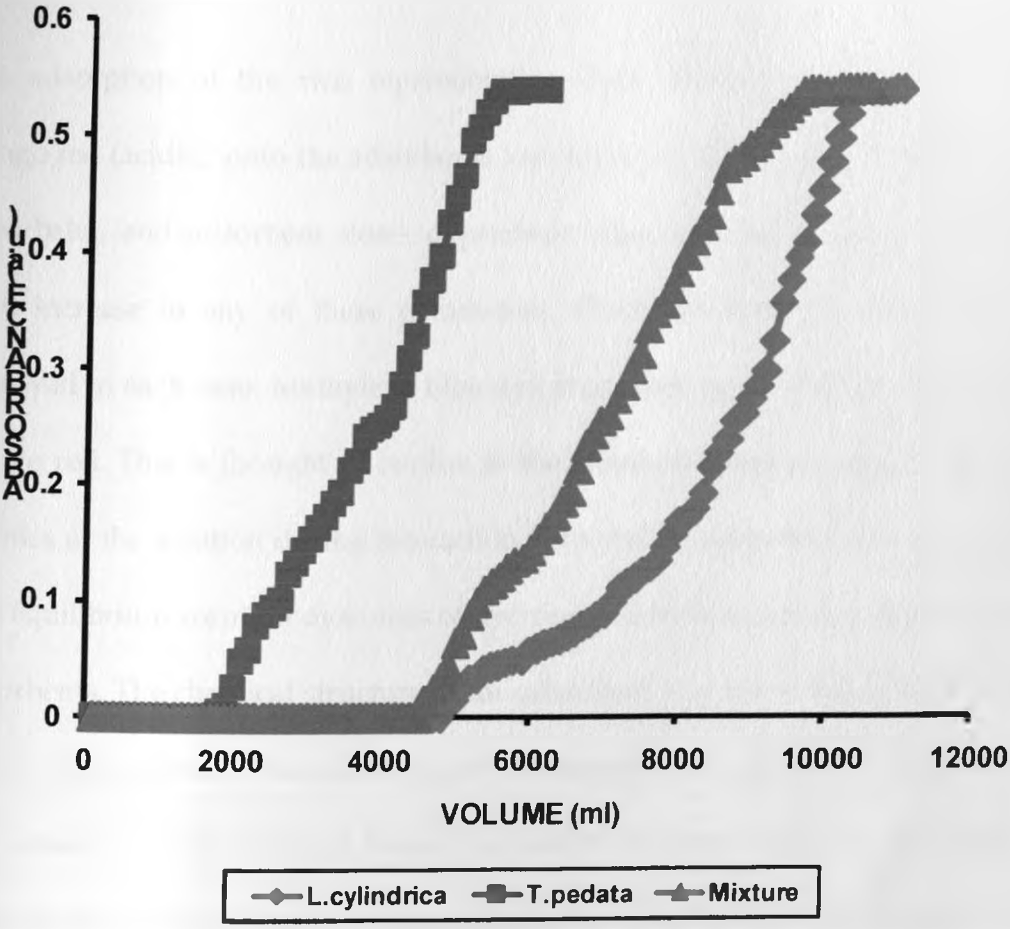


Figure 68: Effect of bed depth at a flow rate of 19 ml/min (on average) in fixed-bed columns containing *L.cylindrica, T.pedata* and their equal-weight mixture separately, in removal of Methylene Blue dye

CHAPTER 6

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

6.1 Summary and Conclusions

This study demonstrates that *L.cylindrica, T.pedata* and their mixture are indeed viable, cost effective adsorbent materials for the removal of dye from dye wastewaters.

The adsorption of the two representative dyes, Methylene blue (basic) and Congo red (acidic), onto the adsorbents was found to be time-, concentration- (of adsorbate), and adsorbent dose- dependent. The removal efficiency increased with increase in any of these parameters. Over 90% removal efficiency was observed in each case. Methylene blue dye was taken up to a larger extent than Congo red. This is thought to be due to the chemical structure of the dyes; the kinetics of the solution during interaction between the adsorbent and adsorbate; and equilibrium sorption dynamics of dye removal from aqueous solution by the adsorbents. The chemical structure of the adsorbent was also contemplated to be a contributing factor. Consequently, the interaction of the adsorbent-adsorbate at the surface of their interface largely depended on their individual chemistry. *T.pedata* was shown to have a higher affinity for Congo red dye as compared to Methylene blue dye.

Other parameters studied-such as the effect of temperature, ionic strength and pH- proved the cost effectiveness of the adsorbents. The studies on the effect of temperature indicated that the phenomenon occurs best at room temperature. The results also indicated that the process is a physical one, and hence exothermic. From an industrial point of view, this is economical owing to the fact that temperatures do not have to be adjusted upwards for maximum efficiency of the process.

Altering the ionic strength of the solution by adding a salt, KCl, resulted in the decrease in adsorption efficiency of both *L.cylindrica* and the mixture while exhibiting an opposite effect on *T.pedata* in the presence of the acidic Congo red dye. The investigation into the effect of pH showed that more alkaline conditions were favored when the adsorbate was the basic Methylene blue dye by *L.cylindrica*, while more acidic conditions were favored for *T.pedata* in the presence of the acidic Congo red dye. *L.cylindrica* and the mixture preferred neutral conditions for Congo red dye.

In all the parameters studied, it was observed that the equal weight mixture adsorbed at either higher % adsorption or mid range % adsorption compared to *L.cylindrica* and *T.pedata;* by a negligible margin. The use of the equimixture, therefore, showed that the % adsorption would remain more or less the same when either the two adsorbents were mixed or were utilized individually. Mixtures of various proportions were not tested.

Tables 1to 4 show constants related to the Freundlich and Langmuir adsorption Isotherms, respectively. The linear correlations of the k_f values and the

2. Further research should be launched to decipher the chemical structure of the adsorbates- *T.pedata* and *L.cylindrica*. This will assist in understanding the mechanism of the sorption process. This will not only shorten the time required to know which industries could use which adsorbent most suitably judging from the chemical composition of dye wastewaters produced, but it will also be an outlet to experiment the materials for other purposes, such as in nanotechnology.
3. The data should be fitted to the Lagergren (1898) model and the Arrhenius law so as to establish the rate-determining step in this particular sorption process. This will further prove that the rate of adsorption is governed by an intra-particle mass transfer. It will also indicate the nature of the order of reaction.
4. The observations made in this thesis are as a result of experiments carried out in the laboratory setting. The comprehensive study can be used to indicate results in an industrial setting. However, this presents some challenges that can be overcome, such as:
    - The design of a column with precise dimensions that will ensure a maximum loading of dyes without significant flow disturbances, channeling effects and clogging; which are prominent features of a column system. An alternative would be the use of large scale batch systems that work just as well.

- The establishment of a flow rate that would ensure economies of scale. The pump used is driven by electricity and this could present financial challenges that could result in a liability if the flow rate is not reasonable.

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Wateraid International (2005), Water Aid

World Health Organization and UNICEF, (2005),Water for Life, Making it Happen

APPENDIX 1

LIST OF ABREVIATIONS	
A^o	Angstroms
BOD	Biochemical Oxygen Demand
C	Carbon
cGMP	Cyclic Guanosine Monophosphate
COD	Chemical Oxygen Demand
DNA	Deoxyribonucleic acid
H	Hydrogen
HCl	Hydrochloric acid
KCl	Potassium chloride
LPS	Lipopolysaccharide
N	Nitrogen
NaCl	Sodium Chloride
NaOH	Sodium Hydroxide
NEMA	National Environment Management Authority
nm	Nanometres
NO	Nitric Oxide
O	Oxygen
PAE	Polyamide-epichlorohydrin
RNA	Ribonucleic acid
rpm	Rotations per minute
SiO_2	Silicon dioxide
UNICEF	United Nations International Children's Education Fund
UV/VIS	Ultra Violet/ Visible
WHO	World Health Organisation

APPENDIX 2

SUPERIMPOSED PLOTS OF THE PARAMETERS AT t= 60 MINUTES

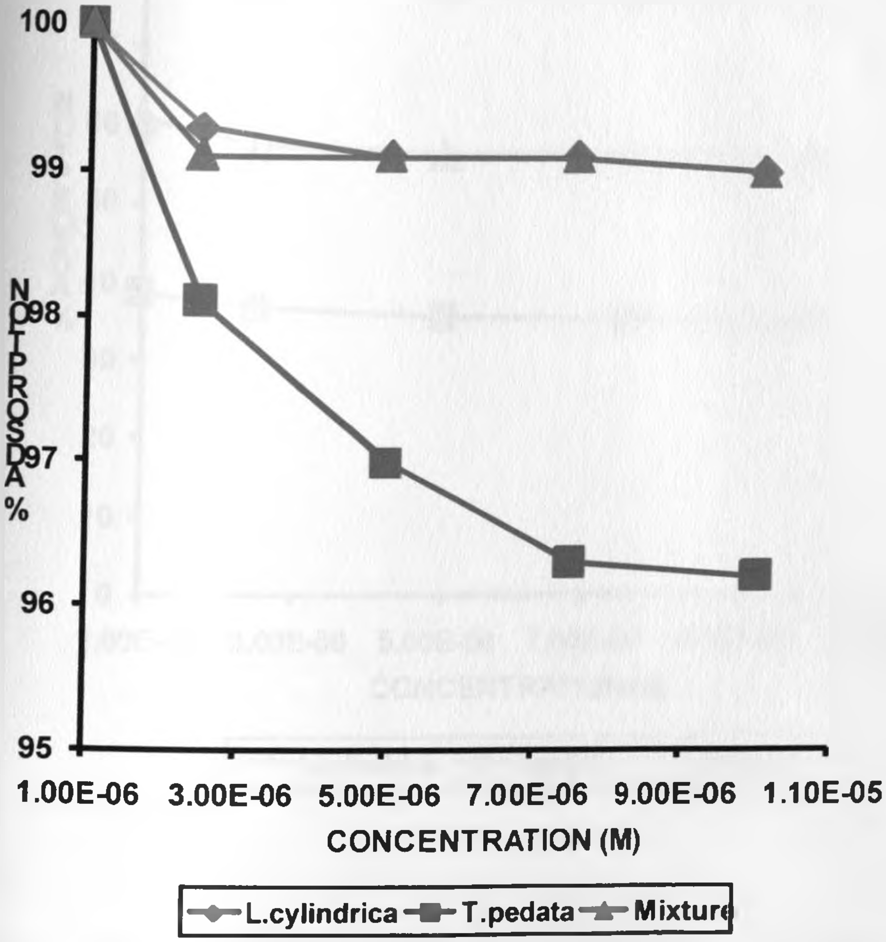

Figure 16b: Plot of % adsorption of methylene blue dye by *L.cylindrica, T.pedata* and their mixture against concentration of dye at t=60 min.

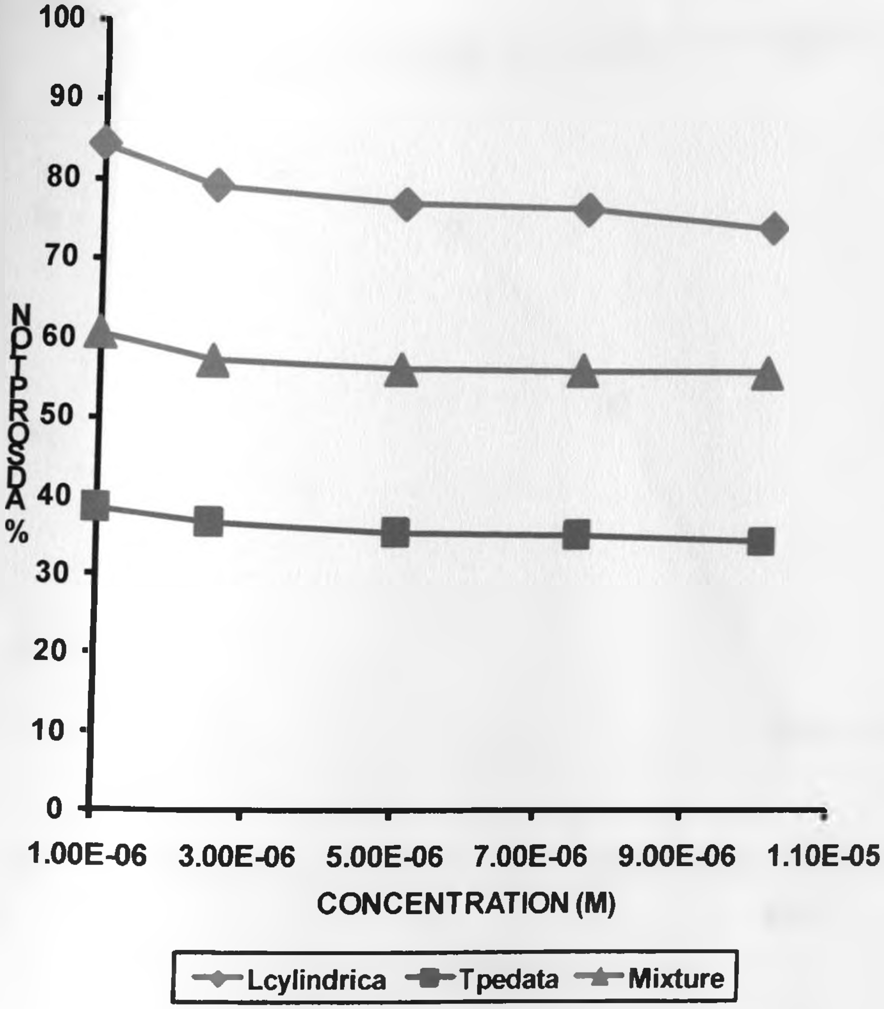

Figure 20b: Superimposed plots of % adsorption of Congo red dye by *L.cylindrica*, *T.pedata* and their mixture versus concentration of dye at t=60 min.

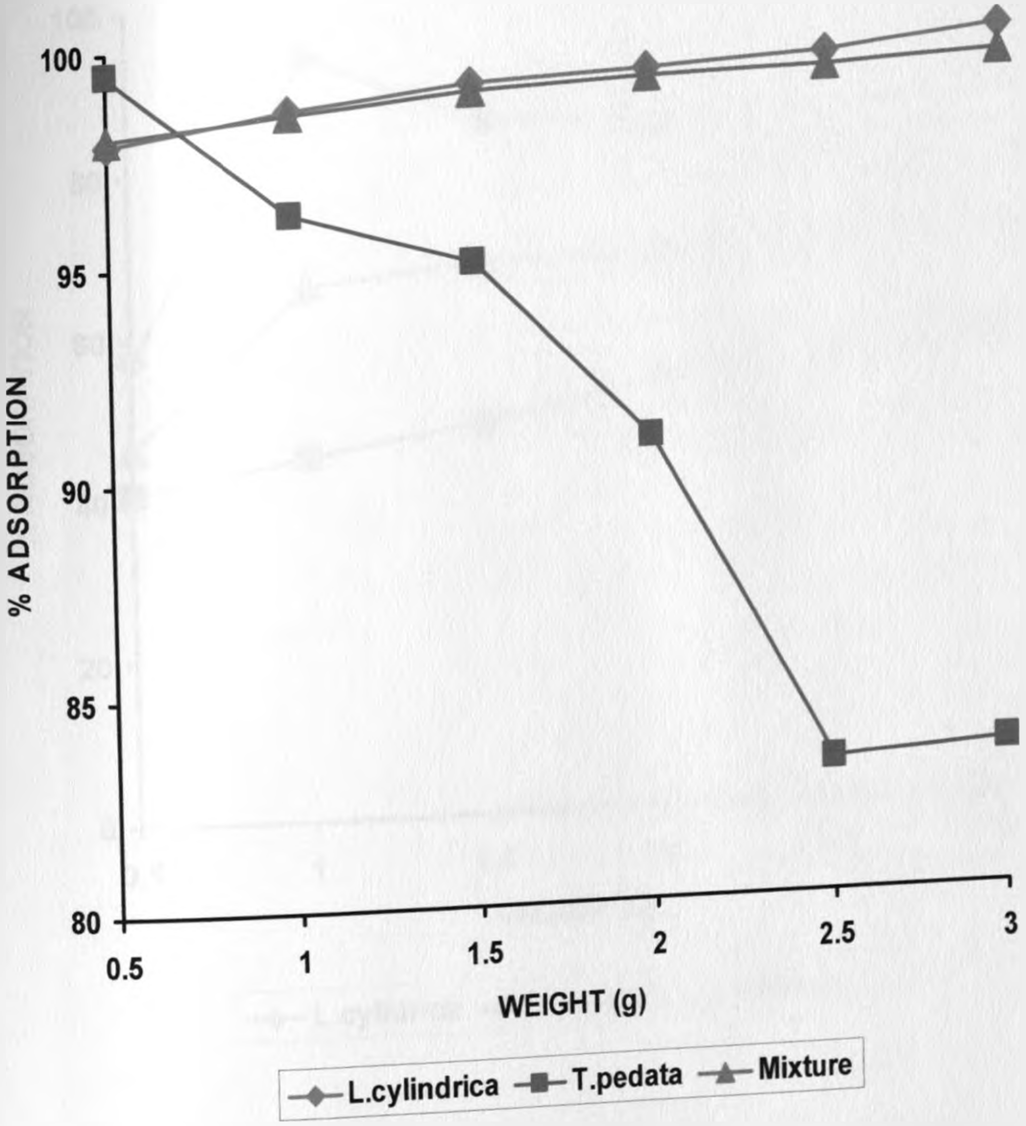

Figure 24b: Superimposed plots of % adsorption of methylene blue dye by *L.cylindrica, T.pedata* and their mixture versus weights of *L.cylindrica, T.pedata* and their mixture at t=60 min.

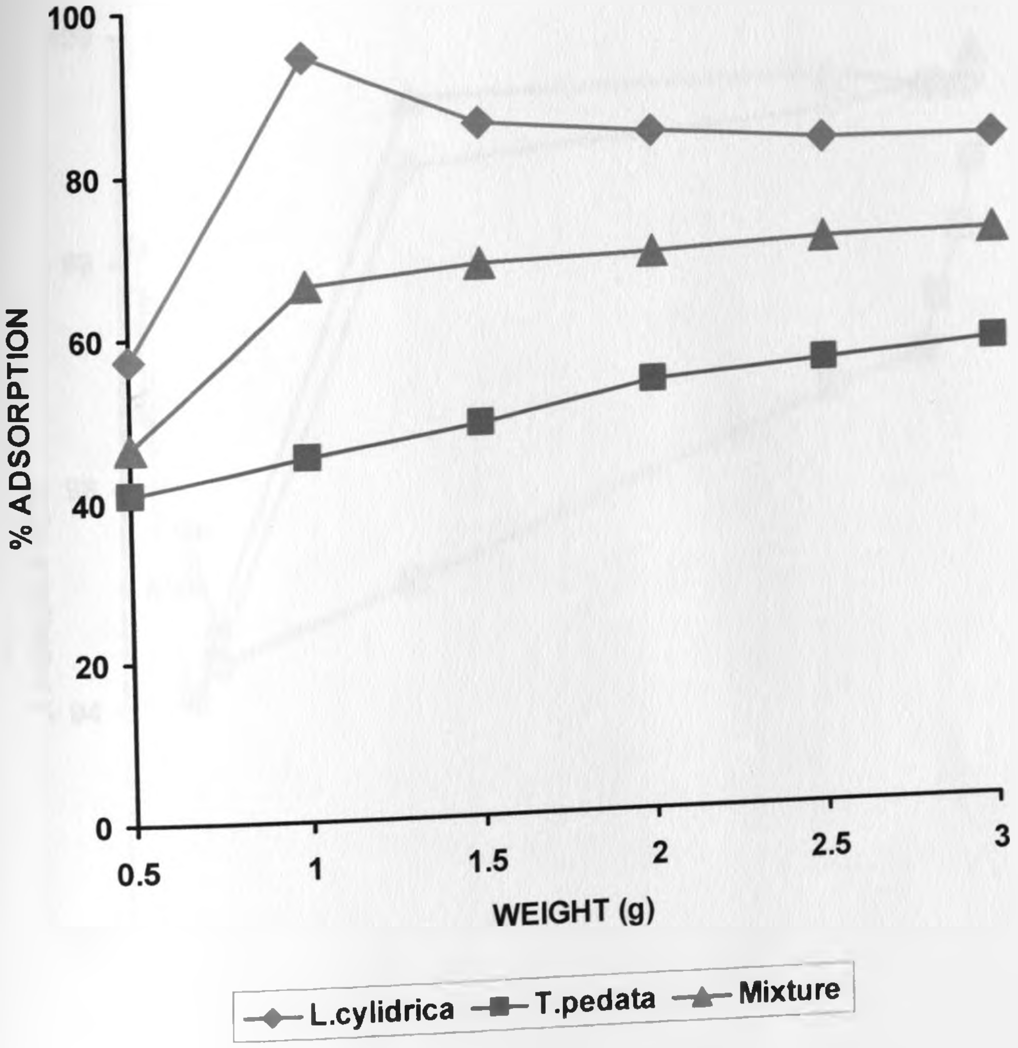

Figure 28b: Superimposed plot of % adsorption of Congo red dye by *L.cylindrica*, *T.pedata* and their mixture against weights of *L.cylindrica*, *T.pedata* and their mixture at t=60 min.

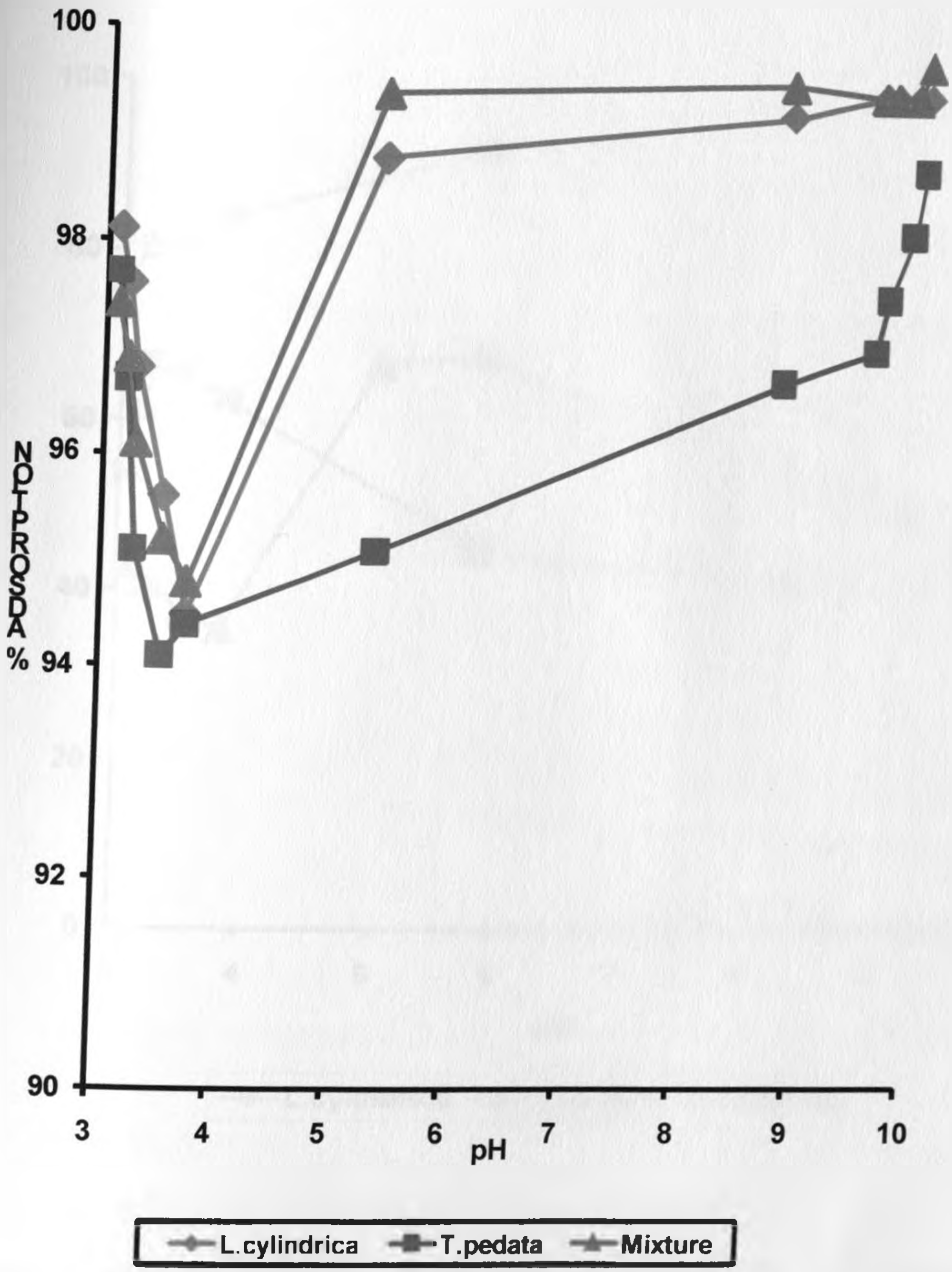

Figure 32b: Superimposed plots of % adsorption of methylene blue dye

by *L.cylindrica*, *T.pedata* and their mixture against pH of the dye at t=60 min.

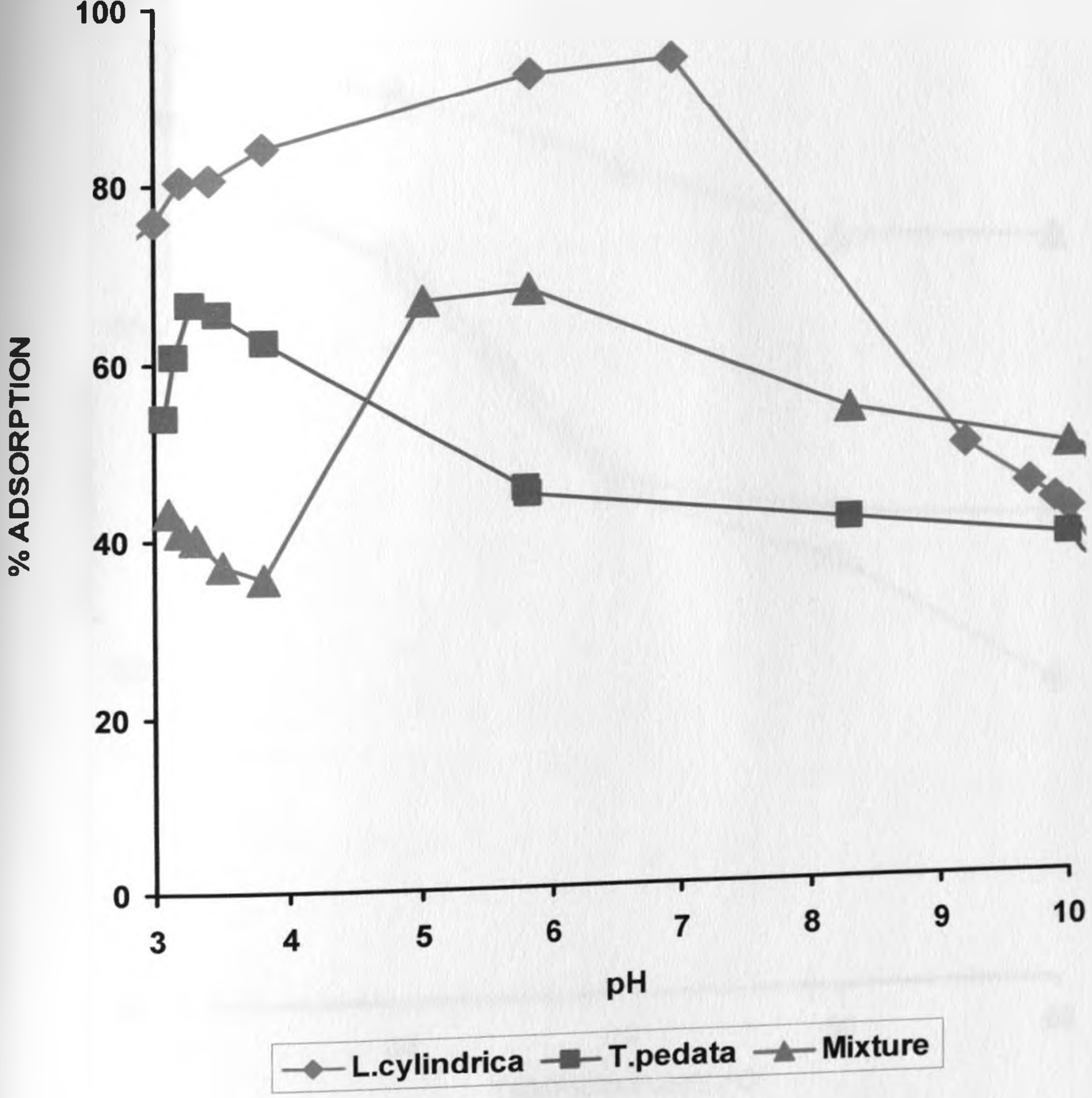

Figure 36b: Superimposed plot of % adsorption of Congo red dye by *L.cylindrica*, *T.pedata* and their mixture against pH of the dye at t=60 min.

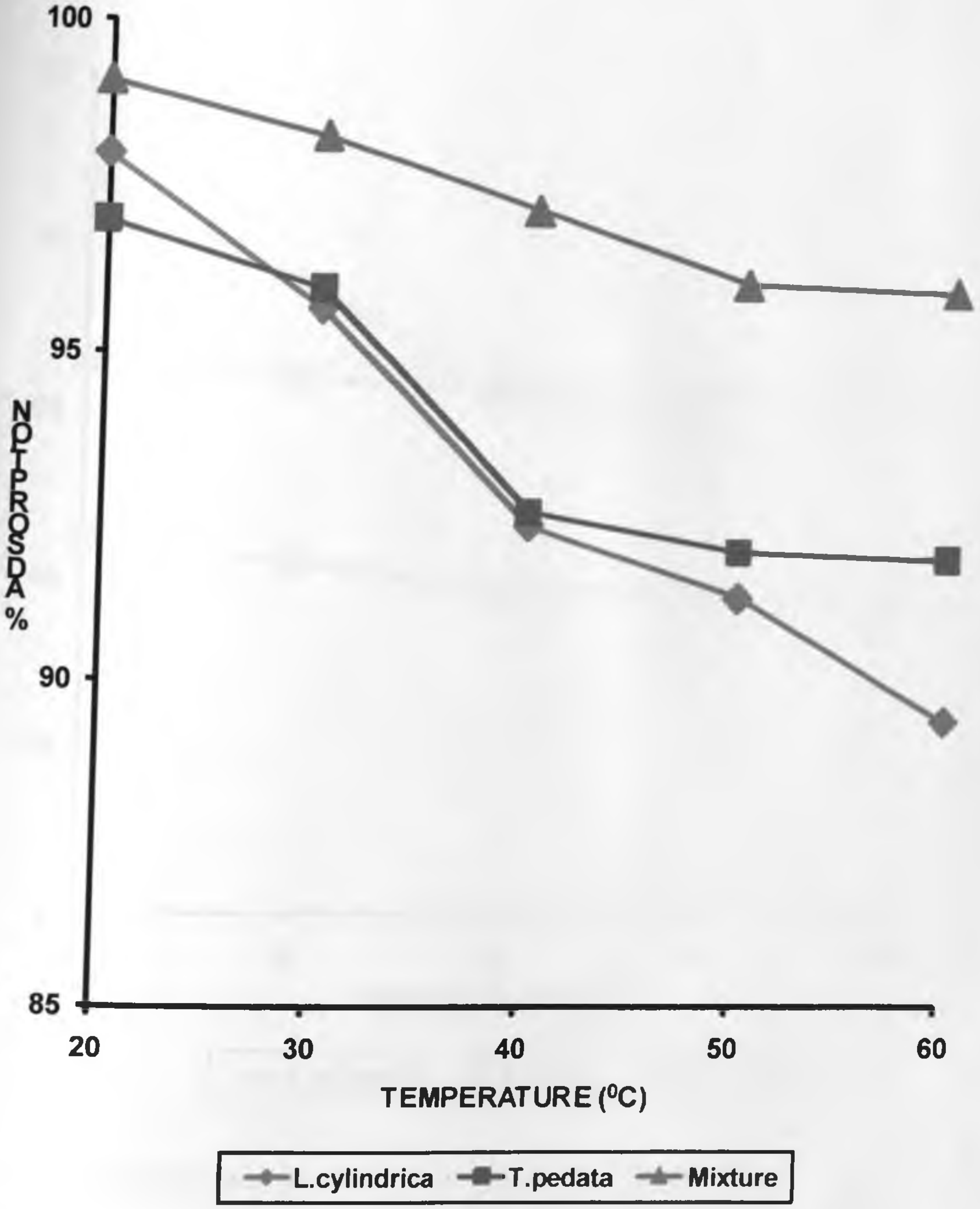

Figure 40b: Superimposed plots of % adsorption of methylene blue dye by *L.cylindrica, T.pedata* and their mixture against temperature of the dye at t=60 min.

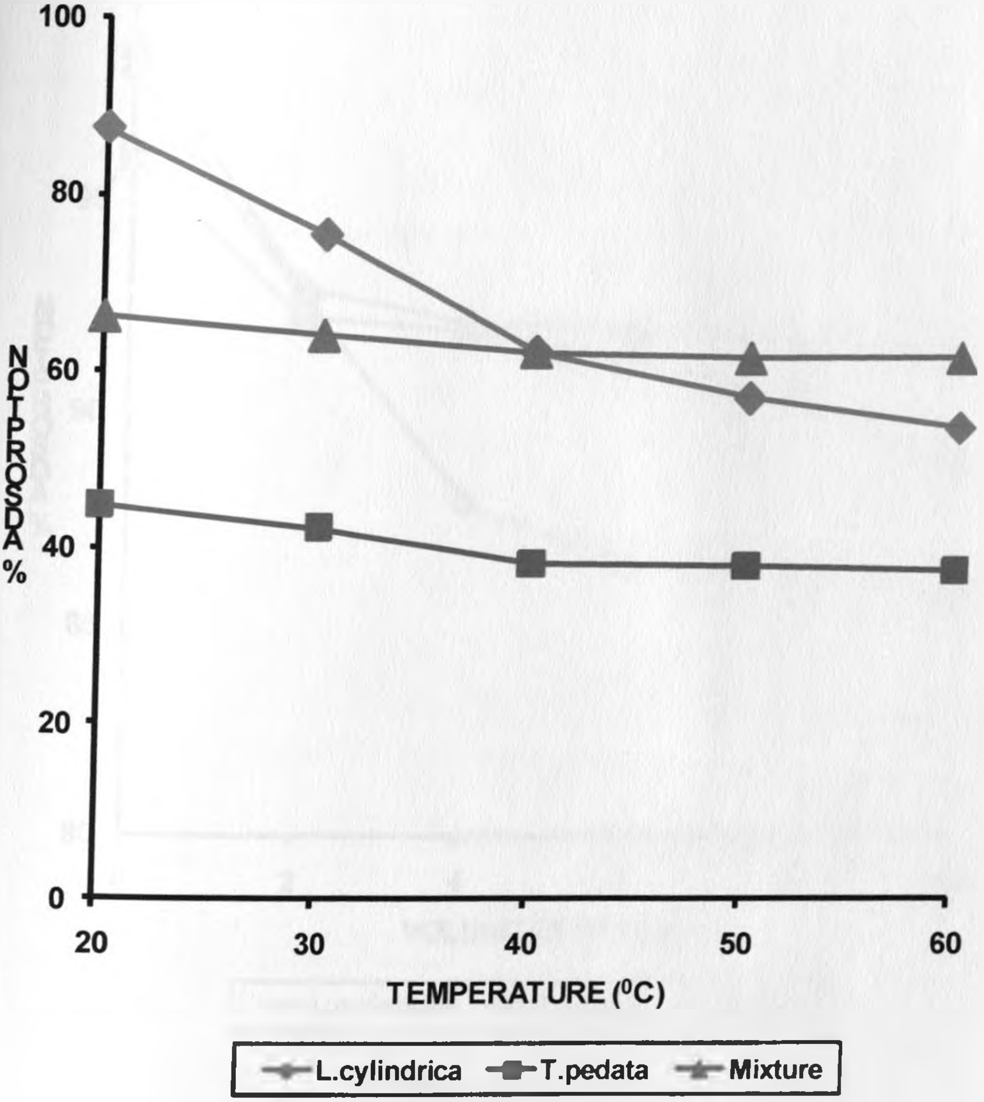

Figure 44b: Superimposed plots of % adsorption of Congo red dye by *L.cylindrica*, *T.pedata* and their mixture against temperature of the dye at t=60 min.

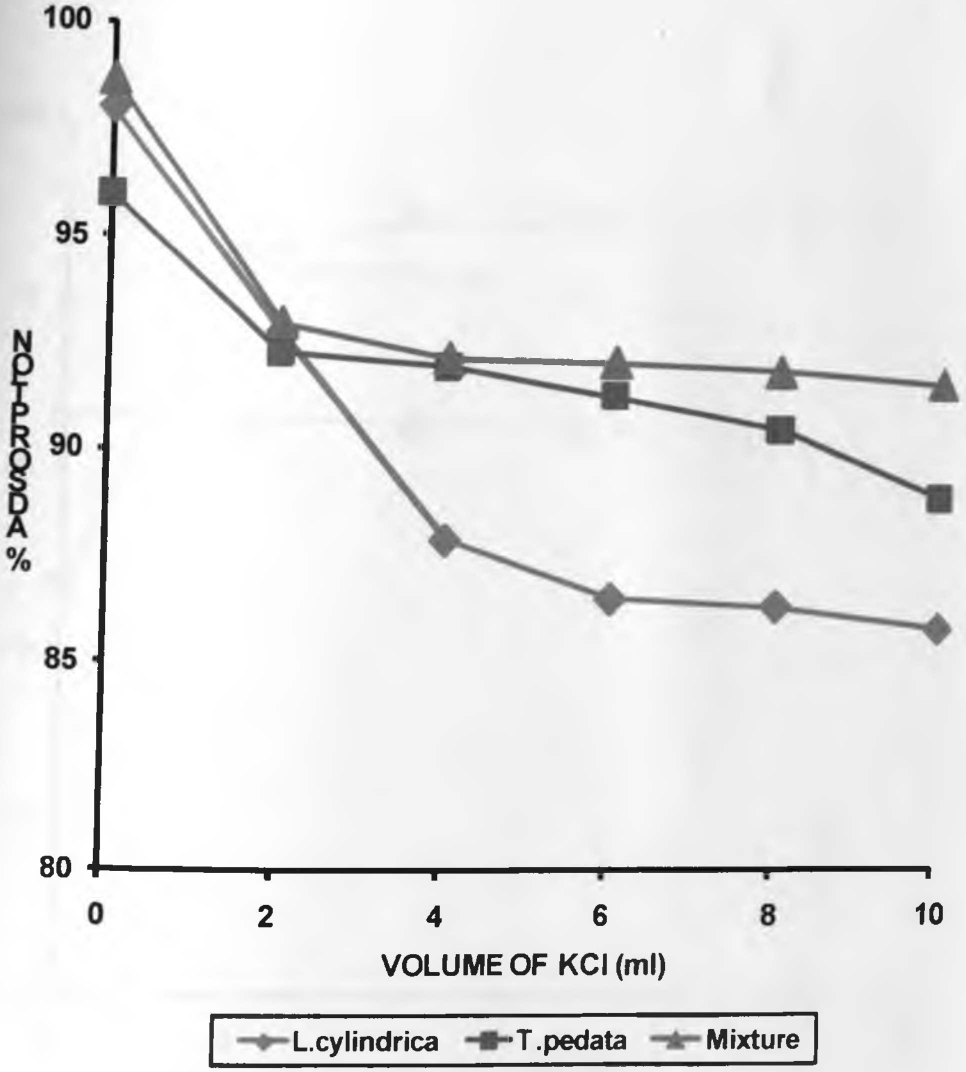

Figure 48b: Superimposed plots of % adsorption of methylene blue dye by *L.cylindrica*, *T.pedata* and their mixture against volume of KCl at t=60 min.

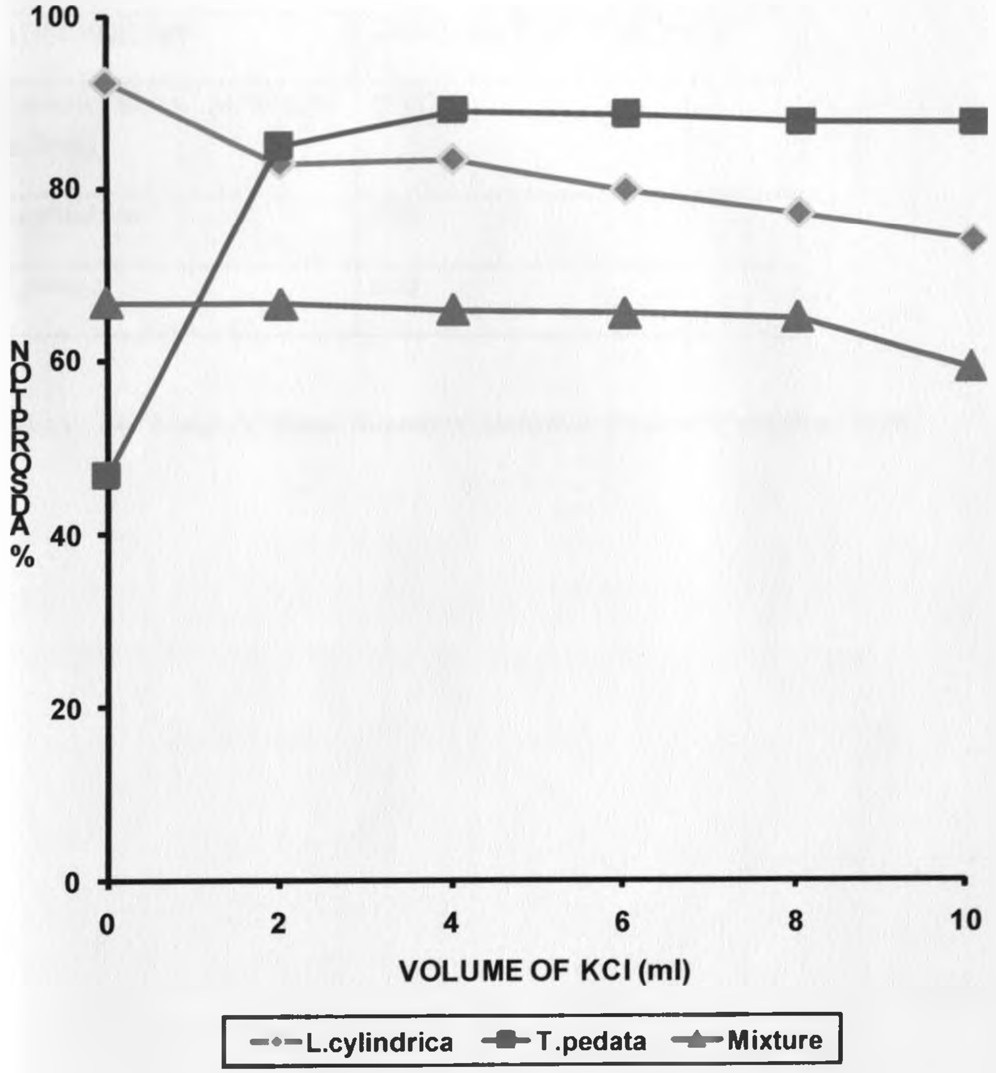

Figure 52b: Superimposed plot of % adsorption of Congo red dye by *L.cylindrica, T.pedata* and their mixture versus volume of KCl at t=60 min.

APPENDIX 3

Table 5: Comparative Cost of Adsorbents

ADSORBENT	**COST IN US $ PER TON.**
Carbon Black (activated carbon)	8500
L.cylindrica	750
T.pedata	600

Source: The Kenya National Bureau of Statistics: Statistical Abstract 2008