OPTIMIZATION OF PARTICLE SIZE OF MAIZE PEAT FOR ADSORPTION OF COLORANTS

BY

BAKALYIL, BIMOHOR AYUBA

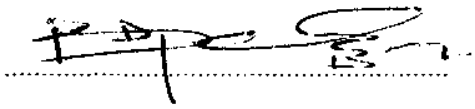
A THESIS SUBMITTED TO THE POSTGRADUATE SCHOOL IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF THE DEGREE OF MASTER OF SCIENCE IN ANALYTICAL CHEMISTRY

DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
AHMADU BELLO UNIVERSITY
ZARIA, NIGERIA

JUNE, 2000

DECLARATION

I hereby declare that this thesis contains the report of my research work and has not been presented in any previous application for a higher degree. All information from other sources have been acknowledged by means of references.



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16:06:2006

DATE

CERTIFICATION

This thesis entitled "Optimization of particle size of maize peat for adsorption of colorants", by Bakalyil, Bimohor Ayuba, meets the regulation governing the award of the degree of Master of Science of Ahmadu Bello University, Zaria, Nigeria and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This work is dedicated to my wife, Mrs. Patience Bakalyil and my two sons: Messrs Mahnwul Bakalyil and Kyeplang Bakalyil.

ACKNOWLEDGMENT

I am grateful to my supervisors Dr. E. J. Ekanem and Prof. S. A. Thomas for their valuable assistance, suggestions and constructive criticisms throughout the course of my work

I express my profound gratitude to the Department of Chemistry which provided me with the required facilities and materials that enhanced the smooth conclusion of my work.

Finally, it is a pleasant duty to thank the following: Engr. E. J. Dasat, Commanders M. A. Dapel and W. K. Lepzem, Messrs D. D. Gufwan and J. S Konyil, who generously provided financial and moral support during the course of my work.

ABSTRACT

The study developed maize cob peat, prepared eleven different particle sizes of the peat and tested the adsorption capability of each particle size on dye solutions and textile effluents, with a view to determining the effective particle size(s) for industrial application.

Each particle size of peat was soaked, squeezed and thoroughly washed to remove the dust and humin content. The cation exchange capacity of the peat was then determined.

The textile effluents were characterised for pH, dissolved, suspended and total solids. The number of dye components in each textile effluent was determined using thin layer chromatography (TLC). Spectral characterisation of the textile effluents and dye solutions was also undertaken.

When column experiments were undertaken, the particle sizes of 150 µm, 300 (am, and 355 µm were found to be quite effective, because using 4 g each of the particle sizes, it was found that 850 cm^3 of dye samples of M and A at maximum dye house concentrations of 100 ppm was decolorised by the stated particle sizes to 11 ppm, 18 ppm, 23 ppm and 28 ppm for dye M and 13 ppm, 21 ppm, 27 ppm and 33 ppm for dye A. The same particle sizes decolorised 70 cm^3 of the dye samples at concentrations of 2800 ppm to 58 ppm, 64 ppm, 79 ppm and 108 ppm for dye M and 111 ppm, 128 ppm and 186 ppm for dye A. Also when 40 cm^3 of the crude effluents of PU and PS at absorbances of 0.460 and 0.340 respectively were administered on 4 g of each of the above particle sizes, the effluents were decolorised to absorbances of 0.055, 0.075, 0.160 and 0.155 for effluent PU and 0.012, 0.035, 0.048 and

0.070 for effluent PS. These results indicate that peat at the above stated particle sizes can be effectively utilized for decolorisation of dye solutions and effluents.

Furthermore, column adsorption experiments were undertaken by placing the same particle sizes in a series of four columns. The method was found to be effective for most particle sizes, because results indicated that when 150 cm^3 of the crude effluent of PU and PS were respectively employed on 4 g of each particle size in the first column and the treated effluent later transferred to the second column and so on; 150 µrn, 300 µm, 250 µm, 335μm, 425 µm, 500 µm and 850 urn decolorised PU and PS at absorbances of 0.460 and 0.350 respectively to 0.006, 0.009, 0.042, 0.063, 0.102, 0.165 and 0.208 respectively for PU and 0.000, 0.000, 0.000, 0.000, 0.019, 0.021 and 0.046 respectively for PS. Although the result is good, prolonged adsorption time and large cumulative void volume resulting in the collection of small volumes of treated effluent far outweighed the advantage of the method.

The performances of 500 urn and 850 µm particle sizes were moderate for all trials while the particle sizes of 1.18 mm, 1.40 mm, 1.70 mm and 2.00 mm performed poorly in all the experiments.

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CHAPTER ONE

1.0 INTRODUCTION

1.1 Water and Water Pollutants

Except for the interaction of light with water which imparts a pale blue colour on the latter, pure water is a clear, colourless, nearly odourless and tasteless liquid which is essential for most plant and animal life (Davies-Colly et. al., 1993). With a freezing point of 0°C, boiling point 100°C at sea level, specific gravity of 1.00 at 4°C, water is the most frequently used of all solvents (Morris, 1969). On the other hand, waters from the various natural sources - rain, sea, oceans, rivers or streams do not have all the characteristics of pure water. This is because of the inherent presence of elemental and chemically dissolved organic and inorganic substances present in them (Snoeyink and Jenkins, 1980). When the concentrations of the dissolved organic and inorganic substances in water exceed an accepted limit, pollution arises. This development affects very much the acceptability of the water for domestic use (Gardiner and Borne, 1978). A water pollutant therefore, is any substance, potentially harmful to animals and plants which enters a body of water in a greater concentration than it would be in the natural condition (Keller and Wilson, 1992). The activities of man, animals and other natural phenomena produce the pollutants (Horne, 1978) and these directly or indirectly alter the composition of watercourses, thereby rendering them less suitable for most of their uses (Ellis, 1988).

1.2 Classification of Water Pollutants.

To embark on a description and the explanation of any available industrial water pollution treatment processes, it is pertinent to classify the various types of pollutants that occur in most industrial wastewaters. The classifications according to Azad (1976), Sollfrank and Gurjer (1991), Henze and Harremoes (1992) and Henze (1992) are:

1.2.1 Floating Pollutants

This category of pollutants consists of oils, grease and other materials lighter than water. The presence of floating pollutants in a receiving water causes unsightly appearance, retards plant growth and is a general nuisance. Oil in particular interferes with natural reaeration, thus endangering aquatic life.

1.2.2 Suspended Pollutants

This type of pollutants can be organic or inorganic in nature. The presence of suspended solids can render a receiving water to become unsightly and can retard aquatic activities. Since suspended pollutants can settle to the bottom of a receiving water, these solids tend to smoother plant life. If suspended solids are organic in nature, they could break-down, utilizing the available oxygen, thereby destabilizing aquatic balance.

1.2.3 Dissolved Pollutants.

These pollutants may be acids, alkalis, heavy metals, insecticides and various types of organics. These pollutants can render receiving waters unusable and may destroy aquatic life. Very small concentrations of certain dissolved pollutants such as phenols, can cause objectionable taste and odour. Again organic decomposition could occur, thereby depleting receiving waters of oxygen and producing obnoxious gases and odour.

1.2.4 Colours

Colour arises from oils, soluble dyes, phenols, nitro compounds, grease and eutrophication. Colour is a pollutant that is objectionable mainly from aesthetic point of view. Colour interferes with normal aquatic life.

1.2.5 Taste and Odours

Alteration in taste and the introduction of unpleasant odours can render a relatively clean water unsuitable for use. Materials such as phenols, mercaptans and hydrogen sulphide in small concentrations can be very objectionable due to their unpleasant odours.

1.2.6 Heat and Radiation

Heat and radiation are responsible for raising the temperature of water bodies. Temperature rise reduces the dissolved oxygen of water and can also cause a lot of discomfort for aquatic inhabitants of all categories.

1.3 Sources of Pollutants in Natural Waters.

The corresponding increase in the volume of waste effluents and the diversity of pollutants discharged into the natural environment has been the result of population explosion, industrial activities, agricultural practices and research developments, e.t.c. (Hart and Stander, 1972; Diamant, 1974). The pollutants produced in most instances, are usually characteristic of the activities taking place at these endeavours.

Large concentrations of population in urban centres has led to the sudden rise in the volumes of waste effluents and pollutants as a result of domestic activities. Following this, huge quantities of soaps, foams, colour additives, food nutrients, human and animal

faeces, various grades of detergents and several other forms of pollutants are discharged into water bodies as a result of improper methods of disposal. Heavy black coloration normally arises as a result of high oxygen demand in the receiving waters (Knight and Simmons, 1980). A wide range of pollutants also manifest from agricultural practices. The pollutants that arise from agricultural activities are: organochlorine and organophosphorus insecticides and herbicides, triazine herbicides, ametryne turbutryne, nitrogenous and organophosphorus fertilizers and animal wastes, e.t.c. The severity of the pollution problems of these agricultural wastes in both surface and underground waters have been expressed as a disaster (Loehr, 1977; Goulden, 1978). Pollution resulting in colouring has been identified as one of the major problems of agricultural practices in water bodies (Azad, 1976).

Effluents and pollutants arise from industrial activities at a rapid rate as a result of their daily operations. Since there is a wide range of industries, the industrial sector tends to produce pollutants in larger quantities and in varieties more than any other sources of pollutants (Sidney, 1978). In the textile industry, waste producing operations and the pollutants generated have been exhaustively discussed (Little, 1976; Sidney,1978; Porter et. al., 1972; Jorgensen, 1978; Durig and Hausmann, 1978). Scouring operations generate grease, solid wax, alkalis e.t.c. Dyeing and printing operations in the textile industry produce residual chromes, sulphide, vat and reactive dyes; sand and salt concentrations. Bleaching operations that take place in the textile industry also produce dissolved solids of inorganic origin like sodium silicates, sodium hydroxide, soaps and colours. Desizing activity in the textile industry also generates oils and grease. A wider range of organic materials used in the textile industry generates organic acids, starch, organic sizes, olein

oils and detergent wastes. As a result intense colours, high turbidity, high biological oxygen demand, high alkalinity and a huge quantity of dissolved solid accompanied by reduced total oxygen demand manifest. Hence, most receiving waters have their characteristics reflecting the waste arising from the activities of a textile industry operating in their vicinity (Gardiner and Borne, 1978). In the tannery industry, the areas of activities are the initial soaking of hydes and the chemical treatment of the hydes. Generally, the end-of-pipe effluents from the tannery are usually characterised by various colours and odours (Jorgensen, 1978).

Foodstuff factories employ a wide range of raw materials which include cereals, root crops, sugars, fruits, vegetables, meat, fish, etc. The common traits of the wastes in the effluents of foodstuff factories are high concentrations of carbohydrates and proteins. There is also a pronounced presence of oils, grease and colours. The discharge of these pollutants into receiving streams usually raises the problem of high biological oxygen demand and visibility problems.

Aromatic amines, phenols, benzo-α-pyrene, benzidine formaldehyde, benzene and a lot of other chemicals are water borne wastes that originate from the laboratories and scientific activities. Although waste from these activities may not be quite enormous in volume, their effects are often pronounced and dangerous (Cook, 1972). Chemical waste similar to that of laboratories and scientific activities occur at commercial areas in urban centres, at photo studios, shops, printing and local dyeing houses, hair dressing saloons, cosmetic centres, hospitals, etc.

A wide range of activities occur in the operations of the oil industry. The major operations are oil explorations and production, transportation by pipelines and land tankers, processing of the oil in the refineries, petrochemical plant complex and the distribution and marketing of the oil products. Major oil leaks arise from these. Dockside sloppiness and the frequent accidents involving the large sea vessels are the major contributors of oil leaks. Natural seepage, both onshore and offshore including deliberate dumping, also represent a major source of petroleum imputs into rivers and natural waters. One major characteristic of oil is that it does not mix with water. Thus when major oil leaks are discharged into natural waters, it can float for a long time. This phenomenon leads to intense surface water coloration and the drastic interception of ultra violet light. The net effect usually, is on aquatic organisms which are killed in large numbers (Diamant, 1974; Bravo, 1998).

Various sources of pollutants in natural water exist which cannot be completely discussed in a single piece of work. Several other activities associated with human endeavours are cropping up and are giving rise to completely new types of pollutants. Since activity is an endless phenomenon, it is the responsibility of the society to develop various methods of treatment of pollutants of interest in the affected water bodies in order to regain the quality of natural water.

1.4 The Objectives of the Study

For some time now, the society, particularly industries and various arms of government have become increasingly aware of the urgent need to clean up industrial effluents and reduce river pollution. The standards set up by the Federal Environmental Protection

Agency (FEPA) are gradually becoming more rigid. Stiff penalties await defaulters of environmental laws. Of course, discharged industrial effluents and any other used water should be cool, clear, odourless and should not form scales or be corrosive (Culp and Culp, 1974). Therefore, new methods of treatment of industrial waste should be continuously investigated and developed to attain improvement in effluent quality.

Many dyes used in the textile industries are particularly difficult to remove by any available conventional methods since they are stable to light and oxidizing agents and are resistant to aerobic digestion (Porter et. al., 1972). Therefore, the removal of dyes in an economic fashion remains a strong need. Most commercial systems in the country currently use activated carbon as the adsorbent for wastewater treatment. Some workers use fuller's earth, while others use bauxite and silica. These adsorbents are usually imported. Considering the present foreign exchange rate, it is expensive. Alternative cheap adsorbents are needed.

The concentration of textile companies in Kaduna is one of the highest in Nigeria. The discharge of untreated coloured effluents into rivers is of great concern to both government and the community. Efficient, simple and cheap methods of removing dyes from textile effluents must be developed. A possible way of doing this is to utilize cheap and readily available naturally occurring materials. Decayed vegetable materials known as peat have been used to achieve this goal (Ottermeyer, 1930; Mckay et. al., 1978; Poots and Mckay, 1979). The capacity of maize cob peat for the removal of colour from textile effluent has already been investigated at a preliminary level (Ibrahim, 1995; Isuaikoh et al., 1998).

In this study, various particle sizes of maize cob peat developed were prepared and tested for colour removal from dye solutions and textile effluents. The performance of each fraction was optimised for effluent colour removal.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Peat and Peat Types

Peat is the material formed as a result of a slow and partial decomposition of a dead vegetable material of any kind (Rose and Arthur, 1956; Bel'Kevick et al., 1972; Considine, 1976; Smith et al., 1977). Peat is formed in areas where water saturates and completely covers the dead material. The water blocks the action of aerobic bacteria and in turn, greatly inhibits the rate of decay of the plant debris. However, if the dead material under the condition of complete saturation is allowed to decompose for too long under pressure, it becomes carbonized instead. Then, the first stage of formation of coal sets in. The extent of saturation of the environment, the type of dead vegetable involved, the pressure and the length of time for the peat to develop determine the category and form. Thus peat types vary with the nature of peat forming material and the period of decomposition. The classification of peat (Bel'Kevick et al., 1972) is based upon these principles. Thus we have the following types of peat:

1. sphagnum peat,
2. cotton-grass-sphagnum peat,
3. pine wood-reed peat,
4. sedge hynum peat,
5. cotton grass transition peat,
6. peat pervifolium peat and
7. sheuczeria-transition peat, etc.

Peat that is formed from the same plant material but in a different type of soil and marshy conditions is bound to have quite different characteristics (Smith et. al., 1978).

2.2 Uses of Peat

The principal uses of peat have been as fuel and for soil conditioning in agriculture (Smith et. al., 1977). When peat is used as fuel, the heat value is related to the moisture content by the equation :

$$\text{Net heat (BTU)} = 100 (x - 10)$$

where x is the percentage of dry peat in the mixture (Coupal and Lalancette, 1976).

In agriculture, the partially decomposed peat is marketed as soil conditioner and fertilizer.

Farnharm and Brown (1972) reported that peat has been used in domestic waste water irrigation because of its characteristics of rapid infiltration and high sorption capacity. Peat is also used for landfill (Coupal and Lalancette, 1976). Forgarty et. al. (1972) described other actual and potential uses of peat which have been considered for a variety of environmental and industrial applications including application of it for removal of dyes and heavy metals in waste effluents.

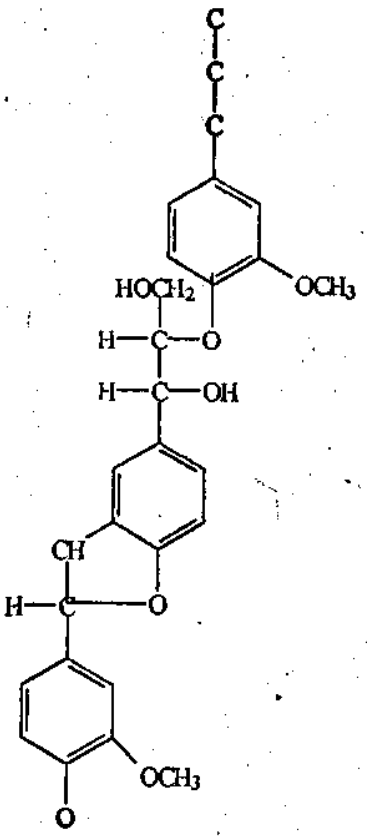
2.3 Chemical Composition of Peat

Souci (1938), Eldeigur (1966), Smith et al. (1978), Pigulevskaya et al. (1979) and Ali et al. (1988), determined the elemental and chemical composition of peat and observed that peat is a complex material, the elemental components being calcium, magnesium, iron, potassium, zinc, copper, sulphur, sodium, lead and nitrogen. The nitrogen in peat is found

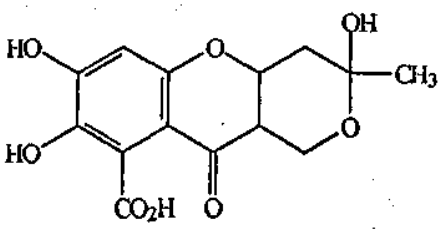
attached to humic acid and it is found to be the most unhydrolyzable heterocyclic component. These elements found in peat may be the basis for the agricultural potential of peat.

The major chemicals found in peat are lignin, fulvic acid, humis and cellulose. The lignin in peat has several polar functional groups like phenolic hydroxyls, ketones, aldehydes, ether, polyuronides, uronic acids, carboxylic groups and thiol groups. These groups are responsible for the ion exchange properties of peat (Bel'Kevick et al., 1972).

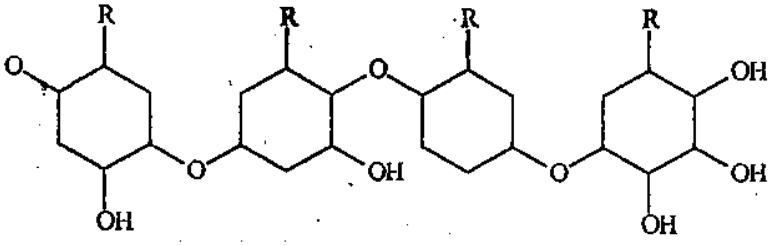
The structures of lignin (Coupal and Lalancette, 1976) and that of fulvic acid, humic acid and cellulose (Poots and Mckay, 1979), found in peat, are:



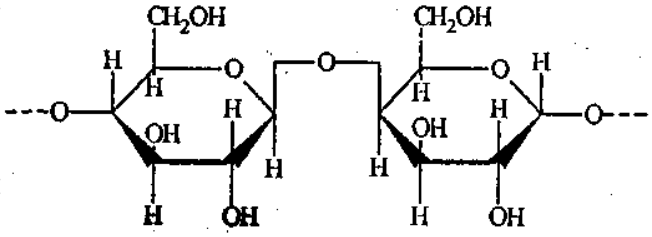
lignin



Fulvic acid



Humic acid



Cellulose

Peat also contains asphalene, wax , paraffin, oils, α-amino acids and monosaccharides. However, the proportions of each of these components vary from one peat sample to another depending on the mode of formation of the peat. According to Smith et al. (1978), any peat formed should have the following descriptions:

i) an organic matter which has undergone considerable breakdown but in which the structure is visible;

ii) an organic matter in an organized state of preservation and, therefore, identifiable;

iii) an organic matter which has degraded below cellular level, composed of what might be termed "humus" and often forming peat matrix and

iv) an inorganic matter derived from cells of some plants.

Due to the polar character of peat materials, specific adsorption for dissolved solids such as transition metals and organic molecules is quite high (Chaney, 1979). This chemical property has enabled peat to be used as an agent for purification of waste water containing dyes and metallic ions (Coupal and Lalancette, 1976).

2.4 Dyestuffs and their Classification

Colorants are dyes. Dyes are used to impart colours or hues on substrates from a solution or a fine dispersion. The principle of dye adsorption involves substances retaining dyes on their surfaces. Some of such substances that can adsorb dyes on their surfaces are wool, silk, hair, vegetable fibres, cellulose, cotton, linen, regenerated cellulose, mineral fibres

(glass) and asbestos. Others are leather, paper, rubber , metal surfaces, foods and solvents.

The structure of a dye dictates the type of colour it can impart. The unsaturated nature of an organic compound is a factor that establishes the character of the colour of a compound. Organic colorants contain conjugated multiple bonds of the type: C=C, C≡C, C≡N, N≡N, C=S, N=S, C=O and N=O. Odd numbers of conjugated atoms have less brilliant colours, but even numbers of conjugated atoms have more brilliant colours (Snell, 1971).

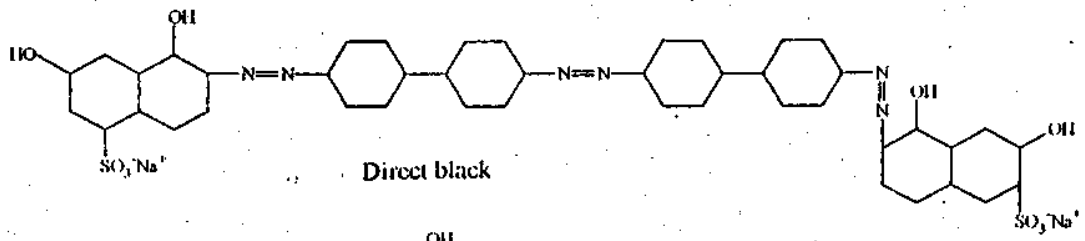
Dyes are classified based on chemical constitution and dyeing behaviour (Reed, 1969; Nkeonye, 1987). Also, classification based on chemical consideration may be done based on their behaviour on reduction. On the other hand, commercial dyers classify dyes according to the dyeing class and hue or tone or colour index (CI). In this classification, numerical figures are always assigned. However, classifications that have relevance with chemical constitution are usually employed for better understanding (Snell, 1971).

2.4.1 Acid Dyes

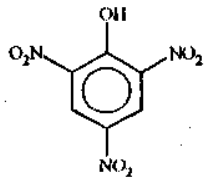
Acid dyes are a class of dyes which contain acid functional groups: $-SO_3^{2-}$, $-COO^-$, $O-SO_3^-$ etc. They are also called anionic dyes. Some examples of acid dyes are:

2.4.2 Direct Dyes

Direct dyes are in the same solubility group as acid dyes. They are acid dyes of high molecular weights possessing certain groups that have direct affinity for cellulosic fibres. The dyes get fixed to the fibre through hydrogen-bonding. In solution, direct dyes tend to aggregate giving rise to larger molecules and tend to gel.



Direct black



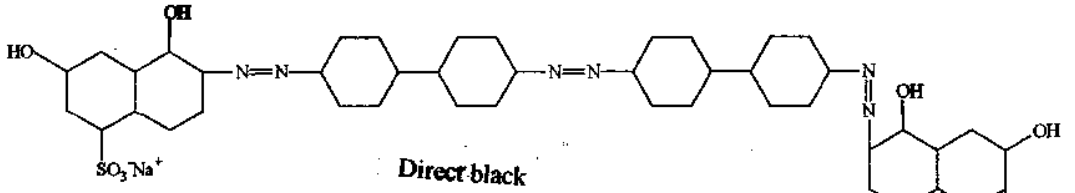
Picric acid

2.4.3 Basic Dyes

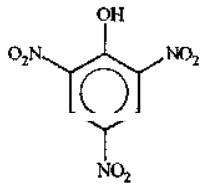
Basic dyes are a class of dyes that are sometimes called cationic dyes and have poor fastness properties. Basic dyes fade away by oxidation. They loose colour fast due to oxidation of the many NH_2 groups. Basic dyes are quite soluble in water.

2.4.2 Direct Dyes

Direct dyes have the same solubility group as acid dyes. They are acid dyes of high molecular weights possessing certain groups that have direct affinity for cellulosic fibres. The dyes get fixed to the fibre through hydrogen-bonding. In solution, direct dyes tend to aggregate giving rise to larger molecules and tend to gel.



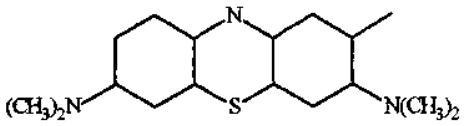
Direct black



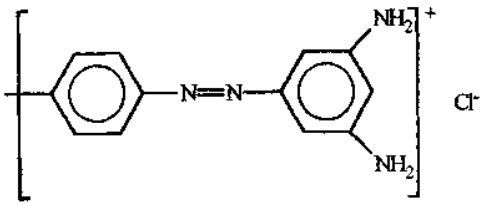
Picric acid

2.4.3 Basic Dyes

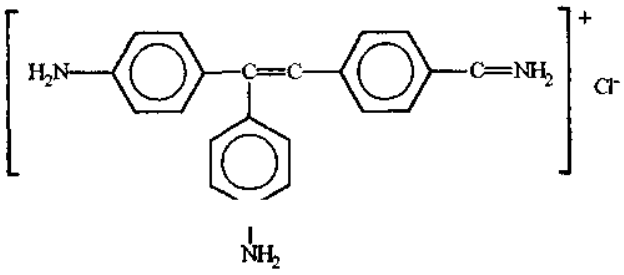
Basic dyes are a class of dyes that are sometimes called cationic dyes and have poor fastness properties. Basic dyes fade away by oxidation. They loose colour fast due to oxidation of the many NH_2 groups. Basic dyes are quite soluble in water.



Methylene blue



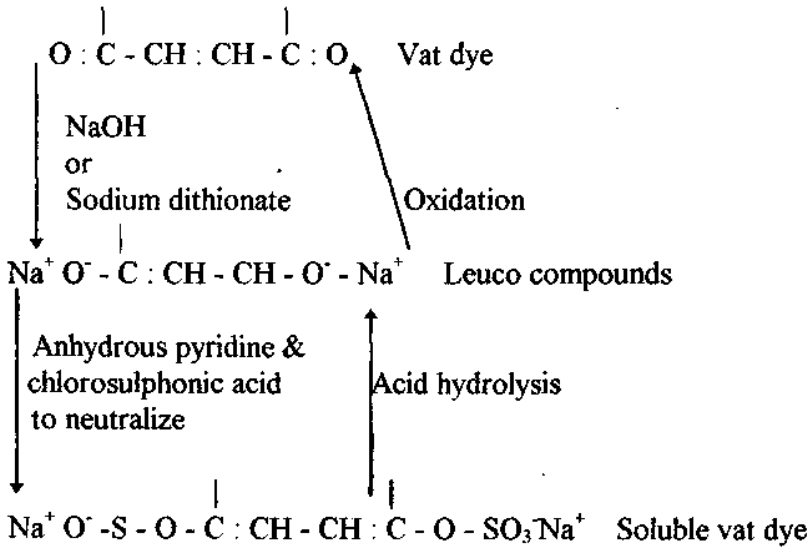
Chryzoidine



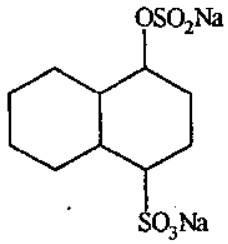
Trianyl methane

2.4.4 Vat Dyes

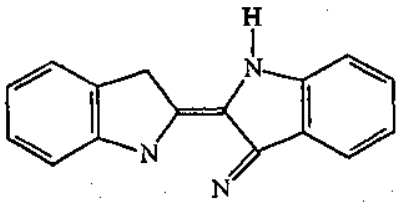
Vat dyes are water insoluble. They can be made soluble by reducing agents like stannous chloride, thiorea dioxide, sodium hydroxide, sodium sulphide, etc. "Vatting" means cooking in water. Vat liquor is usually colourless and is due to the action of sodium sulphide. Vat liquors are too alkaline for protein treatment. Sulphonation converts them to stable water soluble products, which can be applied like acid dyes. The original dye can then be regenerated from fibre on acid oxidation.



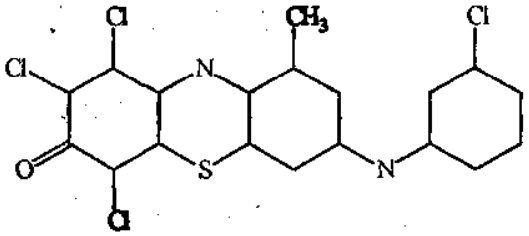
Due to their tendencies to return to their insoluble states on fibres, vat dyes give good wool hues. Some examples of vat dyes are:



(Leuco Ester Vat dye soluble)



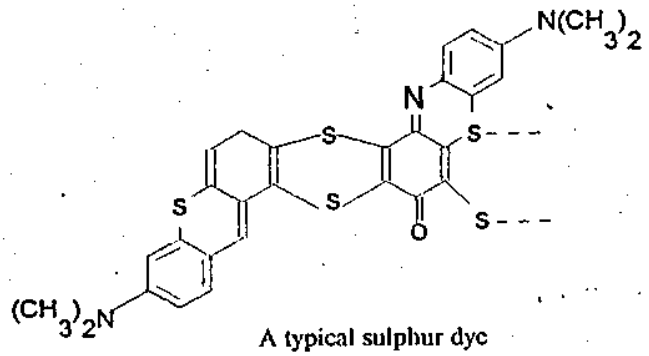
(Indigo blue insoluble)



Vat Violet

2.4.5 Sulphur Dyes

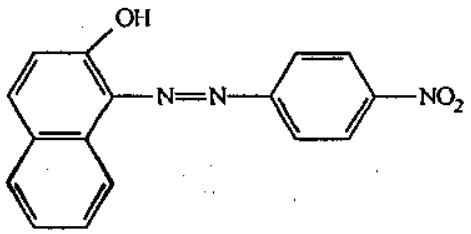
These are dyes that have the disulphide incorporated in the molecule. However, the constituents of these dyes are not well known, their method of manufacture is largely empirical resulting in very complex mixtures (Reed, 1980). They are generally insoluble in water and are made soluble by vatting with sodium sulphide acting both as the alkali and the reducing agent.



A typical sulphur dye

2.4.6 Dispersed Dyes

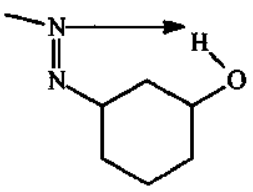
Dispersed dyes are water soluble. The dyes are prepared by grinding pigment powder or paste with a dispersing agent. Dispersed dyes are also soluble in organic solvents. The dyes can penetrate and dissolve in synthetic fibres. This is because organic solvents act as their carrier. Para red is an example of a dispersed dye.



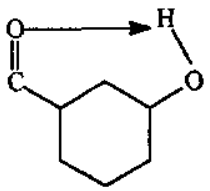
Para red

2.4.7 Mordant Dyes

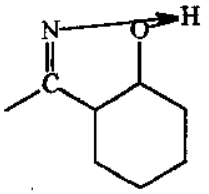
Mordant dyes have some groups that allow ready and firm combination with metals, i.e, O-hydroxyazo, O-hydroxycarbonyl and O-hydroxyazomethane groups. In the dye molecule, the hydrogen atom that is used for hydrogen-bonding is replaced by a metal atom and the compound becomes chelated.



O-hydroxyazo

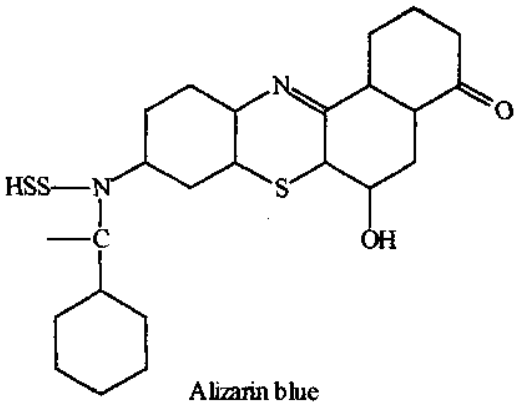


O-hydroxycarbonyl

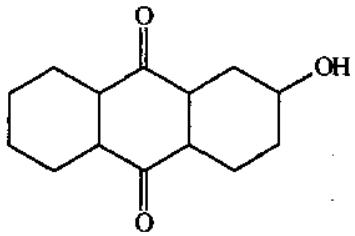


O-hydroxyazomethane

The complexing metals are usually chromium, zirconium, copper and iron. Some examples of these dyes are alazirin, alazirin blue and mordant black 1.



Alizarin blue



Alizarin

2.4.8 Other Classes of Dyes

Metal complex dyes, oxidation dyes, pigment dyes and many other classes of dyes that are classified based on chemical constitution were described in the work of Juster (1962).

2.5 Characterisation of Dyes

In order to arrive at a good clue in the examination of the colour of dyestuffs, the following are usually considered for the characterisation (Reed, 1969).

Source of Colour: Brilliant colours are exhibited by those dyes that possess extensive systems of conjugation while dull colours are from those dyes that have less extensive systems of conjugation. In this group, we have

$N{=}C\text{-}(CH{=}CH)_n\text{-}N^+$ cationic

$O{=}CH\text{-}(CH{=}CH)_n\text{-}O^-$ anionic

$O{=}CH\text{-}(CH{=}CH)_n\text{-}N$ mixed

Solubility: These are dyes that have solubility groups and tend to be very soluble.

Molecular size: Small molecular size dyes are acid dyes. Large molecular size dyes are direct dyes. Vat dyes, anthraquinone dyes and sulphur dyes etc. belong to this same group.

2.6 Adsorption and Chromatographic Methods

Chromatography is a separation method in which the mixture is applied as a narrow band to a stationary, porous adsorbent and the components are caused to undergo differential migration by the flow of a mobile phase which may be a liquid or gas (Zweig and Sharma, 1974). Chromatography employs adsorption phenomena to separate mixtures. Adsorption is a surface phenomenon (Touchstone, 1993). Adsorption can be between solid-solid, gas-solid, liquid-solid and liquid-liquid surfaces (Weber and Morris, 1964). Here, the substance adsorbed is the adsorbate . The adsorbing surface is the adsorbent. When adsorption occurs, the adsorbate molecules become attached to the surface of the adsorbent.

There are two major classifications of chromatography: solution or liquid chromatography (LC) and gas chromatography (GC). In liquid chromatography, the liquid carries the dissolved solute through the adsorbent which can be a column, paper or thin layer. In the case of GC, an inert gas (carrier gas) carries the mixture through the sorption column. Further classifications are based on the stationary phases. Gas-solid chromatography (GSC) involves a column packed with a stationary solid (adsorbent). Gas-liquid chromatography (GLC) involves a solid coated with a stationary liquid as the adsorbent. Liquid-solid chromatography (LSC) involves the solid adsorbent being the stationary phase. Other sub-divisions of non-column liquid chromatography are paper chromatography (PC) and thin layer chromatography (TLC). Liquid-liquid or liquid-solid chromatography may be further classified into normal phase partition chromatography (fixed polar liquids) and reversed phase partition chromatography (fixed non-polar liquids). Furthermore, there are other classifications which involve ion exchange materials: either organic or inorganic. Here, the mixtures are separated as a result of exchange of ions. This is termed ion exchange chromatography (IEC). But when it is a non-ionic polymeric gel (e.g. polystyrene or sephadex) that is involved in the chromatographic technique, it is termed gel permeation chromatography (GPC) or gel filtration chromatography (GFC) or molecular exclusion chromatography (MEC) (Pavia et al., 1976).

2.7 Column Adsorption Chromatography

Column adsorption chromatography is a technique that depends on adsorptivity capability and solubilities. It is a solid-liquid phase partitioning technique. The adsorbents for the column chromatography that are mostly used are alumina ($Al_2O_3.xH_2O$), silica gel

($SiO_2.xH_2O$), activated carbon, charcoal, cellulose, etc. Of recent however, several workers have employed various agricultural products and agricultural by-products which have shown good exchange properties in both modified and unmodified forms in column chromatography (Smith et al., 1977; El-Geundi and Aly, 1995; Ekanem, 1996).

2.8 Ion Exchange Materials and their Classification

Ion exchange materials are charged matrices or adsorbents that can exchange the charged ions with other ions of similar charges. Separation by ion exchange (Hadjiioannou et al., 1988) is based on reversible ions between an outer liquid phase and an ionic solid phase. This is an ion exchange process between solid and liquid phase. In the case of a liquid ion exchanger, the process involves a mixture of two immicible solutions. Ion exchange resins can be developed from modification or activation of the adsorbent (Bassett et al., 1978). To make a resin a cation exchanger, it should be modified into the acid form or hydrogen form. However, to obtain an anion exchanger, it may be required to be modified to a basic or hydroxide form. Hence ion exchange resins are classified as cation exchange resins and anion exchange resins depending on the type of ionisable groups. The degree of ionisation of ion exchange resins allows for classification into strongly acidic, weakly acidic, strongly basic and weakly basic resins. Sodium hydroxide is used fo strongly basic resins e.g. $RN(CH_3)OH$, while tetraoxosulphate(VI) acid is used for strongly acidic resins e.g. RSO_3H. An example of a weakly acidic resin is RCOOH while an example of a weakly basic resin is $R(CH_3)Cl$. R for all the examples of resins represents the uncahrged part of the resin polymer. Procedure for developing a strong cation exchange, the resin must be soaked in a beaker with about twice its volume of 2 mol dm^{-3} hydrochloric acid for about 30

- 60 minutes with occasional stirring.The particles are removed by decantation (Bassett et. al., 1978).

Inorganic oxides like silica and alumina, clays, zeolites and high molecular mass organic polymeric compounds (based on styrene) and carbohydrate derivatives are examples of solid resins that can be modified to cationic or anionic ion exchange resins. An example of a liquid anion exchange material is Amberlite LA1 [N-dodenyl(trialkymethyl) amine]. Liquid cation exchangers are alkyl and dialkyl phosphoric acid. Ion exchange resins are used in columns for adsorption or ion exchange chromatography (Hadjiioannou et. al., 1988).

2.9 Mechanism of Ion Exchange

The selectivity of a resin refers to its increased preference for a certain ion over another. The ion exchange reactions are feasible based on that principle. In general

1) $M^+ + X^+R^- \longrightarrow X^+ + M^+R^-$ cation exchange

2) $M^- + R^+X^- \longrightarrow X^- + R^+M^-$ anion exchange

3) $RSO_3H + NaCl \longrightarrow RSO_3Na + HCl$

4) $2RSO_3Na + CaCl_2 \longrightarrow (RSO_3)_2Ca + 2NaCl$

5) $RN(CH_3)_3OH + HCl \longrightarrow RN(CH_3)_3Cl + H_2O$

6) $RN(CH_3)_3Cl + NaNO_3 \longrightarrow RN(CH_3)_3NO_3 + NaCl$

The selectivity coefficient is equal to the equilibrium constant of the exchange reaction. Considering (1) above, the selectivity coefficient is given by

$$K_X^M = \frac{[X][MR]}{[M][XR]} = \frac{[X][M]_r}{[M][X]_r}$$

For (3), $K_H^{Na} = \frac{[H^+][Na^+]_r}{[Na^+][H]_r}$

where [X] and [M] represent the concentration of the like-charged ions in the solution (Meq/mL) and [XR] or $[X]_r$ and [MR] or $[M]_r$ represent their concentrations in the resin (Meq/g). K_X^M is constant only if activities are used.

The distribution of an ion between the resin and the solution is described by distribution coefficient, K_D. For a general ion exchange reaction,

$$M + XR \longrightarrow X + MR$$

where the concentration of M is quite small, so that the amount is not larger than 5% of the exchange capacity of the resin, then at equilibrium state we have

$$K_D = \frac{[MR]}{[M]} = \frac{amount\ of\ ion\ /\ g\ dry\ resin}{amount\ of\ ion\ /\ mL\ of\ solution}$$

Where an element is not present in the same form in the resin and the solution, the distribution ratio, D is used.

2.10 The Desirable Properties of Adsorbents Used as Ion Exchange Material

According to Kirkland (1971) and Small (1989), ion exchange materials have three important elements:

(i) an insoluble matrix (organic or inorganic in nature) with fixed ionic sites hitherto attached to an integral part of the matrix. Associated with these fixed sites are counter ions. They are mobile throughout the ion exchanger and most importantly they exchange ions with other like exchangers when placed in a solution containing such. These properties give the materials their names.

(ii) the ion exchange material should provides a stationary phase that is chemically stable. The particles are usually preferably uniform spheres so that they have good flow properties when they are placed in a column.

(iii) their exchange sites should normally be modified.

2.11 Ion Exchange Capacity

The ion exchange capacity of a resin is the number of milliequivalent of H^+ or OH^- per unit weight (g) of dry resin (meq/g) or [per unit weight (ml)] of the liquid-swollen resin, (meq/ml) which can be adsorbed by the ion exchanger (Hadjiioannou et.at., 1988). The ion exchange capacity of a resin is dependent upon the total number of ion-active groups per unit weight of material. The procedure involved in the determination of ion exchange capacity of a material has to do with packing the activated resin which may be in the dry form or as a slurry. When the level of water is allowed to drain to the level of the resin beads, then a specified volume of sodium tetraoxosulphate (VI) is run through the column at a given rate. The displaced hydrogen ion is titrated with 0.1 M NaOH using an indicator. For example,

at a given rate. The displaced hydrogen ion is titrated with 0.1 M NaOH using an indicator. For example,

$$2\text{-}RH^{+} + 2Na^{+} \longrightarrow 2H^{+} + 2RNa$$

The capacity of the resin is determined as $\frac{aV}{w}$

where a is molarity of NaOH

V is the volume of NaOH in cm^3

w is the mass of the resin packed in the column.

2.12 Preparing the Column

The column is a cylindrical glass or metal tubing, but could be of any desirable size and length. Usually the column is clamped upright in a vertical position. At the bottom of the tube, a piece of flexible tubing is often attached and a Hoffman clamp is used to stop or regulate the flow . Care is always taken on the type of tubing to be used because certain solvents employed for elution may dissolve the tubing. A list of such solvents and the tubings they damage has been reported (Pavia et al., 1976). Usually before a column is ready for chromatographic experiments, certain steps have to be undertaken. They are:

2.12.1 Preparing a Support Base of the Column

In preparing a support at the base of the column, the column is partially filled with a quantity of the solvent to be used in the elution. A loose plug of glass wool is pressed lightly down into the bottom of the column using a long but thin glass rod, until entrapped air is forced out as bubbles. Next, a thin layer of clean, white sand is formed on top of the

surface of the sand. All sand adhering to the side of the column is washed down with a small quantity of the solvent. The sand forms a base which then supports the column of the adsorbent and prevents it from washing through the flexible tubing. The column is now ready for adsorbent packing.

2.12.2 Packing the Column

Column packing is a very crucial operation in column chromatography. When packing the column with the adsorbent, care is taken to ensure that the column is evenly packed in order to avoid irregularities, air bubbles and gaps. This is essential because the compound to be separated usually moves down in a band or zone. Also the column should be held exactly vertically. Channeling usually occurs when part of the band front of the test compound advances ahead of the major part of the band. Two methods of packing exist; the wet and dry packing methods.

Wet Packing Method: In this method, the adsorbent is packed into the column as a slurry, the slurry being a mixture of a solvent and undissolved adsorbent. Usually, the slurry is prepared in a separate container by adding the solid adsorbent a little at a time, to a quantity of the solvent. Adequate adsorbent is usually added to the solvent, with swirling, to form a thick, but flowing slurry. During the operation of pouring the slurry, the column is tapped consistently and gently on the side. The tapping promotes the even settling and mixing and provides an evenly packed column free of air bubbles. The solvent from the collecting beaker may be re-added to the slurry if it becomes too thick to be poured into the column at a time. The solvent collected during the packing process should

be recycled through the column several times to ensure that settling is complete and the column firmly packed.

Dry Packing Method: In this method, the column is filled with the solvent and it is allowed to drain slowly. The dry adsorbent is added a little at a time, while the column is being tapped constantly until the column has the desired quantity of the adsorbent. A glass rod may be employed to slightly press the adsorbent as it settles in the column. In another dry packing method, the entire column is filled with the adsorbent dry, without any solvent. After this, the solvent is allowed to percolate down the column at a slow rate until the entire column is moistened.

2.13 The Choice of a Packing Method

The choice of a packing method is determined by the type of adsorbent involved. For instance, silica gel and alumina cannot be packed by the dry-packing method, because they accumulate air bubbles and also crack when they are dry-packed. Uneven packing also results when alumina and silica gel are dry-packed (Pavia et al., 1976). The selection of a packing technique depends on the prevailing circumstance. Markl and Schmid (1975) observed that non-spherical particles having low particle size down to about 50 μm can utilize dry packing method while smaller particles of the same material usually would not give high resolution when dry packing technique is employed. Horwitz and Bloomquist (1972) made a useful and remarkably detailed comparison of dry and slurry packing methods on celite when they loaded d-(2-ethylhexyl)phosphoric acid into high resolution columns. They found that their data showed a definitely improved performance of columns by slurry technique.

2.14 Applying the Sample to the Column

In the procedure described by Pavia et al. (1976), the solvent is first lowered to the top of the adsorbent in the column by draining. The sample which may be a liquid, dissolved solid or effluent, is added with the aid of a small pipette or from an overhead of the column using a separatory funnel. A small layer of the sample is then formed on top of the column adsorbent. The sample is allowed to drain into the column until the top of the column just begins to dry. A small layer of the solvent is usually added again. This small layer of solvent is allowed to drain into the column until it just dries. The process is usually repeated until it is obvious that the sample is strongly adsorbed on top of the column. If the sample is coloured and the fresh layer of solvent acquires this colour, the sample has not yet been properly adsorbed. When this procedure has been done, the level of the adsorbent may be protected by carefully layering the top of the column with solvent or sample and introducing a small plug of glass wool or sprinkling clean sand to the column so as to form a source of protection on top of the adsorbent (Pavia et al., 1976). Elution progresses by adding sample or the solvent at the rate at which samples leave the column.

2.15 Monitoring the Column

Monitoring the column is an important procedure which should be carefully observed after sample introduction. If the sample employed in the chromatographic column is coloured, the separation or extent of adsorption can be followed visually and the various bands are collected separately as they elute from the column. Where the components to be adsorbed or separated are not coloured, fractions of constant volume in pre-weighed flasks are collected. The flasks and contents are evaporated and the flasks reweighed. A

plot of fraction number versus the weight of residues after evaporation of solvent gives a typical chromatographic separation or adsorption plot . Monitoring the column could also be done by mixing inorganic phosphorus into the adsorbent that is used to pack the column. When the column is illuminated with an ultra violet light, the adsorbent will fluoresce and separation may be followed visually. Also, adsorption from solution is facilitated if instruments like spectrophotometers or refractometers are used to monitor changes in solute concentration on a continuous basis (Wing, 1992).

2.16 Column Parameters

A knowledge of column parameters is essential for the determination of the efficiency of a column. Partition data, the number of theoretical plates, breakthrough curves are derived through the determination of column parameters (Markl and Schmid, 1975). Detailed theoretical treatment of column parameters outlined below have been the elaborate work of Zweig and Sharma (1974), and Christian (1994).

2.16.1 Retention Time (t_R)

Retention time is the time elapsed between the introduction of the sample at the inlet of the column and the appearance of the maximum peak or sample.

2.16.2 Retention Volume (V_R)

The retention volume of a sample component represents the number of millilitres (mL) of mobile phase that must pass through the column to elute the sample. In gas chromatography, it is the volume of carrier gas required for elution of a substance. In

general, retention volume is simply equal to the mobile phase flow rate (F_C) multiplied by retention time,

$$\text{i.e. } V_R = t_R F_C.$$

2.16.3 Stationary Phase Volume

Stationary phase volume is determined by dividing the mass of the stationary phase put into the column by its density at the experimental temperature.

2.16.4 Mobile Phase Volume

Mobile phase volume is referred to as the interstitial volume, void volume or free volume of the column. It is usually determined by measuring the elution of break through volume of a "non-partitioning" substance which can be detected in the eluate by a simple sensitive method. Gamma emitting radionuclides such as ^{137}Cs are frequently employed for this purpose. The determination of the mobile phase volume through the employment of slurry and dry methods has been described (Markl and Schmid, 1975).

2.16.5 Support Material Volume

Support material volume is determined through the weight of the loaded support material used to make the bed and its density (either known or expressly determined).

2.16.6 Bed Volume

Bed volume is the sum of the volume of support material, the volume of the stationary and the volume of the mobile phases. Bed volume is determined by measuring the amount of water between two marks indicating bed length.

2.17 Column Operation

2.17.1 Elution Analysis

In elution analysis, a small portion of the sample mixture is applied onto the column. Here, a narrow band is formed at the head of the bed. Columns are eluted using a solvent which is less strongly adsorbed than the sample components; or generally the same pure solvent is used. Based on different degrees of retention caused by the difference in partition equilibria and/or mass transfer kinetics, the different components of the sample migrate with the mobile phase, at various speeds. The different migration rates of the sample components on their way through the bed leads to a separation of the mixtures. Separated bands are usually obtained from the columns.

2.17.2 Frontal Analysis

In frontal analysis, the sample is fed continuously into the column, the sample solution being used as the mobile phase for the elution. At the on set, the sample components are retained in the stationary phase. With time, the migration rate of the sample begins to differ based on different degrees of retention. The components with the least retention will come out first, then others follow. In essence, only one pure component can be obtained from this. Later, a mixture of increasing complexity is obtained with time.

2.17.3 Displacement Analysis

In the displacement analysis technique, a single portion of the sample mixture is introduced into the column as in elution analysis. Here, the displacer which is more strongly retained in the column than any other components of the mixture is introduced. This substance completely displaces the sample components from the stationary phase and

moves them down through the column. Displacement also takes place between sample components that show different retention and hence, on their movement down the column, the sample components are dispersed in different bands and contains the pure substance now washed out. Displacement also produces few pure components after which a mixture will be obtained with time.

2.17.4 Resolution

The objective of chromatography is to separate analytes into descrete bands. The quality of the separation is further enhanced by the extent to which the band centres move apart and also on the extent of band dispersion. Hence, resolution describes the quality and quantity of chromatographic separation (Small, 1989). The determination of widths involves measurements of peak of elution volumes and band widths and a value that expresses quantitative extent of resolution can be obtained. The expression used is

$$R = 2(V_2 - V_1)/(W_1 + W_2).$$

where R is resolution, V_1 and V_2 are elution volumes of two adjacent eluates, W_1 and W_2 are the peak widths at the base determined by drawing tangents through the point of inflection of the peaks.

2.18 Adsorption Kinetics

Kinetics is a useful tool employed to explain adsorption steps. Smith (1968), Weber (1972), Weber and Van Vliet (1980), Faust and Aly (1983) proposed that adsorption of organics by an adsorbent can be kinetically explained in three steps:

Step 1 involves transport of the adsorbate from the bulk solution to the surface of the adsorbent granule by molecular diffusion. This is the external or film diffusion. The mass transfer coefficient in film theory is related to the free liquid diffusivity of the solute, D_e, and the thickness of the diffusional layer, δ, as follows:

$$K_f = D_e / \delta$$

The concentration gradient in the liquid film around the granule is the driving force in the film diffusion.

Step 2, termed internal diffusion, involves the transport of the adsorbate from the particle surface interior sites by diffusion within the pore-filled liquid and migration along the solid surface of the pore diffusion.

Step 3 involves the adsorption of the solute on to the active site on the interior surfaces of the pores. Here, the overall rate of adsorption process will be controlled by the slowest step, which would be either film diffusion or internal diffusion. However, control may be also distributed between intraparticle and external mechanism in some systems.

2.18.1 Adsorption Processes

Adsorption is a physicochemical process (Poots and Mckay, 1979; Chermisinoff and Ellerbusch 1978). This statement implies that a physical or chemical process or both may be involved in a liquid-solid column chromatography. Physisorption and chemisorption take place when the adsorbate is in the liquid form. The adsorbate molecule becomes attached to the surface of the adsorbent thereby overcoming the kinetic energy of the

liquid contaminant. Therefore the forces involved here are physical or chemical (Wing, 1992).

2.18.2 Physisorption

Physisorption is a phenomenon whereby a molecule adheres to the surface with which it is in contact. This is the result of the force of attraction at the surface. The process by which surface energy attracts and holds molecules arises from the differences generating Van der Waals forces (Weber and Morris, 1964). The adsorbate becomes physically fastened to the adsorbent surface. It is a kind of multilayered adsorption where each molecule layer forms on top of the previous layer, the number of layers being proportional to the concentration of the effluent. Physisorption can be reversed in a condition where the strength of attraction between the adsorbate and the adsorbent collapses. Adsorbent regeneration after the process of physisorption may be feasible.

2.18.3 Chemisorption

Chemisorption occurs when a chemical reaction occurs during the adsorption process between the adsorbate and the adsorbent and a compound is formed. Energy is usually involved during the process of compound formation. Whether the energy involved in the process is evolved or absorbed, the process is not reversible and desorption is not feasible. Regeneration of the adsorbent at instances where chemisorption had occurred is not always possible because the process of adsorption in this case had evoked a chemical change of solutes (Zweig and Sharma, 1974).

2.19 Adsorption Isotherms

Adsorption isotherm is the relationship at a given temperature between the amount of substance adsorbed and its concentration in the surrounding solution (Culp and Culp, 1971). Weber and Morris (1964) presented three models based on the work of Langmuir, Brauner-Emete-Teller (BET) and Freundlich. In the Langmuir model, the degree of adsorption of a solute from an effluent or a solution of a dye onto an adsorbent is taken as defining the distribution of a solute in the effluent between the adsorbent and the liquid phase. The distribution rate is a measure of the degree of equilibrium in the adsorption process. This depends on the concentration of the solute in effluent and the concentration and nature of the adsorbent. Mathematically, the expression is put as the quantity X/M as a function of C at a fixed temperature, X/M being the quantity of solute from effluent or solution of dye adsorbed per gram of solid adsorbent. C is the concentration of the solute remaining in solution or effluent at equilibrium. An expression like this is called adsorption isotherm when a series of data of X/M is plotted against C for a given solution of dye or effluent. An adsorption theory must have to fit into an experimental isotherm. The usual relationship between X/M and C is possible for a system in which adsorption from a solution yields a deposition of only a single layer of solute molecule from a dye solution or waste water onto the surface of the adsorbent. The single layer adsorption is the Langmuir model. The model is based on the assumption that an energy of adsorption is on the surface. In the model, three assumptions are made:

(1) that maximum adsorption corresponds to a saturated monolayer of solute on the adsorbent surface;

(2) that there is no transmigratory activity of adsorbent molecule on the plane of the surface;

(3) that the energy of adsorption is constant.

Based on the above, Weber and Morris (1964) derived that,

$$\frac{X}{M} = \frac{AC}{C_s - C}[1+(A-1)\frac{C}{C_s}] \qquad \text{.....(1)}$$

where C = measured concentration of solution at equilibrium

X/M or X_m = the number of moles of solute per gram of adsorbent forming a complete monolayer on adsorbent surface,

X = the number of moles of solute adsorbed per gram of adsorbent at concentration C,

A = a constant expression of the energy of interaction with the surface,

C_s = the saturation concentration of solute and

C = equilibrium concentration

Equation (1) could be reduced to

$$X = \frac{X_m bC}{1 + bC} \qquad \text{.....(2) , if b is set to be eqaul to } A/C_s$$

where b is taken as a constant related to the energy of adsorption. If C is taken as negligibly small compared to C_s and A is assumed to be greater than 1, it means that two convenient forms of the Langmuir equation that arise are:

$$\frac{C}{X} = \frac{1}{bX_m} + \frac{C}{X_m} \qquad \text{.....(3)}$$

$$\frac{1}{X} = \frac{1}{X_m} + \frac{1}{bX_m}\left(\frac{1}{C}\right) \quad \text{.....(4)}$$

Equations (3) and (4) are used for the linearization of data that agree with the Langmuir model.

One other equation for isothermal adsorption the Freundlich or van Bermelen equation

$\frac{X}{X_m} = KC^{1/n}$, also assumes a monolayer adsorption and has been widely used for many years (Weber & Morris, 1964). In the equation, X/X_m is similarly defined as in Langmuir.

C = equilibrium concentration

K = constant.

Again it can be mathematically written as

$$\log\frac{X}{X_m} = \log_{10} K + \frac{1}{n}\log C$$

A log-to-log plot of X/X_m Vs C gives a straight line gragh for dilute solutions, log K is the intercept and $\frac{1}{n}$ is the slope (Culp and Culp, 1971). When C approaches C_S the total capacity of the adsorbent is given by the value X, and at this stage, the adsorbent is said to agree well with Freundlich or Langmuir equation.

The Brauner-Emete-Teller (BET) model is described as one representing many isotherms reflecting a multilayer adsorption process. The equation like that of the Langmuir is based on the assumption of uniform energies of adsorption on the surface. BET model is based on the following assumptions:

1. that n layers of adsorbate molecules form at the surface of the adsorbent and that the Langmuir equation applies to each layer;
2. that $(n\text{-}i)^{th}$ layer initiated prior to the completion of the $(n\text{-}i\text{-}j)^{th}$ layer in which i and j represent integral numbers such that $n > i > j > 0$;
3. that the equilibrium condition involves several types of surfaces. The number of layers of molecules on each surface site are equal. This assumption also considers that layers beyond the first one have equal energies of adsorption, the BET equation takes the simplified form

$$\frac{X}{X_m} = \frac{AC}{C_s - C}[1+(A-1)\frac{C}{C_s}] \qquad \text{.....(5)}$$

where all terms are as defined in the langmuir model. Rearranging,

$$\frac{C}{(C_s - C)X} = \frac{1}{AX_m} + \frac{A-1}{AX_m}(\frac{C}{C_s}) \qquad \text{.....(6)}$$

A plot of $\frac{C}{(C_s - C)X}$ vs $\frac{C}{C_s}$ gives a linear plot with a slope $(A - \frac{1}{AX_m})$ and with an intercept of $\frac{1}{AX_m}$ for data that agree with the BET model.

2.20 Factors Affecting Adsorption

2.20.1 Residence Time of the System

Contact time is a very important parameter in adsorption experiment. Adequate time is required to allow the adsorbate move from the bulk solution to the surface of the adsorbent particle (Chermisinoff and Ellerbusch, 1978). Also, if adequate time is allowed

between adsorbent and adsorbate to contact properly, an avenue would be created for the adsorbate to migrate to the adsorption site onto the surface of the adsorbent particle. Moderate flowrates are therefore essential to allow time for effective contact. In most adsorption experiments, a preliminary work is always done to estimate the residence or contact time required to attain equilibrium. The procedure requires taking say, V cm^3 portion of the adsorbate and then agitating it in test tubes with various masses of the adsorbent (Chermisinoff and Ellerbusch, 1978; Poots et. al., 1976). At the end of each residence time, the adsorbate is carefully removed after centrifugation. The concentration of the adsorbate is then spectrophotometrically determined to measure the extent of adsorption. The procedure is repeated several times for a given volume of the effluent and a given mass of the adsorbent until such a time when the concentration of the adsorbate remains constant. Using these data, the quantity of adsorbate that remains in the effluent after each periodical agitation is plotted as a function of time. The graphs are recognised as isotherms of contact experiments.

If a flow rate is too slow and a sample overstays in the column, the rate of diffusion of the substance in the effluent may become greater than the rate at which the substance moves down the column. In this circumstance, the bands grow wider and more diffuse and the separation will become poorer. Also, an eluting solvent that elutes too fast would not separate constituents, since time is not allowed for proper contact to allow adsorption (Pavia et al., 1976; Christian, 1994).

2.20.2 The Effect of Temperature

The process of adsorption is a spontaneous one (Faust and Aly, 1983). Adsorption is accompanied by a decrease in the system's free energy. There is always a decrease in the entropy due to loss of a degree of freedom of the solute passing from the dissolved to the adsorbed state (Young and Crowell, 1962). In this case it follows that from the relationship

$$\Delta G = \Delta H - T\Delta S$$

ΔH must always be negative regardless of the nature of interaction of forces. Lowell (1979) reported that the enthalpy change, ΔH, for a physical adsorption is in the range of 8 - 63 kJ/mol. An increase in temperature, would , therefore, result in reduction of the equilibrium adsorptive capacity, and lower temperature affects the viscosity and thermal stability of the test sample. For example, when the temperature for an adsorption experiment of activated carbon with benzene phonates was increased from 9.5°C to 18.5°C, the adsorption capacity of the activated carbon was found to decrease (Morris and Weber, 1964). Similar results were reported by Zogorski (1975).

2.20.3 The Effect of pH

pH is also a very important factor in the adsorption process. pH adjustments should be made with care so that the changes in pH do not degrade or decompose a particular component of the adsorbate or adsorbent (Chermisinoff and Ellerbusch, 1978). Chaney (1979) found that the adsorption capacity of peat was poor due to leaching of metallic ions in industrial effluents at pH 4.5 - 8.3 but the adsorption capacity of the peat was found to be good at pH 9 and pH 10.2. Coupal and Lalancette (1976) and Smith et al. (1978) reported similar results in their earlier works.

2.20.4 Nature of the Adsorbent

The chemical nature of the adsorbent, as well as its physical nature with respect to polarity, determine the process of adsorption. When the surface of an adsorbent is negatively charged, the adsorbent is unlikely to remove anion from an effluent and vice versa (Smith et al., 1978). Modification of some ion exchangers is usually done in order to match its function with the nature of the effluent encountered. Once the polarity of the surface of the adsorbent is similar to that of the adsorbate, adsorption is unlikely. Wood dust was found to adsorb acid dyes with much difficulty from waste water, while peat was found to adsorb the same dye with less difficulty. The poor performance of wood was due to the similarity of the polarity of the wood surface and that of the acid dye (Poots et al., 1976).

2.20.5 The Nature of the Adsorbate

Giles and Nakhwa (1962) observed that for an adsorbate to be properly adsorbed, it should have the following properties:

1. the adsorbate should be highly polar in order to ensure the attachment of the whole surface of the polar adsorbent;
2. the adsorbate should be partly hydrophobic to ensure adsorption by a non polar adsorbent;
3. the adsorbate should have a small molecular size, preferably with a planer configuration;
4. the adsorbate should not be surface active to avoid the formation of three dimensional geometry at the surface;
5. the adsorbate should be readily soluble in both water and non-polar solvents.

London dispersion, hydrogen-bonding, electrostatic and charge transfer are forces that can determine a physical or chemical adsorption, yet, their roles depend on the nature or polarity of the surface of the adsorbent and the polarity of the adsorbate (Zweig and Sharma, 1974).

2.20.6 Effect of Particle Size of Adsorbent

Particle sizes of adsorbents or matrices play an important role in the enhancement of any adsorption process. The rate of a heterogeneous reaction such as adsorption on a solid surface varies with available surface area and the particle size for a constant mass of the adsorbent (Weber and Morris, 1964). Breaking up a large particle size into smaller ones introduces a secondary effect, thus opening up tiny sealed channels in the adsorbent which in turn become available for diffusion and adsorption. The effect also slightly increases the specific area of a given mass of adsorbent . Sample retention volume and adsorbent retention capacity are each proportional to the specific surface area of adsorbent. For example, 50 μm particles give a significantly better column than larger particles for a given set of experimental conditions (Synder, 1971). The advantages of smaller particle sizes in the enhancement of adsorption efficiency of adsorbents has been severally reported (Markl and Schmid, 1975; Poots et al., 1976; Mckay et al., 1978; Chermisinoff and and Ellerbusch, 1978; Faust and Aly, 1983; Touchstone, 1993). Beyond a certain limit of smallness of particle sizes, however, the advantage of smaller particle size in the improvement of adsorption performance of adsorbents becomes outweighed by the disadvantages (Markl and Schmid, 1975). Here, excessive pressure is required in order to force the mobile phase through the packed column. The difficulty encountered in reaching

a uniform packing is additionally experienced in extremely fine material. Hence decreasing particle size beyond a particular limit results in the undesired decrease in permeability with no gain in the efficiency of separation (Halasz and Naefe, 1972). With the problem of an extremely small particle fraction of a given adsorbent envisaged, the report of Smith et al. (1978) put the lower limit for industrial application at 0.2 mm - 1.2 mm. However, with high pressure, (10,000 psi), column chromatography employing 1 μm particle size can be achieved (Synder, 1974).

2.20.7 Effect of Column Size and Adsorbent Quantity

In order to achieve a good result in the separation of a given amount of an adsorbate in an adsorption experiment, appropriate particle size and the quantity of the adsorbent are usually selected in a proportionate fashion in relation to the size of the column (Pavia et al., 1976; Synder, 1971). The amount of adsorbent should normally be 25 to 30 times as (by mass) large, as the amount of material to be separated by chromatography. Additionally, the column used should have a height to diameter ratio of about 8 : 1. About 30 cm long and 1 cm internal diameter columns including 50 ml analytical burettes have been recommended for column chromatography (Zweig and Sharma, 1974). The choice of size and length of the column, however, depends on the difficulty of separation. Compounds which do not separate with ease may require larger columns and more adsorbent, while compounds that can easily be separated may require reduced column size and less adsorbent. On the other hand, larger columns are at the expense of the efficiency of separation (Synder, 1971). The quantity of adsorbent required for a given sample size that can be placed on a given column is defined by the adsorbent linear capacity $\theta_o 1$. This is the weight of sample per gram of adsorbent which causes 10% reduction in the specific

retention volume, V_r^o, of some standard compound, relative to the contact retention volume observed for a smaller sample (Synder, 1971). Consequently sample quantity should be less than the linear capacity of the column both for constant sample migration rates and for maximum separation efficiency.

2.21 Related Works on Peat Adsorption of Colorants in Effluents and Dye Solutions

Ottermeyer (1930) employed peat and wood dust for the purification of dye waste water. The dyes employed for the research were vat, direct, basic, disperse, acid and substantive dyes. The peat and wood dust was mixed with water and pressed to remove soluble humin. It was dried at 110°C. 0.001% solution of each dye sample was passed through columns or tubes containing the wood dust and peat materials. The times for the filtrate to show slight coloration were noted. The result of the work indicated that basic and substantive dyes gave better adsorption rate than acid dyes. Mordant dyes were completely adsorbed in alkaline solutions. However, when peat and wood dust were used separately, peat showed considerably higher adsorptive power than wood dust, and it was said to be about twenty times the power of coke ash.

Poots et al. (1976) treated Telon acid blue on sphagnum peat. The peat was washed with distilled water at 90° for 1 hr. It was broken into various fractions for use. Adsorption and contact time experiments were conducted for each of the particle sizes. All the adsorption processes in the work was done in columns. Measurements of extents of adsorption was undertaken using a uv-spectrophotometer.

Coupal and Lalancette (1976) used peat moss for the treatment of waste water. The chemical and physical characteristics of the peat were discussed. Metal ions of concentrations up to 1.0 ppm were precipitated first, using either sulphide or hydroxides, and the water was allowed to stand for some time before it was circulated over peat. Metal ions with concentration less than 1.0 ppm were simply removed by peat by adjustment of pH between 6 and 8. For metal ions in the hexavalent form, the waste water was treated with $FeCl_3$ and Na_2S at pH 5.0 and pH 7.0 before the removal on peat was undertaken. For cyanide, the blue ferrocyanide was formed by treatment with ferrous tetraoxosulphate(VI). The prussian blue colour was removed on peat. For colorants, the appropriate flocculating agent was $FeCl_3$. The colorants removed were from five samples of waste water from different sources. The research concluded that the system could treat 240 gallons of effluent of concentration 100 ppm on 0.68 kg of peat. Regeneration of the peat could not be achieved, rather the spent peat was burnt and was reduced to a small volume of ash.

Mckay et al. (1978) conducted a comparative study between wood dust, fuller's earth, alumina, diatomaceous earth, activated carbon and peat. The dyes employed in the study were astrazone blue (CI basic blue 69), telon blue (CI acid blue 25), chlorazol blue (CI direct blue) and cibacet turquoise blue G (CI disperse blue 7). Uniform size particles of 150 -250 microns were used. Experimental isotherms for various dyes were obtained using the X/M vs C_e plots. Contact isotherms were conducted. Moderate temperatures and high concentrations of effluents increased adsorption capacity. The pH effect varied from one dye to another. Finally, the study concluded that peat was second in adsorption

performance next to carbon. Cost analysis however showed that peat was the cheapest of them all. The experiments were performed in columns.

Poots et al. (1978) determined the adsorption parameters of astrazone blue I on peat. Contact time experiments were demonstrated for the various particle sizes. The contact time experiments showed a complexity of mechanism where the rate determining steps involved intraparticle diffusion and boundary diffusion. The findings of this study were in agreement with the Langmuir and Freundlich isotherms. It was concluded that peat was an excellent adsorbent for the astrazone blue I. Smaller particle sizes adsorbed better than larger particle sizes. All experiments were conducted in columns.

Smith et al. (1978) reported the oil removing capability of peat. In the experiment, an oil-in-water emulsion was prepared in distilled water with Exxon 260 diesel fuel of density 0.8 g/ml. Columns of 6 mm internal diameter were used. The particle size of the Irish peat was 0.5 to 1.0 mm diameter. The oil concentrations after adsorption was measured by infrared (ir) adsorption of CCl_4 extracts.

Poots and Mckay (1979) conducted an experiment to determine the surface area of peat. The peat was washed with distilled water and dried at 80°C for 30 minutes. The dyes that were employed were p-nitrophenol, methylene blue and acid telon blue. Contact time experiments were conducted for telon blue. 100 ppm initial concentration of the dye was employed. The adsorption isotherms were in agreement with Langmuir isotherms. Strong cation exchange between dye ions and the acidic hydrogen ions in the carboxylic and phenolic hydroxy groups of peat was reported. The adsorption process was reported to be

predominantly chemisorption and enhanced a multilayer adsorption. An optical spectrophotometer was used for the measurements of dye concentrations.

Konzun and Nitievskaya (1983) treated petroleum waste water using filters with turf peat, meadow peat and peat moss. The peats were found to be quite effective for adsorption of petroleum product waste water.

Kubota et al. (1988) established the capability of peat for adsorption of colorants and gases in industrial waste. In the experiment, the peat fibre was washed with alkali, dried and then loaded with denitrifying bacteria in order to improve removal of ammonia. 50 cm internal diameter columns were employed. The columns were washed with 0.5% $Ca(OH)_2$, dried and then loaded with denitrifying bacteria. The workers reported that the system treated 50 mg/l of NH_3-containing gas from faecal waste treatment plant. 90% of ammonia from the odorous gas was reported removed

Sokolova (1982) used granulated meadow peat to remove some coloured metals in a solution of waste water. The metals were Zn^{2+}, Cu^{2+} and Ni^{2+}. Sorption effectiveness of the granulated peat was determined to be capable of effectively treating about 200 m^3 of waste water. Allen and Mckay (1978) employed peat for the removal of dyes from a multicomponent system waste effluents. Various methods of waste water decolorization were discussed. Peat was found to be remarkably efficient in adsorbing the dyes in the effluents.

Ibrahim (1995) carried out a preliminary investigation on maize peat and found it very effective in the treatment of textile waste. Maize peat has also been used in a combined matrix to remove colorants from textile effluent (Isuaikoh et al., 1998).

CHAPTER THREE

3.0 SOURCES OF MATERIALS

3.1 Reagents

All laboratory reagents used in this work were of analytical grades and no further purification was undertaken. Distilled water was used in all preparations and dilutions

3.2 Preparation of Standard Stock Solutions

Standard stock solutions were used in various experiments and were prepared as follows:

Preparation of Ammonium buffer pH 10: The ammonium buffer (pH 10) was prepared by dissolving 70.0 g ammonium chloride and 5.70 g ammonium hydroxide in 1000 cm^3 of aqueous solution.

Preparation of Phthalate buffer pH 4: Phthalate buffer (pH 4) was prepared by dissolving 10.12 g dry potassium hydrogen phthalate (KHP) in 1000 cm^3 of aqueous solution.

Preparation of 0.25 mol dm^{-3} Sodium Tetraoxosulphate(VI): 8.85 g sodium tetraoxosulphate(VI) was dissolved in 50 cm^3 of distilled water and transferred into a 250 cm^3 volumetric flask and diluted to the mark with water.

Preparation of 0.1 mol dm^{-3} Sodium Hydroxide: 1.0 g sodium hydroxide was dissolved in distilled water and diluted with more water to the mark in a 250 cm^3 volumetric flask.

Preparation of 5% Sodium Chloride: 5.0 g sodium chloride was dissolved in 25 cm^3 of distilled water and made up to the mark in a 250 cm^3 volumetric flask with water.

Preparation of 0.1 mol dm^{-3} Trioxonitrate(V) acid: 8.3 cm^3 of the acid (1.57 g/cm^{-3}, > 90%) was diluted in 100 cm^3 of distilled water and made up to the mark with water in a 1000 cm^3 volumetric flask.

Preparation of 0.3 mol dm^{-3} Silver Trioxonitrate(V): 50.4 g silver trioxonitrate(V) was dissolved in 250 cm^3 of distilled water and diluted with water to the mark in a 1000 cm^3 volumetric flask.

Preparation of 0.6 mol dm^{-3} Sodium Chloride: 35.10 g sodium chloride was dissolved in 200 cm^3 of distilled water and made up to the mark with water in a 1000 cm^3 volumetric flask.

3.3 Sources of Dye Samples

Anthraquinone acid blue (BDH) and Methylene blue, analar grade (BDH) were obtained from the Chemistry Department store, Ahmadu Bello University, Zaria and were used without further purification.

3.4 Sources of Textile Effluents

The effluents were obtained off the drains of the United Nigeria Textiles, Plc and Supertex factory, both located in Kaduna, Nigeria.

The test effluents were obtained separately from the following units of the United Textiles, Plc.

1. Treatment plant
2. Printing and dyeing
3. General outlet
4. Pretreatment
5. Indigo dyeing
6. Engraving
7. Wax recovery

Effluents from the Spertex factory were obtained from the following operational units:

1. Indigo dyeing
2. Washing
3. Wax recovery

For further use, all samples of the effluents were stored separately in plastic containers inside the refrigerator. In addition, equal portions of the separate effluents were pooled together to yield combined effluent for each factory.

3.5 Sample Description

The dyes and effluent samples were coded as follow:

Material	Code
Mehtylene blue	**M**
Anthraquinone acid blue	**A**
UNT Treatment plant	U_1
UNT Printing and dyeing	U_2
UNT General outlet	U_3
UNT Pretreatment	U_4
UNT Indigo dyeing	U_5
UNT engraving	U_6
UNT Wax recovery	U_7
Pooled UNT effluent	PU
Spertex Indigo dyeing	$\mathbf{S_1}$
Supertex Washing	$\mathbf{S_2}$
Supertex Wax recovery	$\mathbf{S_3}$
Pooled Supertex	PS

3.6 Development of the Maize Cob Peat

About 10 kg of the maize cob sample that was collected from Area F, Ahmadu Bello University, Zaria, was soaked in water in a 150-litre plastic jar. It was ensured that the maize cobs were completely covered in water to prevent evaporation which may expose them during the long period required for the decay. The plastic container and its content was left in the laboratory for about thirteen months in order to allow the peat to develop. The peat that developed appeared black and was soft enough to be broken with bare hands. The peat was removed from the plastic jar and was properly washed using a large

quantity of distilled water. The peat was dried for two weeks to enable it to be milled into various particle sizes.

3.7 Milling and Sieving the Peat

The peat was pounded using a wooden mortar and its pestle, and was sieved through a set of test sieves, model BS 410/1986, equipped with a bottom pan with the following sieve sizes: 150μm, 250μm, 300μm, 355μm, 425μm, 555μm, 850μm, 1.18 mm, 1.40 mm, 1.70 mm and 2.00 mm. For the sieving, the set of sieves with their covers and bottom pan was secured into an Endecott mechanical test shaker. The milled peat was continuously introduced into the arranged sequence of sieves with 2.00 mm at the top and 150 μm at the bottom. It was shaken at medium speed until all the milled peat was sieved into the various particle fractions.

3.8 Removal of Dust and Humin from the Peat

50 g of each particle size was separately covered with distilled water. Periodical squeezing and stirring was employed to remove yellow humin in the peat into the bulk of the water, white the washings were discarded (Ottermeyer, 1930). At the end of the process which lasted for about six days, the washed peat was air dried and stored in stoppered plastic bottles until required. The volume of water consumed by each particle size varied. The result is indicated in Table 4.1. A further rinsing to remove traces of humin after packing 4.0 g columns required various amounts of water, also indicated in Table 4.1.

3.9 Characterisation of the Effluents

Characterisation of the textile effluent was undertaken to determine some physical properties of the effluents.

3.9.1 Visual Characterisation

The colours of the effluents were visually observed as recorded in Table 4.2. samples PU and PS were also characterised using a Lovibond 3000 colour metre. The results are indicated in Table 4.2.

3.9.2 Spectral Characterisation

The absorption spectra of the effluents were determined using a Corning colorimeter 253. A small portion of each effluent solution was measured using distilled water as blank. The absorbances were measured at spectral intervals of 10 nm over the spectral range of 400 - 700 nm. The wavelength of maximum absorption (λ_{max}) was also recorded for each effluent. The spectral absorption maxima are shown respectively in Figures 4.1 - 4.4 and the summary of absorption maxima in Table 4.4.

3.9.3 Determination of Total Solid by Evaporation

50 cm^3 of each of effluents PU and PS was measured into a preweighed evaporating dish. The samples were evaporated to dryness and transferred into an oven at 103°C. The residue of each fraction was dried to constant weight, cooled in a desiccator and weighed according to the procedure of Vesilind (1975). Each experiment was carried out in triplicate. The total solid was calculated using the expression (Vesilind, 1975).

$$Ts = \frac{(D_S) - (D)}{V_S \text{ X } 10^{-6}}$$

where Ts = total solid in mg/L

Ds = weight of dish and solids

D = weight of dish

Vs = volume of effluent in cm^3 used.

The results are included in Table 4.4.

3.9.4 Determination of Suspended Solid by Filtration

50 cm^3 of each pooled effluent was introduced into a preweighed Gooch crucible with filter paper. After filtration, the crucible and its content was placed in an oven at 105°C for 24 hours. It was cooled in a dessicator. The process (Vesilind, 1975) was repeated until a constant mass was obtained. The suspended solid was calculated from the average of three results using the equation (Vesilind, 1975)

$$SS = \frac{(F_c) - (I_c)}{V_s \ \chi \ 10^{-6}}$$

where SS = suspended solid in mg/L

F_c = final weight of crucible and its content

I_c = initial weight of crucible

V_s = volume of effluent used in cm^3

The results are included in Table 4.4.

3.9.5 Determination of Dissolved Solids

Reasonable quantities of each PU and PS were separately filtered and kept. A 50 cm^3 portion of each sample was separately introduced into preweighed evaporating dishes

(Vesilind, 1975). Each evaporating dish was heated over a steam bath to dryness and was transferred into an oven at 105°C for 24 hours, to ensure complete drying. The evaporating dishes and their contents were cooled in a desiccator. The processes of drying and cooling were repeated until a constant mass was obtained for each sample. Three experiments were performed for each sample and the average computed. The dissolved solid was calculated according to the equation, (Vesilind, 1975)

$$D_s = \frac{(F_d) - (I_d)}{V_s \times 10^{-6}}$$

where D_s = dissolved solid in mg/L

F_d = final mass of evaporating dish and its content

I_d = initial mass of evaporating dish and its content

V_s = volume of sample is in cm^3

The results are included in Table 4.4.

3.9.6 Determination of pH

A Crison micro pH 2000 pH meter equipped with electrodes was calibrated using pH 4 and pH 10 buffers. The pH of each effluent was then measured. The results are shown in Table 4.5.

3.9.7 Solubility of Effluent Residues in Selected Solvents

Residues of PU and PS were developed by evaporating 50 cm^3 of each sample in an evaporating dish. When constant masses of the residues were obtained, the solubilities were determined in the following solvents: acetone, heptane, benzene, water, chloroform,

1,4-dioxane, methanol, butanol, acetic acid, petroleum ether and methyl ketone. The results of the solubility test are indicated in Table 4.6.

3.10 Thin Layer Chromatography (TLC) of Effluents

Textile effluents are characterised by the presence of a mixture of dyes. Thin layer chromatography is usually employed to establish the number of components in effluents (Rhys, 1978).

3.10.1 Preparation of Alumina and Silica Gel Plate Coatings

The procedure described below is that developed by Touchstone(1993). 30 g of alumina was accurately weighed and dissolved in 40 cm^3 of distilled water in a 250 cm^3 round bottom flask. The flask was shaken for five minutes to homogenise the mixture. The slurry was immediately coated over five (20 cm x 20 cm) glass plates whose surface had earlier been cleaned with petroleum spirit (60° - 80°). The coating was performed using a manual spreader with groove 0.25 μm. The plates were allowed to air-dry for thirty minutes and then activated in an oven for about 30 minutes at 114°C. The plates were stored in dessicators for use.

A similar procedure was employed for plate coating with silica gel in which 25 g of silica gel was dissolved in 50 cm^3 of distilled water in a 250 cm^3 volumetric flask. To obtain 1.00 mm preparative plate of silica gel, 60 g of silica gel was dissolved in 40 cm^3 of distilled water in a 250 cm^3 round bottom flask. The coating was done with the manual spreader using the 1.00 mm groove.

3.10.2 Spotting the Plates

0.1 g of residues of each of PU and PS was dissolved in 5 ml of distilled water in separate containers. The samples were spotted 2 cm from the base of the plate using a melting point tube. The spotted plates were allowed to air-dry for about 15 minutes before they were developed.

3.10.3 Plate Development

To develop a plate, a series of solvent mixture ratio (Touchstone, 1993) were tried as follows:

Methylketone-Acetic Acid-Methanol System on Alumina: Methylketone-acetic acid-methanol were mixed (120: 15 : 15) in a 250 cm^3 beaker. The mixture was swirled for about one minute. About 110 cm^3 of the mixture was transferred into a Shadon chromatographic tank and firmly covered. It was allowed to stand for about 45 minutes to equilibrate. Equilibration was accelerated by placing a sheet of thick absorbent Whatman No 1 ('seed' paper) at the side of the tank standing it in position to enhance plate development. After equilibration, the spotted plate was dipped into the tank ensuring that the spots were a little above the solvent level. Development of the plate lasted for about 1 hour. The colour and the shapes of the spots formed after development were noted. the results are summarised in Tables 4.7 and 4.8 for PU and PS respectively.

Butanol-Ethanol-Water System on Alumina: Butanol-ethanol-water (50 : 50 : 50) mixture was prepared. About 110 cm^3 of the mixture was transferred into the chromatographic tank and allowed to stand for 45 minutes to equilibrate, with the seed

paper in place. The effluents, PU and PS were separately spotted on the alumina plate and the latter was carefully dipped into the tank which was then firmly covered. The development of the plate lasted for about 3 hours. The results are summarised in Tables 4.7 and 4.8 for PU and PS respectively.

Benzene-1,4-Dioxane-Acetic Acid System on Silica Gel: Benzene-1,4-dioxane-acetic acid combination was 90 : 25 : 4. The development lasted 2 hours. An intense blue spot was formed by each sample. Both spots later faded away. A preparative plate was employed so that the fading blue substance could be obtained in their larger quantities for further identification.

Benzene-1,4-Dioxane-Acetic Acid System on Silica Gel - PREP TLC: In the procedure, effluents PU and PS were each streaked on a 20 cm x 20 cm plate coated with 1.00 mm silica gel. The plate development was performed in a similar way to those earlier described. The intense blue spots which appeared were immediately marked and scooped. The scooped sample was dissolved in water. Similar portions were also dissolved in 1,4-dioxane. Also, the absorption spectra of the scooped samples were determined on the Corning colorimeter-253. The results are shown in Tables 4.9 and 4.10 for PU and PS respectively and plotted in Figures 4.5 and 4.6 respectively.

Visualization of Chromatographed Plates: All chromatographed plates were visualized either with the naked eye or with the aid of a 254 nm uv lamp in the dark room. All the spectra observed are presented in Figures 4.5 - 4.6 for PU and PS respectively.

Determination of R_f Values: The R_f values of different components on the developed plates were determined for all the TLC experiments using the equation,

$$R_f = \frac{\text{distance moved by product spot}}{\text{distance moved by the solvent front}}$$

The values are summarised in Tables 4.7 and 4.8 respectively.

3.11 Determination of Natural Cation Exchange Capacity of Maize Cob Peat

2.0 g of the maize peat fraction of 150 μm was dry-packed on a small glass wool in a column. 250 cm^3 of 0.25 M sodium tetraoxosulphate(VI) solution was run from a separate funnel through the packed column at a rate of 2 cm^3 min^{-1}. The effluent received from the dripping column was collected into a 500 cm^3 conical flask. The contents of the flask was mixed with 3 drops of phenolphthalein and titrated to the pink end point with 0.1 M sodium hydroxide. The sodium tetraoxosulphate(VI) displaced the H^+ from the maize peat according to the equation (Bel'kevick et al., 1972; Bassett et al., 1986).

$$O\text{—}H + Na^+ \longrightarrow O\text{—}Na + H^+$$

The cation exchange capacity was calculated using the equation,

$$C = aV/w$$

where C = cation exchange capacity in meq/g

a = molarity of sodium hydroxide

w = mass of maize peat used

V = volume of NaOH used in cm^3

The ion exchange capacity was determined for other fractions of the maize peat. An average of the readings was obtained for each particle size. The results are shown in Table 4.11.

3.12 Determination of Cation Exchange Capacity of Maize Cob Peat Conditioned to the H Form with Trioxonitrate(V) Acid

250 cm^3 of 0.1 M trioxonitrate(V) acid was steadily supplied from a separatory funnel onto 1.50 g of neatly packed 150 μm particle size peat in a medium porosity filter paper resting in a funnel at a rate of 2 cm^3 min^{-1}. The acid effluent was received in a volumetric flask and discarded. The acid-treated peat was rinsed thoroughly until it became acid free. 1.0 g portion of the wet acid free peat was transferred into a 500 cm^3 erlenmeyer flask. 200 cm^3 of 0.1 M sodium hydroxide solution which contained 5% of sodium chloride was added. The erlenmeyer flask and its contents was stoppered and was allowed to remain overnight. 50 cm^3 of the supernatant was titrated with 0.1 M hydrochloric acid to the phenolphthalein end point. The remaining sample that was left on the medium porosity filter paper was dried to a constant mass at 80°C for eight hours (Snell and Ettre, 1972). The solid content of the dry sample, S, was computed by the equation;

$$S = \frac{W \text{ X } 100}{w}$$

w = weight of wet sample in gram

W = weight of dried sample in gram

The cation exchange capacity was computed using the equation;

$$C = \frac{(V)(M)(10)(100)}{(w)(S)}$$

Where V = volume of sodium hydroxide solution used for titration

M = molarity of sodium hydroxide

S = solid content of dried sample

w = weight of the wet sample

The average of two readings was computed for each peat fraction. The results are included in Table 4.12.

3.13 Void Volume Determination by Dry Packing

4.0 g of each particle size of peat was separately dry-packed in a series of 1 cm x 35 cm columns by adding each particle size of peat in their respective columns a little at a time. Each column was being tapped constantly until the columns had the desired quantity of the adsorbent. A known volume of water was carefully added drop-by-drop from a separatory funnel until the first drop of water was collected. The volume of water retained by each peat fraction in the column before the first drop of water appeared was noted. Careful note was taken to ensure that results were not recorded for columns in which channeling interfered. Two measurements were averaged for each peat fraction. The results are shown in Table 4.13.

3.14 Void Volume Determination by Wet Packing

4.0 g each peat fraction was packed as a slurry in a column. Water was run through each fraction in the columns. Next, a solution of 0.6 M sodium chloride was added drop-by-drop from a graduated separatory funnel just when the water level was a little above each

peat fraction in the columns. The volume of water retained by each peat fraction was gradually displaced as the sodium chloride eluted. The eluate was monitored with 0.3 M silver trioxonitrate(V) to detect its turbidity. The first drop of sodium chloride that appeared was noted. The volume of the water displaced before the first drop of sodium chloride appeared was recorded as the dead volume for each peat fraction in its respective column. Two results were averaged for each peat fraction. The results are shown in Table 4.14.

3.15 Determination of Wavelength of Maximum Absorption of Dye Samples

A solution of concentration 1000 ppm of each of samples M and A was prepared. The wavelength of maximum absorption (λ_{max}) was determined for each sample. The absorbance values were taken at intervals of 10 nm over the spectral range 400 nm - 700 nm.. The spectral values indicating the maximum peaks are shown in Figures 4.17 and 4.18 for M and A respectively.

3.16 Preparation of Calibration Curve

A solution of concentration 100 ppm of each of samples M and A was prepared. Each solution was stepwisely diluted to obtain other concentrations : 80 ppm, 60 ppm, 40 ppm, 20 ppm, 2 ppm and 0.4 ppm. To obtain an analytical line, a four fold dilution of each concentration was made to obtain 20 ppm, 15 ppm, 10 ppm, 5 ppm, 2 ppm, 0.5 ppm and 0.1 ppm. The absorbances of these concentrations were determined at the λ_{max} earlier determined in section 3.15. The calibration plots are indicated in Appendices A and B for samples M and A respectively.

3.17 Adsorption of M, A, PS and PU Using Test Tube Agitation.

15.0 cm^3 of 100 ppm solution of each of samples A, M, PU and PS was transferred into a test tube (2.5 cm x 15.5 cm) each containing 1 g of each particle size of the peat. The test tubes were firmly stoppered using rubber bungs, each test tube was securely clamped onto the test tube shaker and was agitated at medium speed for six hours. The test tubes were allowed to stand for 45 minutes. The contents were carefully decanted and the absorbances of the clear liquid portions determined using the Corning colorimeter-253. The concentration of the dyes adsorbed was determined with the aid of the respective calibration curves. The results of the preliminary experiment for each particle size on the set of samples are shown in Table 4.15 for M, 4.16 for A and 4.17 for PS and 4.18 for PU.

3.18 Determination of Equilibrium Time of Peat Adsorbent

The definition and the importance of contact time in adsorption experiments have been discussed elaborately in section 2.19. For the contact time determination, 15.0 cm^3 of 100 ppm solution of A was agitated with 1 g of peat fractions of 150 μm, 350 μm, 850 μm and 2.00 mm for four hours. At 30 minutes intervals, the dye sample was withdrawn from the test tubes by carefully decanting, and their absorbances were determined. A similar procedure was employed for samples M, PU and PS. Plots of concentrations of dyes left in solution after agitation against time were obtained. The results of extent of adsorption of the selected particle sizes for given samples are shown in the equilibrium plots of Figures 4.8 - 4.9.

3.19 Column Adsorption of M and A on Peat

In the column adsorption of M and A by each peat fraction, an initial concentration of solution of 100 ppm of each dye sample was employed to determine the efficiency and effect of particle size of peat. The initial concentration of 100 ppm was initially chosen because it is the maximum concentration expected to be found in a dye house effluent (Poots and Mckay, 1979).

Method

4.0 g of each maize cob peat fraction was packed as slurry in 1.0 cm x 35 cm column. The peat was thoroughly cleaned in the column. Next, the solution of concentration 100 ppm of the dyes were run each from the funnel drop-by-drop when the water level was just below the peat level.

850 cm^3 of the solution of concentration of 100 ppm of each dye was applied on each particle size in the respective columns. The results are shown in Tables 4.19 and 4.20. The results for a solution of concentration of 2800 ppm of the dyes adsorbed on the particle fraction are shown in Tables 4.21 and 4.22.

3.20 Column Adsorption of PU and PS on Peat

4.0 g of each particle size of peat was packed as a slurry. It was ensured that the peat was thoroughly cleaned in the column by monitoring using the Corning colorimeter-253.

40.0 cm^3 of each of the effluents PU and PS was employed on each particle size in the respective columns. The effect of particle size on adsorption efficiency are shown in

Tables 4.23 and 4.24. The time required by each particle size for the same volume of effluent is also included in these tables.

3.21 Adsorption of PU and PS on Peat Using Columns in Series

For each peat fraction, a set of four columns mounted in series were packed with 4 g of the peat as slurry. 150 cm^3 of effluent was treated on the first column. After adsorption in the first column it was transferred to the other columns in sequence until it was passed through the fourth column.The efficiency and extent of adsorption and the time taken by each fraction are shown in Tables 4.26 and 4.27.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSIONS

4.1 Removal of Dust and Yellow Humin from Peat

Table 4.1 indicates the quantity of water required for bulk washing and final cleaning of peat in the columns. From the Table, it is evident that smaller particle sizes required more water than larger particle sizes.

Table 4.1. Dust and Yellow Humin Removal

Particle size	Total wash water (l)	Cleaning in colum water (l)
150 μm	21	0.640
250 μm	13	0.524
300 μm	9	0.500
355 μm	9	0.500
425 μm	8.5	0.300
500 μm	5.0	0.26
850 μm	4.8	0.210
1.18 mm	3.5	0.160
1.40 mm	3.5	0.100
1.70 mm	2.8	0.100
2.00 mm	2.0	0.100

4.2 Lovibond and Visual characterisation of Effluent

Lovibond and visual colour of the test effluents are indicated in Table 4.2. The colours of U_1, U_3, U_4, S_1 and S_3 are exactly the same while the intensities of the blueness of U_2, U_5, U_6, U_7, and S_2 vary. The colours of the pooled effluents PU and PS are reflection of the general blue colour of the respective component effluents. Lovibond tinctometer also indicated high colour intensities for the pooled effluents.

Table 4.2. Lovibond and Visual Colour Data

Sample	Visual colour	Lovibond
U_1	Light blue	
U_2	Blue	
U_3	Light blue	
U_4	Light blue	
U_5	Deep blue	
U_6	Brownish	
U_7	Pale blue	
PU	Prussian blue	(4.4)B (23.0)R
S_1	Light blue	
S_2	Greenish blue	
S_3	Light blue	
PS	Blue	(54.4)B (43.0)R

4.3 Spectral Characterisation of Effluent

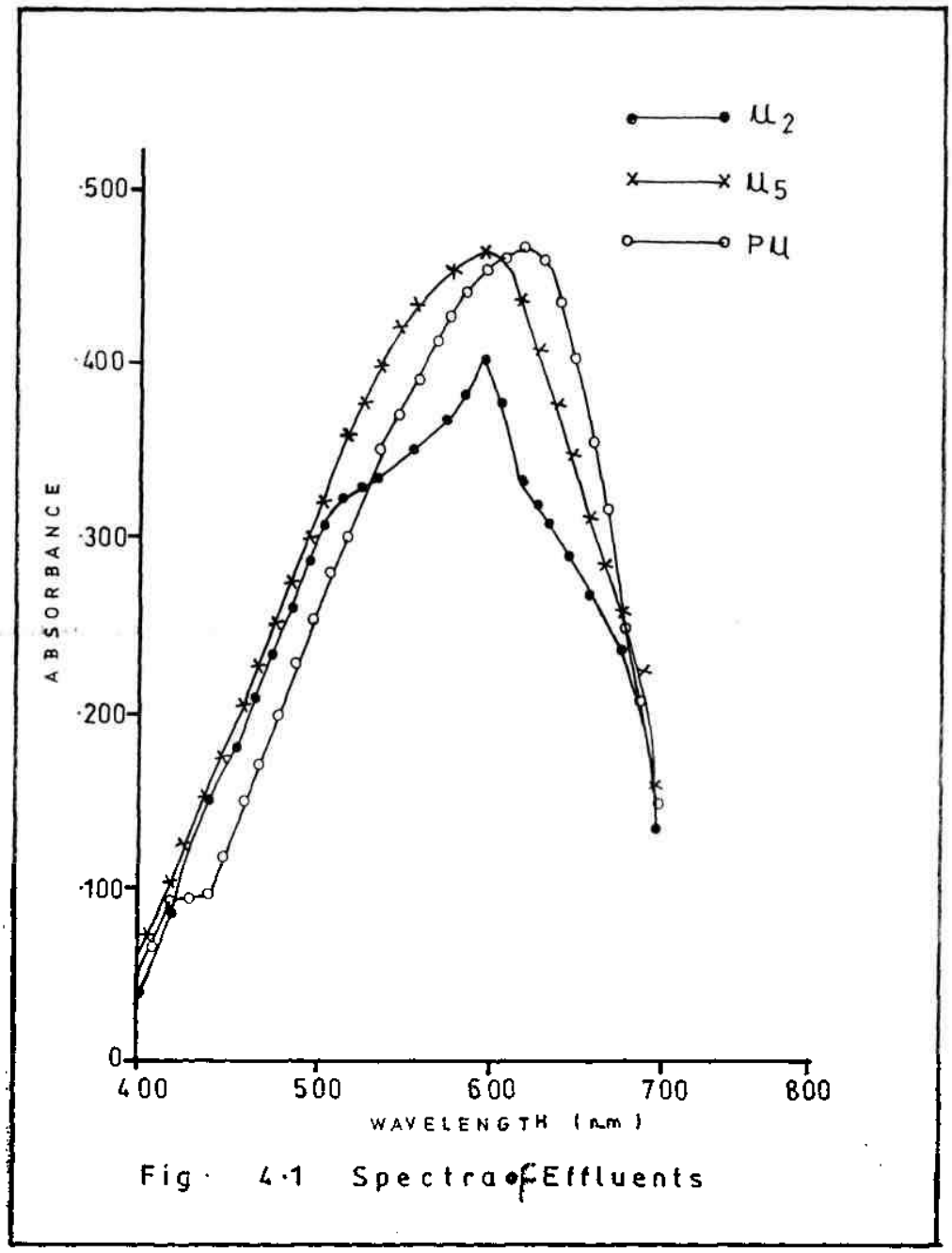
The absorption spectra of the test effluents are indicated in Figures 4.1 - 4.4 and which relevant information are summarised in Table 4.3. From the summary, S_3, U_1, U_2, U_4, U_5 and U_7 have the same λ_{max}, 600 nm. The similarity may be an indication that the component effluents contain the same chromophore. Also, S_1 and S_2 absorb maximally at 605 nm. U_3 and U_6 however, have λ_{max} of 610 nm and 570 nm respectively. The pooled effluent PU, has a λ_{max} of 620 nm. This value is higher than all its component effluents. The longer wavelength is as a result of the effect of the pooling of the component effluents together which has given rise to a change in medium (William and Fleming, 1980). PS has a λ_{max} of 509 nm. The value is smaller than those of its component effluents. It is also the result of change in medium arising from the pooling of the component effluents.

It may be argued that the similarities in the λ_{max} of wax recovery effluents of the two factories is an indication that the same dye is being employed in the wax recovery units of both factories.

Maximum absorbances (Table 4.3) of the effluents are different for all except U_1 and S_3 which are the same, with absorbance unit of 0.330. The absorbance value indicates the relative concentration of the colourant in an effluent.

Table 4.3. Summary of λ_{max} of Test Effluents

Sample	λ_{max}	Maximum absorbance
U_1	600	00.350
U_2	600	0.400
U_3	610	0.210
U_4	600	0.300
U_5	595-600	0.460
U_6	570	0.070
U_7	600	0.270
PU	620	0.465
S_1	600-605	0.380
S_2	605	0.171
S_3	600	0.350
PS	590	0.340



Fig· 4·1 Spectra of Effluents

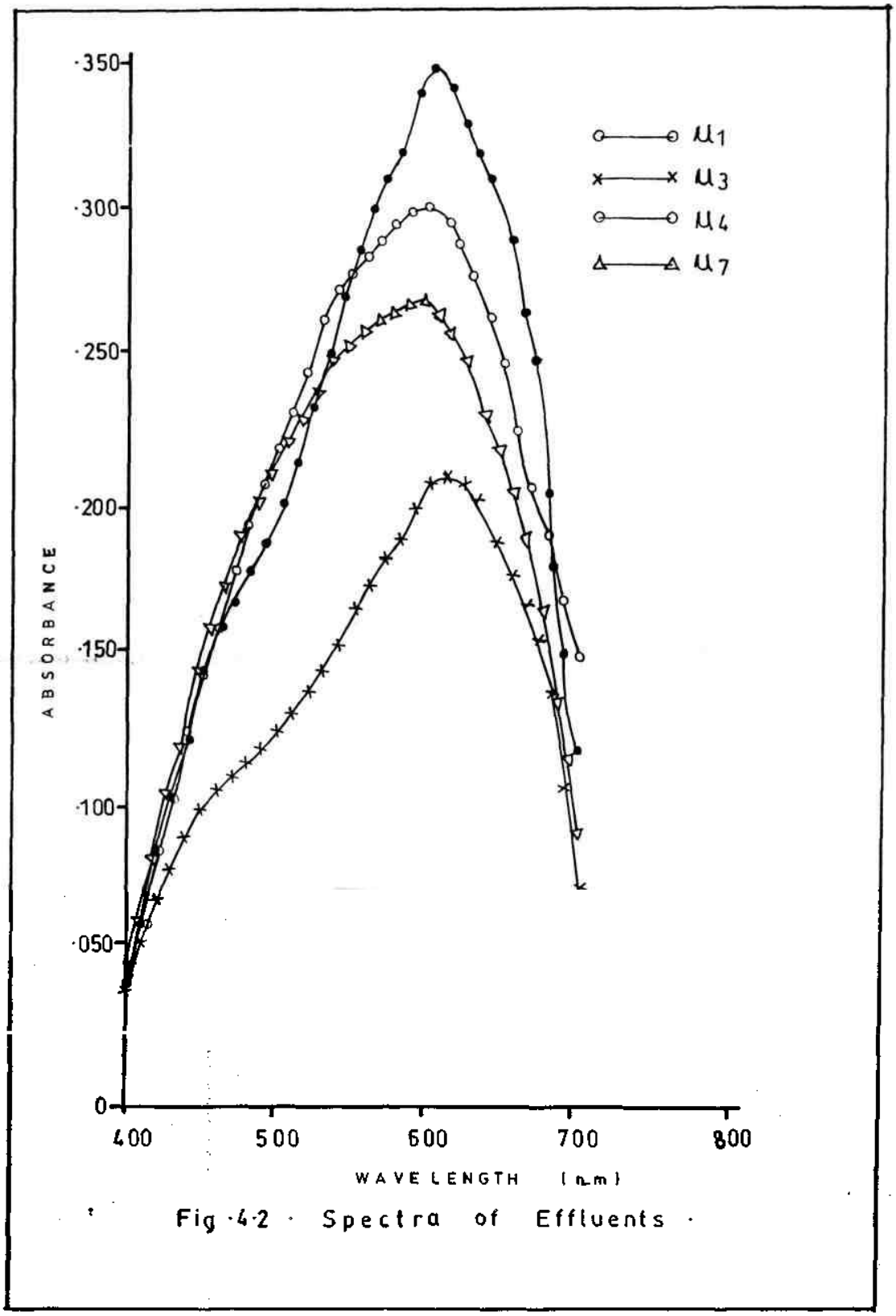


Fig ·4·2 · Spectra of Effluents ·

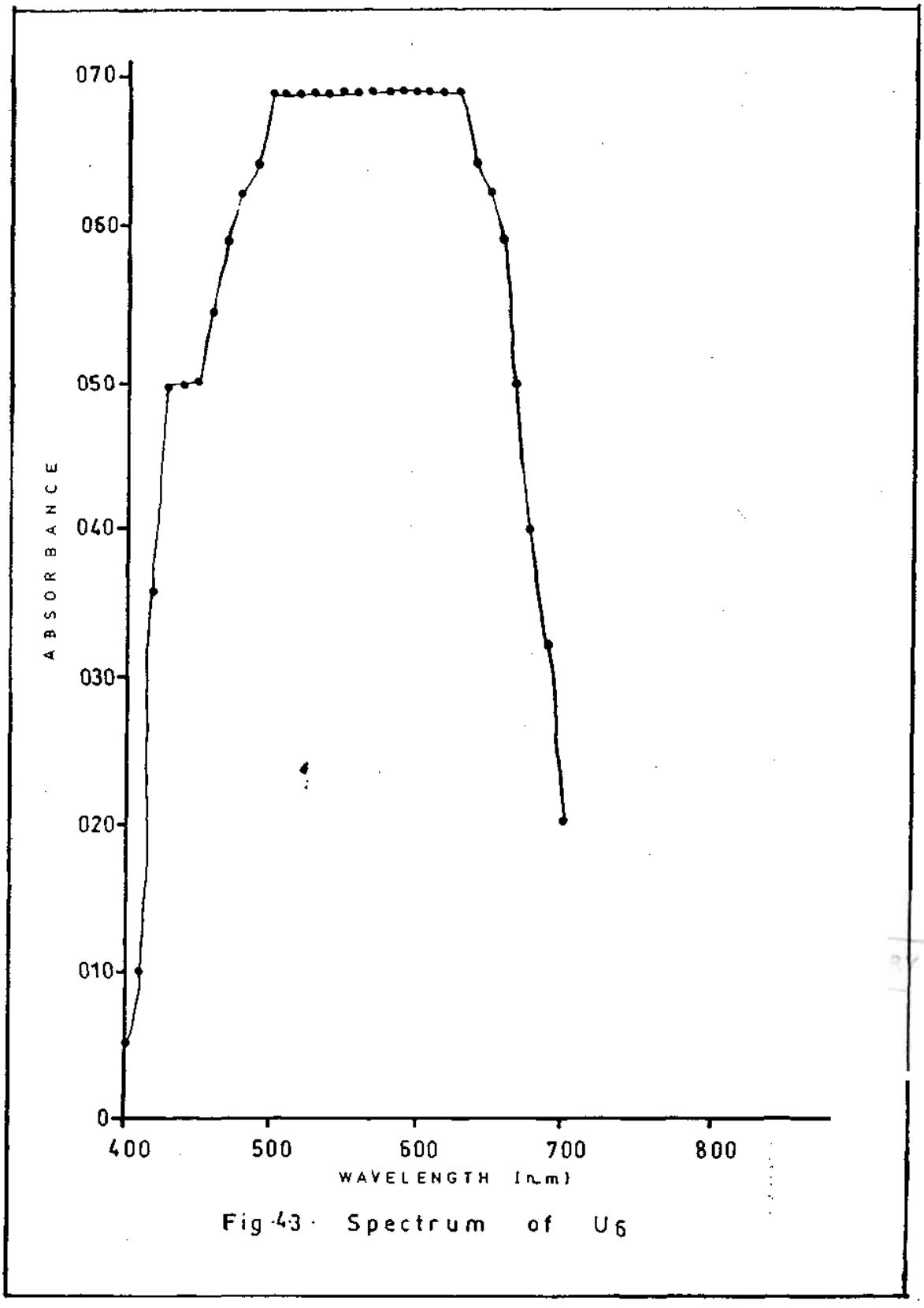


Fig 4.3 Spectrum of U_6

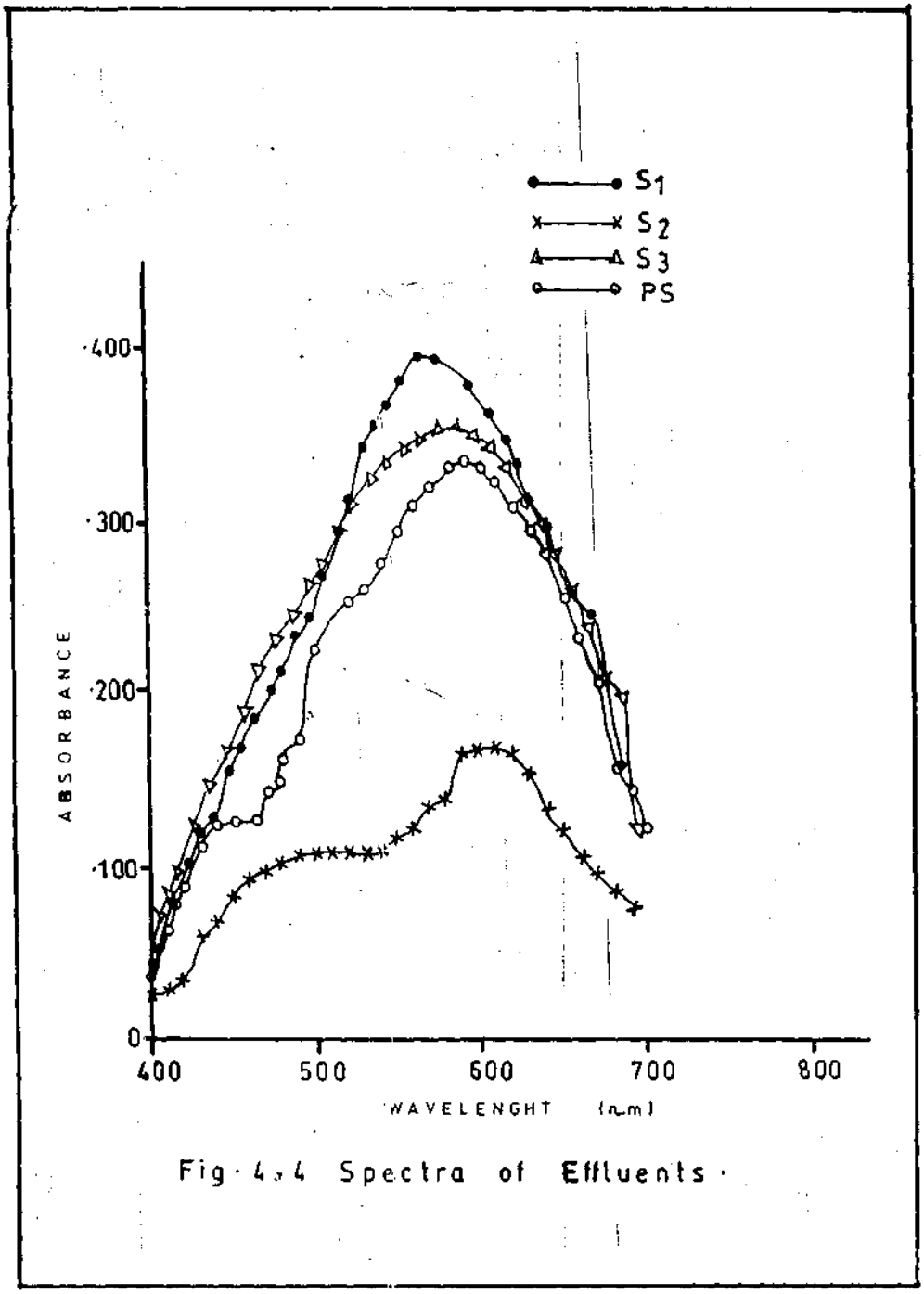


Fig. 4.4 Spectra of Effluents.

4.4 Suspended, Dissolved and Total Solids of PU and PS

The results of suspended, dissolved and total solids for PU and PS are indicated in Table 4.4. The suspended solids contents of both PU and PS exceed the recommended upper limit of 50 mg/l (Rhys, 1978). Effluents whose suspended solids contents exceeds the 50 mg/l would collect in the peat column causing excessive head loss down the column. Therefore these effluents are required to undergo filtration or crude settling before adsorption on peat (Coupal and Lalancette, 1976).

Although the values of dissolved and total solids appear high for both PU and PS, they are not unusual. Effluents from wool and clothing factories as is the case here, are characterised by high dissolved and total solids contents (Porter et al., 1972).

Table 4.4. Suspended, Dissolved and Total Solids

Test effluent	Total solids (mg/l)	Dissolved solids(mg/l)	Suspended solids (mg/l)
PU	2600	2020	580
PS	1670	1460	**210**

4.5 pH of Test Effluents

The rsults of the pH for single and pooled effluents are indicated in Table 4.5. The pH values are within the range 8 - 9 for all the effluents except for U_6 which has a low pH of 4.3. The different values obtained for the test effluents are characteristic of textile

effluents (Gardiner and Borne, 1978). Overall pH range of 8 - 11 is considered as normal for textile effluents while pH greater than 12 is considered as very high (Porter et al, 1972).

Table 4.5. pH of Test Effluents

Effluents	**pH**
U_1	**7.9**
U_2	**8.5**
U_3	**8.0**
U_4	**8.6**
U_5	9.0
U_6	**4.3**
U_7	8.1
PU	8.0
S_1	**8.8**
S_2	8.2
S_3	8.0
PS	8.6

4.6 Solubility of Residues of PU and PS

The results of solubility tests conducted for residues of PU and PS are shown in Table 4.6. PU and PS residues are respectively insoluble in acetone, heptane, benzene, and acetic acid. Varied solubilities were observed for both PU and PS in the other solvents and were found to be the same for both residues except for PU which did not dissolve in chloroform. Both residues were highly soluble in water.

Table 4.6. Solubilities of PU and PS Residues

Solvent	Residue	Solubility remark
Acetic acid	PU, PS	Fairly soluble
Acetone	PU, PS	Not soluble
Benzene	PU, PS	Not soluble
Butanol	PU, PS	Slightly soluble
Chloroform	PS only	Fairly soluble
Dioxane	PU, PS	Slightly soluble
Heptane	PU, PS	Fairly soluble
Methanol	PU, PS	Not soluble
Methylethyl ketone	PU, PS	Slightly soluble
Water	PU, PS	Highly soluble

4.7 Thin Layer Chromatography of PU and PS

The results of thin layer chromatography undertaken in section 3.10.1 - 3.10.3 are shown in Tables 4.7 and 4.8. Thin layer chromatography was undertaken to afford a knowledge of the number of components of dyes in each pooled effluent.

Table 4.7 shows that PU has three components, a yellow, blue and white dye with R_f values of 0.961, 0.722 and 0.922 respectively. PS also has a similar set of dye components with R_f values of 0.967 and 0.733 for the yellow and blue dyes respectively while that of the white dye is 0.896. The development time for the blue and yellow components was 3 hours and 2 hours respectively for both PU and PS, while the development time for the white dye in PU was $^3/_4$ hours and that of PS, 1 hour. The results indicate that PU and PS are multicomponent effluents.

Table 4.7. Thin Layer Chromatography of PU

Solvent system	Distance moved by solvent front (cm)	Distance moved by component (cm)	No/colour, shape of spots	Development time (hr)	R_f value
Butanol-ethanol-water on alumina	15.5	14.9	1, yellow, oval	3	0.961
Benzene-1,4-dioxane-acetic acid on silica gel	18.0	13.0	1, blue round	2	0.722
Methlethyl ketone-acetic acid -acetone on silica gel	15.4	14.2	1, white, oval	$^3/_4$	0.922

Table 4.8. Thin Layer Chromatography of PS

Solvent system	Distance moved by solvent front (cm)	Distance moved by component (cm)	No/colour, shape of spots	Development time (hr)	R_f value
Butanol-ethanol-water on alumina	15.3	14.3	1, yellow, oval	3	0.935
Benzene-1,4-dioxane acetic acid on silica gel	18.0	13.0	1, blue round	2	0.722
Methlethyl ketone-acetic acid -acetone on silica gel	15.4	13.8	1, white, oval	1	0.896

4.8. Preparative Thin Layer Chromatography of PU and PS

Figures 4.5 - 4.6 show the results of the preparative thin layer chromatography of PU and PS. A summary of the λ_{max} of the scooped dye components are shown in Tables 4.9 and 4.10 for Pu and PS respectively.

The λ_{max} for the yellow dye in PU was 480 nm while that of the blue component was 600 - 605 nm. The spectra of the white dye could not be taken due to the small quantity recovered. The blue component was unstable to light in 1,4-dioxane while the yellow dye was relatively stable. The λ_{max} of the yellow dye was 490 - 510 nm while that of the blue

component was 600 - 605 nm; exactly like that for PU. The blue dye component of PS was also seen to decolorise in 1, 4-dioxane when a portion of it was exposed to light.

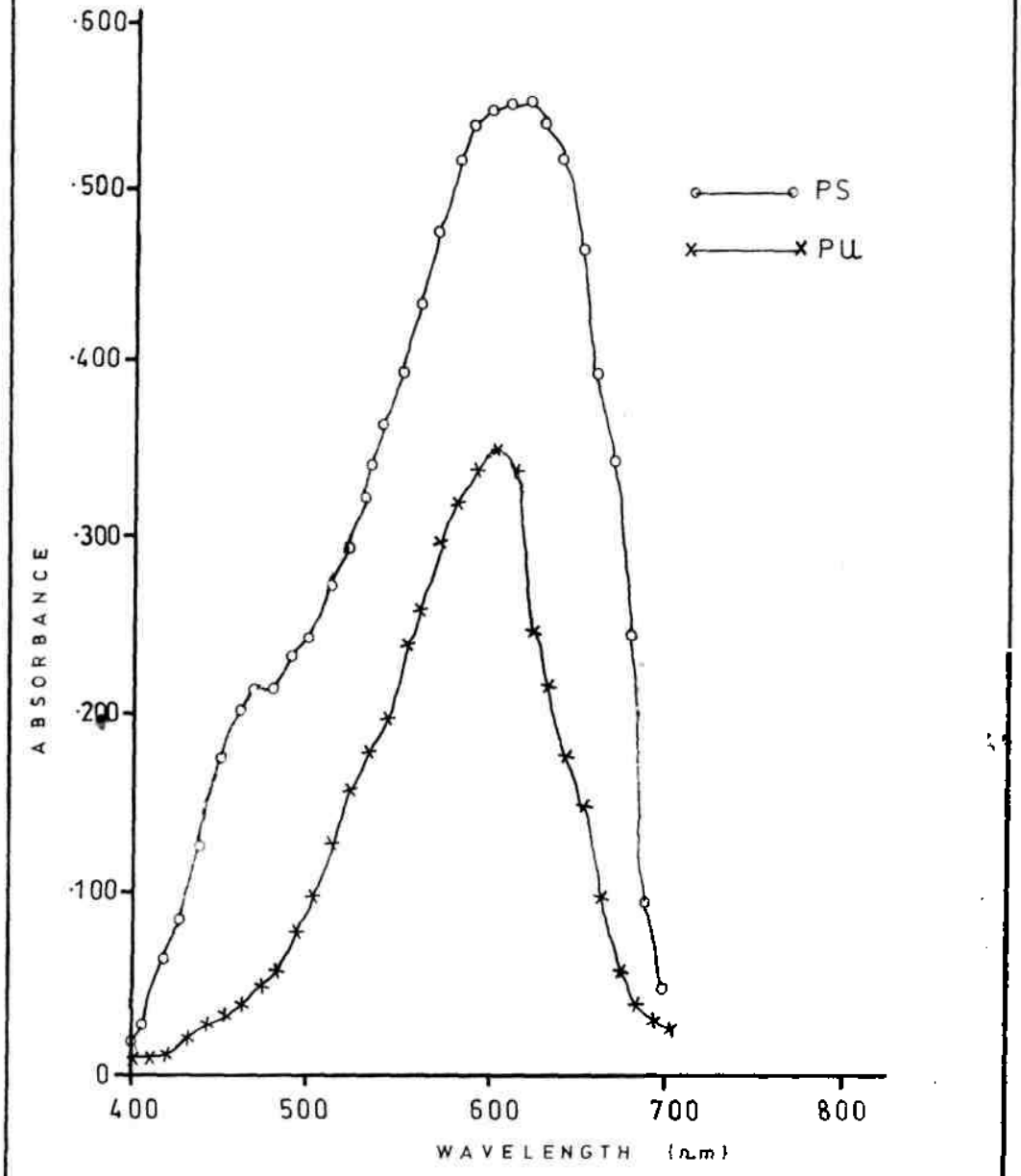
The gradual decoloration of the blue dyes in PU and PS on exposure to sunlight, may be the result of oxidation, a characteristic that is inherent in basic dyes (Reed, 1969). Both the blue components in PU and PS, whose maxima are at 600 nm, Figures 4.5 and 4.6 respectively indicate the possibility of an indigo dye, because in blue dyes, the principal blue dye encountered is 'indigotin' whose main source is an isatistintoria (Biodun, 1995).

Table 4.9. Preparative Thin Layer Chromatography of PU

Solvent system	Colour of streak	λ_{max} (nm)	Lability of scooped TLC
Butanol-ethanol-water on alumina	Yellow	480	Non-labile
Benzene-1,4-dioxane acetic acid on silica gel	Blue	600-605	Labile on exposure to light
Methlethyl ketone-acetic acid - acetone on silica gel	White	Not scaned	

Table 4.10. Preparative Thin Layer Chromatography of PS

Solvent system	Colour of streak	λ_{max} (nm)	Lability of scooped TLC
Butanol-ethanol-water on alumina	Yellow	490-510	Non-labile
Benzene-1,4-dioxane acetic acid on silica gel	Blue	600-605	Labile on exposure to light
Methlethyl ketone-acetic acid - acetone on silica gel	White	Not scaned	-



Fig·4·5 Spectra of Blue Dyes in Pooled Effluents Scooped from Prep·TLC·

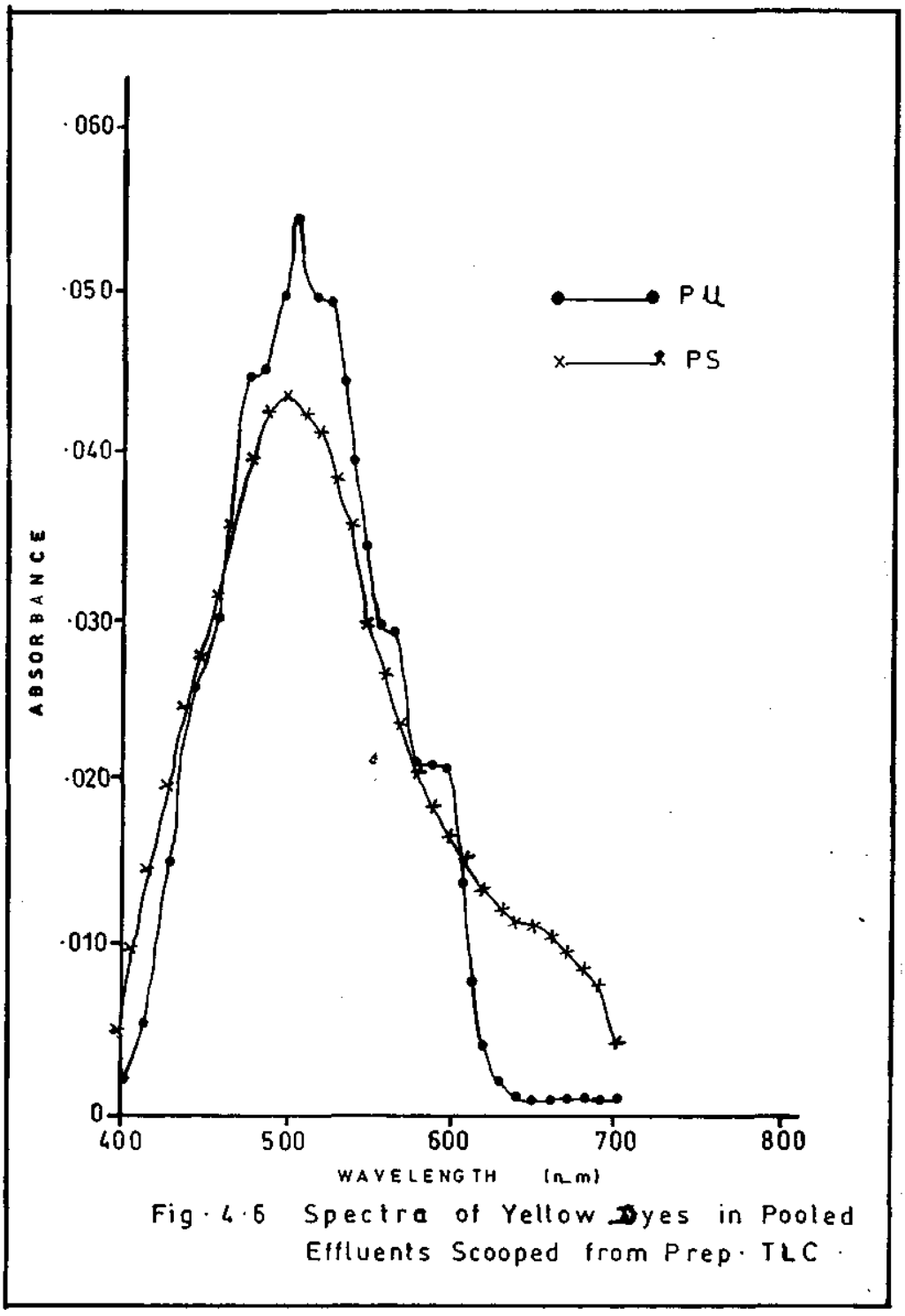


Fig · 4 · 6 Spectra of Yellow Dyes in Pooled Effluents Scooped from Prep · TLC ·

4.9. Natural Cation Exchange Capacity of Peat

The natural cation exchange capacity of peat for the various particle fractions is shown in Table 4.11. From the Table the trend is that the ion exchange capacity increases with decrease in the particle size of the fraction. 150 μm, the fraction of smallest particle size has the highest exchange capacity of 0.090 meq/2g of maize cob peat and 1.40 mm has the lowest exchange capacity of 0.006 meq/2g of peat, while 1.70 mm and 2.0 mm could not be recorded. The natural cation exchange capacity of the maize cob peat is generally low i.e. 0.002 - 0.090 meq/2g of maize cob peat compared to 98 - 100 meq/2g reported for certain other peats with barium ions as exchangers (Bel'Kevic et al, 1972). Ion exchange capacity of peats are on the general scale, low, because their exchange materials are known to be COOH and phenolic groups which are characterised as weak ion exchangers (Snell and Ettre, 1972).

4.10 Cation Exchange Capacity of Peat with H of HNO_3

The cation exchange capacity of peat with HNO_3 is shown in Table 4.12. Here too, the trend is that 150 μm particle fraction exchanges cation with H of HNO_3 > 250μm > 300μm > and continued in that order ending with 2.00 mm particle size with the lowest. The exchange capacity range was 0.003 - 1.65 meq/g of peat. The peat was leached to a large extent into solution when it was in contact with HNO_3, introducing difficulty in the detection of end-point.

Table 4.11. Natural Ion Exchange Capacity of Peat

Particle size	Volume of NaOH (cm^3)	Exchange capacity (meq/g)
150 μm	2.7	0.090
250 μm	2.5	0.085
300 μm	2.1	0.069
355 μm	1.7	0.053
425 μm	1.2	0.040
500 μm	0.9	0.030
850 μm	0.5	0.017
1.18 mm	0.5	0.016
1.40 mm	0.2	0.006
1.70 mm	-	-
2.00 mm	-	-

Table 4.12. Cation Exchange with H of HNO_3

Particle size	Ion exchange (meq/g)
150 μm	1.650
250 μm	1.250
300 μm	1.150
355 μm	0.980
425 μm	0.640
500 μm	0.470
850 μm	0.380
1.18 mm	0.083
1.40 mm	0.056
1.70 mm	0.011
2.00 mm	0.003

4.11. Void Volume by Dry Packing

Void volume provides adequate information on when to begin to collect treated effluents from a packed column (Pavia et. al., 1976). Void volume also determines how much of solvent or solution of effluent a matrix can retain. The results for the void volume of the various particle sizes by dry-packing are shown in Table 4.13. From the results, 150μm and 250 μm retained less volume of water than 300 μm, 355 μm, 425 μm, 500 μm and

800 μm while the retention volume of 1.18 mm, 1.40 mm, 1.70 mm and 2.00 mm are the least.

The trend is like that because tiny particle fractions are closely packed, therefore less air space is allowed between particles for water to occupy. Medium particle sizes on the other hand, have air spaces between them and therefore more water volume occupies the spaces. On the other hand, larger particle sizes do not pack as closely as the medium particle fraction. The inability of the larger particle sizes to pack closely provides a smaller surface area. Since retention volume and adsorbent retention capacity decrease with decrease in surface area, larger particle fractions have less retention of volume (Weber and Morris, 1964; Synder, 1974).

Table 4.13. Void Volume by Dry Packing

Particle size	Void volume (cm^3)
150 μm	14.60
250 μm	17.10
300 μm	19.10
355 μm	19.60
425 μm	21.00
500 μm	22.70
850 μm	23.00
1.18 mm	21.00
1.40 mm	8.80
1.70 mm	7.76
2.00 mm	6.60

4.12 Void Volume by Wet Packing

The results are shown inTable 4.14. The retention of volume (volume of water retained) by the method follows the same trend as in 4.11. However, all the particle fractions had retained volume less than their corresponding particle sizes that were dry-packed. This development arises because the particle sizes that were packed by the slurry method may have swollen thereby blocking up most openings or air spaces between packed particles.

Table 4.14. Void Volume by Slurry Method

Particle size	Void volume (cm^3)
150 μm	13.00
250 μm	15.80
300 μm	18.20
355 μm	18.00
425 μm	18.90
500 μm	20.00
850 μm	22.00
1.18 mm	9.80
1.40 mm	7.20
1.70 mm	6.10
2.00 mm	5.60

4.13 Absorption Maxima of M and A

Figure 4.7 shows the absorption spectra of M and A. The λ_{max} of M was 600 nm, while that of A was 605 nm. Both values were found to be similar to that in literature (Poots and Mckay, 1976), which were found to 595 nm and 600 nm respectively.

4.14 Calibration Graphs for M and A

Calibration curves prepared for M and A are shown in Appendices A and B respectively.

4.15 Adsorption of Peat Tested with M and A

Tables 4.15 and 4.16 show the adsorption of 15 cm^3 of 100 ppm of M and A by 1 g of each particle size of peat. In both results, the adsorption capacity showed a gradation in the order 150 μm > 250 μm > 300 μm > 355 μm > 425 μm > 500 μm > 850 μm > 1.19 mm > 1.40 mm > 1.70 mm > 2.00 mm. The trend here indicates that smaller particles sizes performed better than larger particle sizes. The peat adsorbed more M, basic dye, than A which is an acid dye. This difference was also reported by Ottermeyer (1930) and Poots and Mckay (1979).

4.16. Peat Tested with PU and PS

Tables 4.17 and 4.18 indicate the result of agitation in test tubes of 15 cm^3 of PU at absorbance of 0.465 and PS at absorbance of 0.340 with 1 g of each particle size. The trend in the adsorption of PU and PS is similar to that observed in section 4.15 where smaller particle fractions performed better than larger particle sizes. Particularly, the performance of the peat fractions 1.18 mm, 1.40 mm, 1.70 mm and 2.00 mm were extremely poor. In general, the performance of peat with PS is better than that of PU.

4.17. Contact Isotherms

The significance of resident or contact time of effluent with adsorption has been discussed (section 2.11.1). The determination of contact time of M, A, PU and PS with some selected particle fractions are shown in Figures 4.8 and 4.9. Smaller particle sizes took less contact time to reach equilibrium than larger particle sizes which took longer contact time. This means that for the same masses of different peat fractions, smaller particle fractions present larger surface areas due to secondary effect opening and it aids faster adsorption compared to larger particle sizes (Weber, 1963).

All the curves (or graphs) exhibited L shapes. The point of inflection of each curve is the point at which the adsorbent has reached its equilibrium and no more dye is adsorbed after that contact time. The L-shaped contact curves for the peat is an indication that the mode of adsorption by the peat is by ionic bond (El-Geundi and Aly, 1994), and since the peat could not be regenerated, it indicates chemisorption.

4.18. Column Test of Peat with M and A

Tables 4.19 and 4.20 are the results of the 850 cm^3 of M (100 ppm) and A (100 ppm) respectively treated with 4 g of each particle fraction of peat. The column adsorption showed that 150 μm and 250 μm treated the dye solution very well by reducing concentration of dye in 850 cm^3 from 100 ppm to 11 ppm and 18 ppm respectively for M and 13 ppm and 21 ppm respectively for A, while 300 μm and 355 μm reduced concentration of M to 23 ppm and 28 ppmm and that of A to 27 ppm and 33 ppm respectively. 425 μm performed moderately. The other larger particle sizes performed below average. Again, it can be observed that more M was adsorbed than A.

As the peat fraction remained for a longer time in solution, expansion of the particles occurred, air spaces got blocked and the flow rates got reduced drastically. That explaines why the adsorption time were quite long. By the trend, smaller particle fractions took longer time.

4.19. Column Test with Higher Concentration of M and A

The results for the increased concentration of M and A to 2800 ppm respectively, treated on 4 g of each particle fraction are shown in Tables 4.21 and 4.22 respectively. The result of the treatment of 70 cm^3 of each of M and A is considered a good performance by the peat. Particularly 150 μm, 250 μm, 355 μm and 425 μm performed well. The treatment capacity of other particle fractions was moderate.

Although the volume of dye solution treated by each fraction was 70 cm^3, the adsorption time was very long because of the high concentration of the dye solution which slowed down the flow rate due to excessive head loss down the column.

4.20. Column Test of Peat with PU and PS

The result of treatment of 40 cm^3 each of PS and PU having initial absorbances of 0.340 and 0.460 respectively are shown in Tables 4.23 amd 4.24. The adsorption performance of peat for the treatment of 40 cm^3 pf PS and PU on 4 g of each particle fraction is quite good, except for 8.50 μm 1.18 mm, 1.40 mm, 1.70 mm and 2.00 mm which adsorbed rather poorly. Again, PS was generally adsorbed more than PU for all the particle sizes.

The trend is in order because Pu has an absorbance of 0.460 while PS has an absorbance of 0.340 indicating that Pu is greater in concentration than PS.

Table 4.15. Peat Tested with 100 ppm M

Particle size	Concentration after adsorption (ppm)	% adsorption	Void volume (
150 μm	0.20	99.80	6.50
250 μm	0.80	99.20	7.50
300 μm	1.00	99.00	8.00
355 μm	2.00	98.00	7.00
425 μm	2.60	97.40	7.50
500 μm	3.00	97.00	8.80
850 μm	3.70	96.20	7.80
1.18 mm	5.80	94.20	8.50
1.40 mm	7.20	92.80	4.80
1.70 mm	9.25	90.80	4.10
2.00 mm	10.30	89.00	4.00

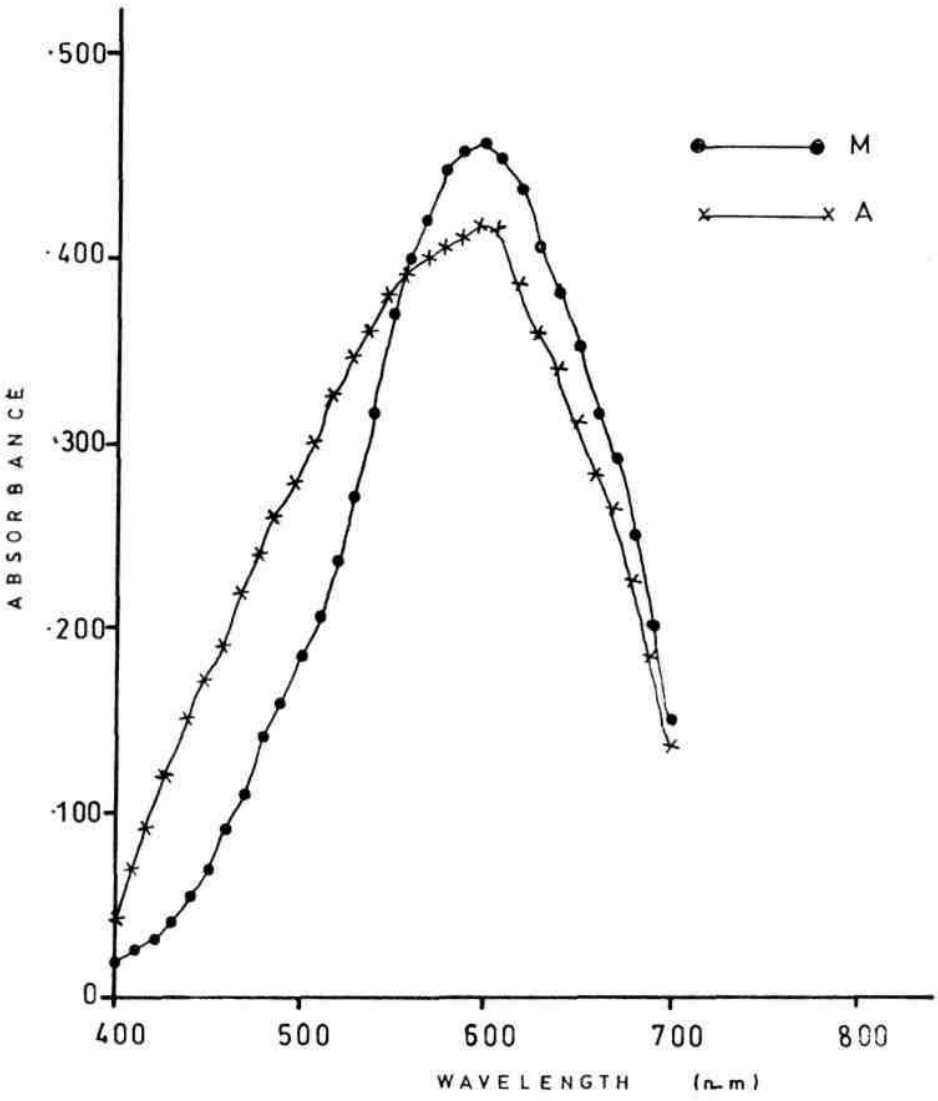


Fig · 4 · 7 Spectra of Adsorption maxima of M and A

Table 4.16. Peat Tested with 100 ppm A

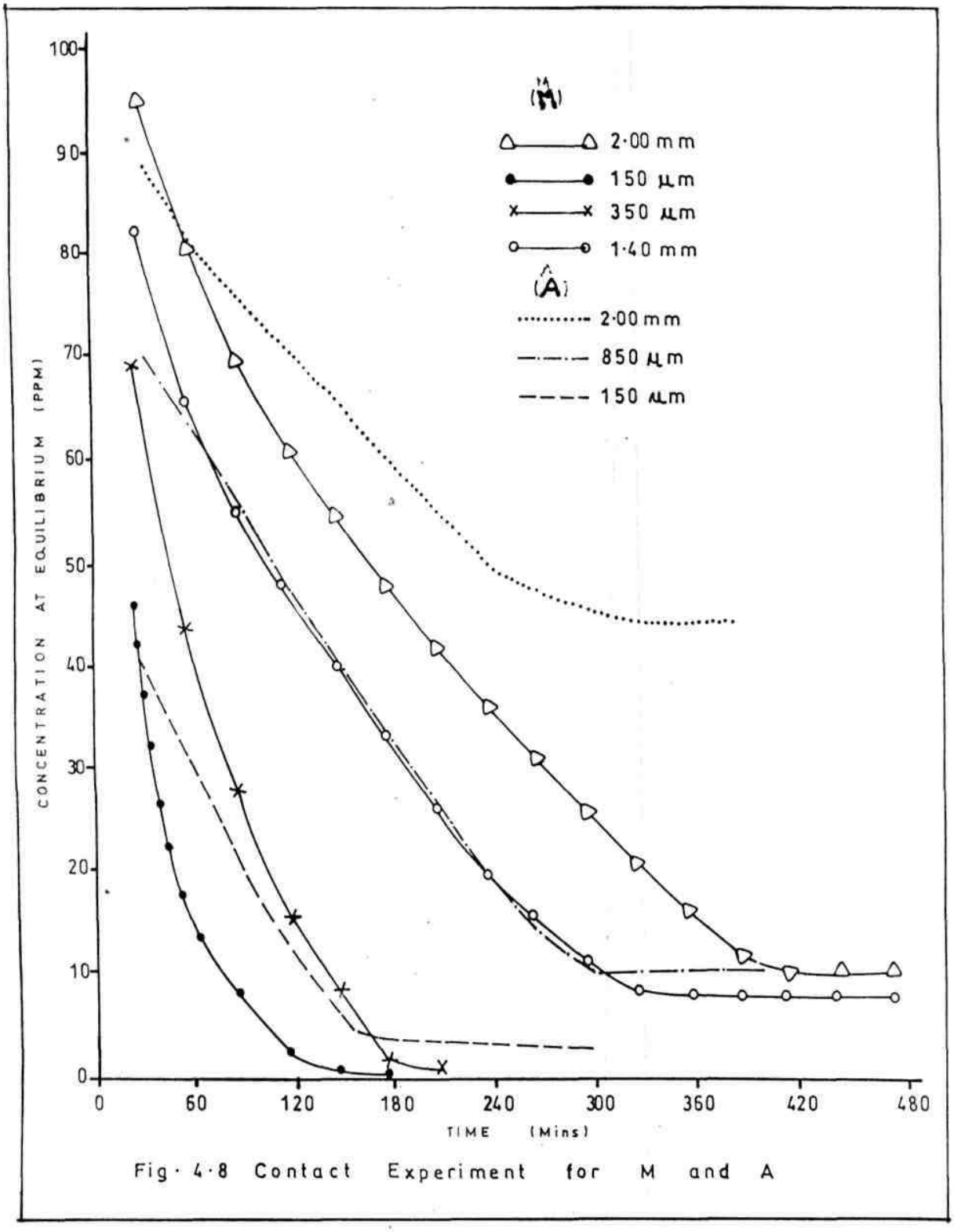
Particle size	Concentration after adsorption (ppm)	% adsorption	Void volume (cm^3)
150 μm	3.90	96.30	6.50
250 μm	5.35	94.65	7.55
300 μm	6.88	93.12	8.00
355 μm	7.12	92.88	7.00
425 μm	7.86	92.14	7.50
500 μm	9.38	90.62	8.80
850 μm	10.36	84.64	7.80
1.18 mm	25.43	74.57	**8.5**
1.40 mm	26.96	73.50	4.80
1.70 mm	33.29	65.71	4.40
2.00 mm	46.00	54.00	4.00

Table 4.17. Peat Tested with PU

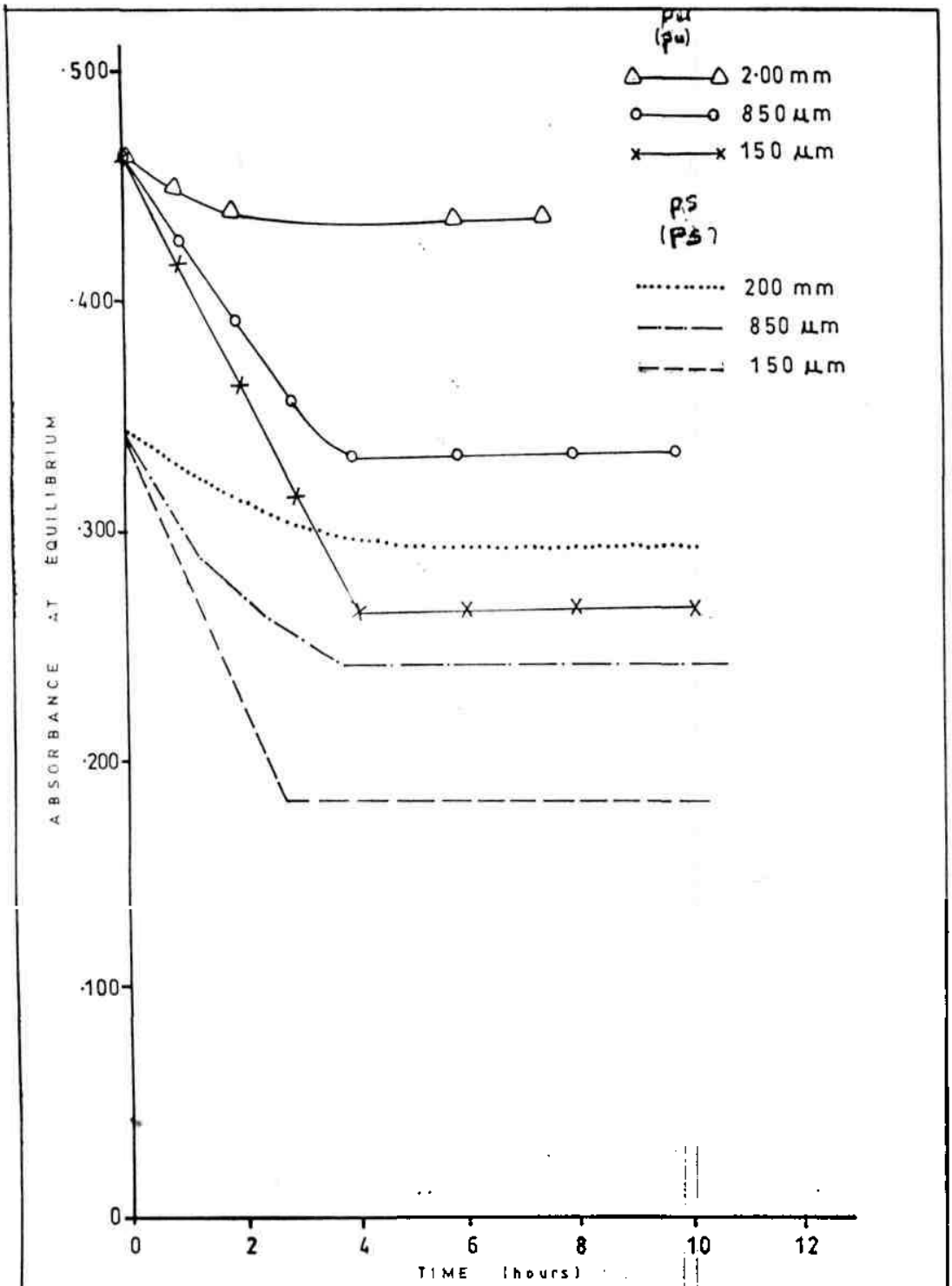
Particle size	Absorbance after adsorption	% adsorption	Void volume (cm^3)
150 μm	0.262	46.60	6.00
250 μm	0.270	41.94	7.00
300 μm	0.278	40.22	9.00
355 μm	0.280	40.00	7.50
425 μm	0.286	38.49	7.50
500 μm	0.310	33.33	6.80
850 μm	0.330	29.03	8.00
1.18 mm	0.350	24.73	5.00
1.40 mm	0.380	18.28	4.30
1.70 mm	0.400	13.98	4.00
2.00 mm	0.435	6.45	3.30

Table 4.18. Peat Tested with PS

Particle size	Absorbance after adsorption	% adsorption	Void volume (cm^3)
150 μm	0.180	47.06	6.00
250 μm	0.195	42.65	7.50
300 μm	0.225	33.82	8.50
355 μm	0.228	32.94	7.00
425 μm	0.230	32.35	7.50
500 μm	0.240	29.41	7.80
850 μm	0.240	25.00	8.20
1.18 mm	0.255	22.53	8.50
1.40 mm	0.260	17.35	6.80
1.70 mm	0.280	4.71	6.30
2.00 mm	0.320	3.00	5.50



Fig· 4·8 Contact Experiment for M and A



Fig· 4·9 Contact Experiment For PU and PS

Table 4.19. Column Test of Peat with M

Particle size	Concentration (ppm) after treatment	Time (hrs)
150 µm	11	72
250 µm	18	58
300 µm	23	65.5
355 µm	28	61
425 µm	34	56
500 µm	44	50
850 µm	53	46
1.18 mm	59	27.5
1.40 mm	63	15
1.70 mm	74	19
2.00 mm	88	14.5

Table 4.20. Column Test of Peat with A

Particle size	Concentration (ppm) after treatment	Time (hrs)
150 µm	13	72.50
250 µm	21	69
300 µm	27	66
355 µm	33	62.50
425 µm	42	56.50
500 µm	55	51
850 µm	69	50
1.18 mm	78	47
1.40 mm	83	28.5.
1.70 mm	89	23.50
2.00 mm	97	15.75

Table 4.21. Column Test with Concentrated M

Particle size	Concentration (ppm) after treatment	% adsorption	Time (hrs)
150 μm	**58**	97.00	91
250 μm	**64**	97.91	89.5
300 μm	**79**	97.15	86.5
355 μm	**108**	96.14	85
425 μm	**181**	93.57	78.75
500 μm	**196**	93.00	78.50
850 μm	**896**	88.29	62
1.18 mm	1300	82.50	39
1.40 mm	1800	64.29	26
1.70 mm	1860	33.57	14.5
2.00 mm	2065	26.25	13

Table 4.22. Column Test with Concentrated A

Particle size	Concentration (ppm) after treatment	% adsorption	Time (hrs)
150 µm	111	96.04	90
250 µm	128	95.42	92
300 µm	**139**	95.04	50.5
355 µm	**186**	93.36	48
425 µm	**199**	92.89	32
500 µm	**560**	80.00	24
850 µm	**890**	68.21	18
1.18 mm	1230	56.21	9.5
1.40 mm	1275	54.46	8.5
1.70 mm	2005	28.39	**8**
2.00 mm	2460	12.14	**3**

Table 4.23. Column Test with PS

Particle size	Absorbance after treatment	% adsorption	Time (hrs)
150 µm	0.012	96.40	**31**
250 µm	0.035	88.71	**28**
300 µm	0.048	85.88	**25**
355 µm	0.070	77.06	20.5
425 µm	0.088	76.47	**17**
500 µm	0.085	74.71	**15**
850 µm	0.109	68.50	**8**
1.18 mm	0.120	64.70	**5**
1.40 mm	0.168	47.06	**3**
1.70 mm	0.199	41.47	**3**
2.00 mm	0.225	25.00	**2.5**

Table 4.24. Column Test with PU

Particle size	Absorbance after treatment	% adsorption	Time (hrs)
150 μm	0.055	88.04	36
250 μm	0.078	85.04	33.5
300 μm	0.100	78.30	32.5
355 μm	0.155	66.30	29.5
425 μm	0.200	56.52	28
500 μm	0.232	49.56	23
850 μm	0.270	41.30	18
1.18 mm	0.290	36.96	8
1.40 mm	0.298	35.22	6
1.70 mm	0.325	29.34	4.75
2.00 mm	0.360	21.74	3.0

4.21. Adsorption with Columns in Series

The result of the successive column adsorption of PU and PS with initial concentration absorbances of 0.441 and 0.320 respectively are shown in Tables 4.25 and 4.26. It was observed that the final volumes of the treated effluents collected for Pu had their absorbances reduced from absorbance of 0.441 to absorbances of 0.006, 0.009, 0.042 and 0.062 by 150, 250, 300 and 355 μm particle sizes respectively. This is considered to be very good. The remaining particle fractions performed moderately. For PS, it was also observed that the final volumes of the treated effluents collected had their absorbances reduced from absorbance of 0.320 to absorbances of of 0.00 respectively by the particle fractions of 150, 250, 300 and 355 microns.

The remaining particle sizes of 425 μm, 500 μm and 850 μm performed well too. The problem of the method is the exccessive void volume and prolonged adsorption period.

4.22. Adsorption at pH 4.0 and pH 10.0

At these pHs, the dye solutions and the test effluent leached the maize cob peat for all the particle fractions and absorbances could not be recorded. This phenomenon was discussed in section 2.12.2.

Table 4.25. Successive Column Adsorption of PU

Particle size	Control (absorbance)	Column 2 (absorbance)	Column 3 (absorbance)	column 4 (absorbance)	Total void volume (cm^3)	Volume treated (cm^3)	Total time (hr)
150 μm	0.355	0.235	0.115	0.006	54.20	45.80	230
250 μm	0.358	0.258	0.129	0.009	65.50	33.50	116
300 μm	0.385	0.291	0.146	0.042	73.90	26.10	122
355 μm	0.395	0.302	0.175	0.063	74.10	25.90	112
425 μm	0.398	0.336	0.205	0.102	78.40	17.40	88.5
500 μm	0.411	0.357	0.228	0.165	82.60	27.12	77
850 μm	0.418	0.395	0.241	0.208	84.50	25.50	65
1.18 mm	0.421	0.398	0.295	0.225	80.40	19.60	41
1.40 mm	0.436	0.416	0.335	0.300	56.00	44.90	39
1.70 mm	0.436	0.425	0.388	0.300	30.00	72.00	26
2.00 mm	0.438	0.430	0.402	0.391	25.00	75.00	23

Table 4.26. Successive Column Adsorption of PS

Particle size	Column 1 (absorbance)	Column 2 (absorbance)	Column 3 (absorbance)	column 4 (absorbance)	Total void volume (cm^3)	Volume treated (cm^3)	Total time (hr)
150 µm	0.202	0.100	0.031	-	56.72	43.28	
250 µm	0.221	0.103	0.055	-	60.00	40.00	227
300 µm	0.236	0.131	0.030	-	71.33	28.67	158
355 µm	0.256	0.151	0.091	-	75.53	24.47	126.5
425 µm	0.271	0.162	0.100	0.019	77.72	22.28	103
500 µm	0.280	0.182	0.106	0.021	83.10	16.90	89
850 µm	0.291	0.212	0.120	0.046	84.86	15.14	72.5
1.18 mm	0.298	0.231	0.141	0.070	81.50	18.50	42
1.40 mm	0.300	0.249	0.201	0.140	55.00	45.00	39
1.70 mm	0.305	0.261	0.210	0.160	27.00	73.00	31
2.00 mm	0.310	0.281	0.230	0.192	23.99	76.00	17

CHAPTER FIVE

5.1. CONCLUSIONS AND RECOMMENDATION

The objectives of the study were to optimize the particle size of the maize cob peat developed for removal of colour from dye solutions and coloured effluents. The following objectives were ultimately achieved:

The maize cob peat developed has a good adsorption capability for removal of dyes in solution and colours in effluents. The effective particle sizes were observed to be 150 μm > 250 μm > 300 μm > 355 μm, while 425 μm, 500 μm and 950 μm performed moderately in the removal of dyes in solutions and colours of effluents. 1.18 mm, 1.40 mm, 1.70 mm and 2.00 mm performed poorly, especially on the test effluents.

It is essential to observe that the effective particle size established for the maize cob peat: 150 μm, 250 μm, 300 μm and 355 μm are relatively smaller particle fractions than the lower limit (0.29 mm - 1.20 mm) recommended by Smith (1978) for industrial application for a given adsorbent.

Some problems were encountered with the maize cob peat: the problems were associated with the long time and larger volume of water required to remove dust and yellow humin. Flow rates were very slow during adsorption experiments. The problem was traced to the fact that the maize cob peat expands in the columns in aqueous solutions; thereby blocking air spaces and reducing flow rates drastically. The availability and use of a peristaltic pump could over come the problem of low flow rates. The sensitivity of maize

cob peat to pH was observed during the cation exchange of HNO_3 with peat. It was also observed at pH 4.0 and 10.0. At all these stages, the peat was leached. The problem is a major one for most peats which have for long remained uncontrolled.

Regeneration of the maize cob peat was not feasible. This has been the general problem of all peats. Ashing of the used peat to a very small volume of material disposed as agricultural soil conditioner is recommended.

For a more effective and wider application, various forms of modifications of maize cob peat should be undertaken in order to discover optimum modifications for exploitation.

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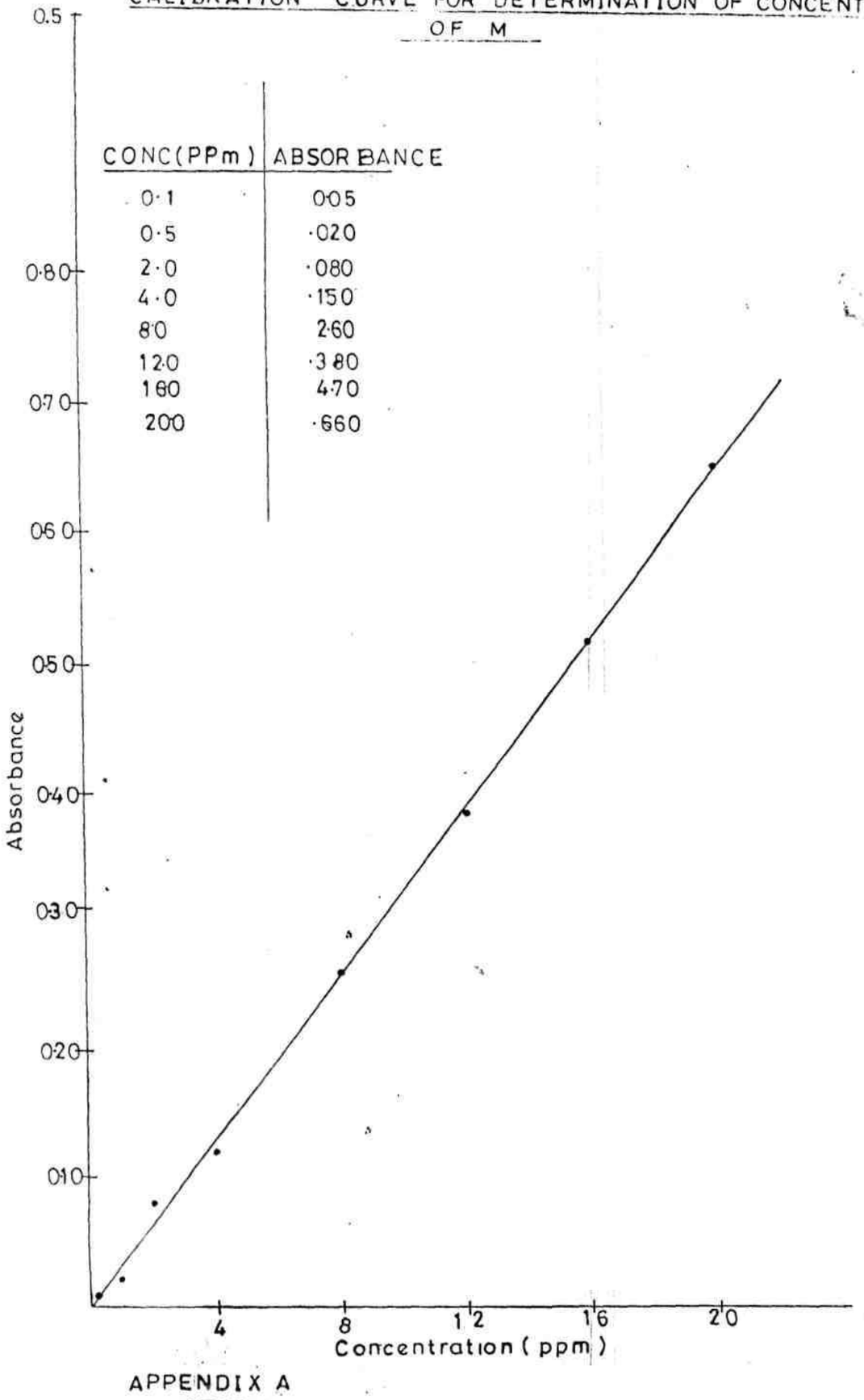
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CALIBRATION CURVE FOR DETERMINATION OF CONCENTRATION OF M

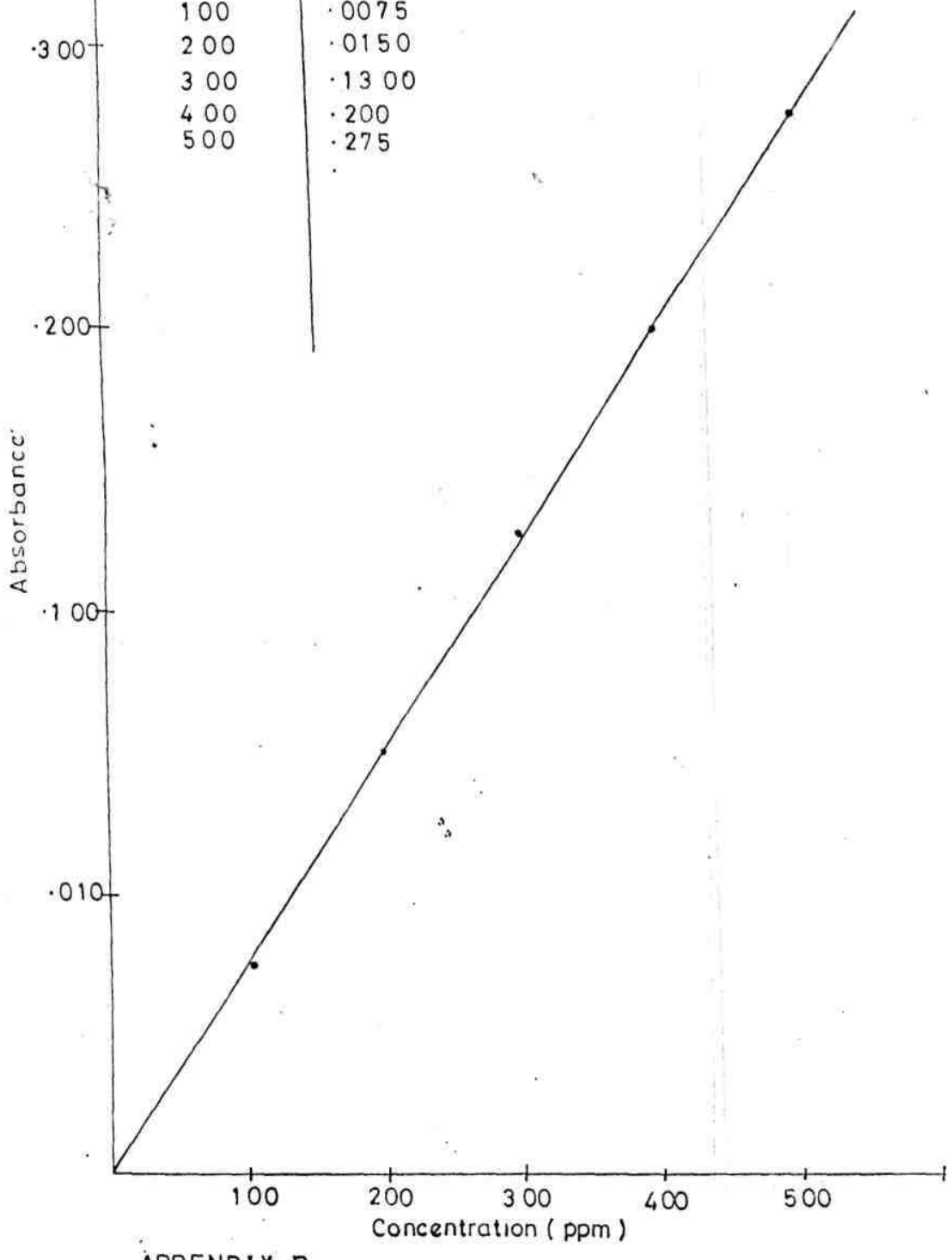
CONC(PPm)	ABSORBANCE
0·1	005
0·5	·020
2·0	·080
4·0	·150
8·0	2·60
12·0	·380
16·0	4·70
20·0	·660



APPENDIX A

CALIBRATION CURVE FOR DETERMINATION OF CONCENTRATION OF A

CONC(PPm)	ABSORBANCE
100	·0075
200	·0150
300	·1300
400	·200
500	·275



APPENDIX B