UNIVERSITY OF NAIROBI

Department of Civil Engineering

ASSESSMENT OF SAWDUST POTENTIAL IN THE REMOVAL OF DYE COLOUR FROM TEXTILE WASTEWATER.

WAIRURI J.K.
Reg.No: F/56/8171/99

Supervisor: Professor B.N.K. Njoroge.

ASSESSMENT OF SAWDUST POTENTIAL IN THE REMOVAL OF DYE COLOUR FROM TEXTILE WASTEWATER.

Candidate: WAIRURI J.K.
Reg.No:F/56/8171/99

Supervisor: Professor B.N.K. Njoroge.

A thesis submitted in partial fulfillment for the award of Master of Science in Civil Engineering.

Declaration

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

J.K. Wairuri_____Date 30/09/03
Candidate

This thesis has been submitted for examination with my approval as University supervisor

Professor.B.N.K.Njoroge_____Date 30/09/2003

TABLE OF CONTENTS.

Acronyms

ADF	Acid Detergent Fibre
ADL	Acid Detergent Lignin
APHA	America Public Health Association
BET	Breunner, Emmet, Teller
EDTA	Ethylenediaminetetracetic Acid
CWC	Cell Wall Contents
NDF	Neutral Detergent Fibre
NPN	Non Protein Nitrogen
UNEP	United Nation Environmental Programme

DEDICATION

I dedicate this work to all men and women whom in the time past and now, have and continue to give their best in time effort and other unquantifiable resources selflessly in stewarding God's magnificent creation.

Acknowledgement

In writing this research, I am greatly indebted to a number of people without who this work could not have been possible

First and foremost I greatly acknowledge Professor.B.N.K. Njoroge for being my supervisor and guiding me through the entire project. He gave thoughtful insights in experimentation, analysis and discussion of the results.

Technical staffs in the Public Health Engineering laboratory for technical advise availing themselves to be consulted when necessary. Chairman and technical staff of Department of Biochemistry for extending some of their facilities and equipment for uses in this project.Technical staff Department of Animal production for the help extended in part of the experimentation.

Staff of Woodmakers Limited for freely availing different varieties of sawdust. Fellow colleagues in the Department of Civil Engineering for their positive critique and sincere encouragement.

Thank you all, may the Lord God always bless you for what you have done for me.

List of Tables

List of Figures

List of Appendices

Abstract

The potential of hardwood and softwood sawdust as low cost adsorbents in the removal of a disazo dye (Congo Red) from water was evaluated. Two softwoods, Cypress *(Cypressus lusitanica*) and Pine *(Pinus spp.)* and two hardwoods Camphor (*Ocotea usambarebsis*), and Meru oak (*Vitex keniensis*) were used in the studies. Those materials were selected on the basis of their relative abundance as a waste in the timber mills industry.

Sawdust was found to have potential in removing Congo red dye from wastewater. The interaction of dye and the sawdust conform to Freundlich adsorption model with softwoods showing a higher potential both in capacity and intensity of removing Congo red dye from wastewater than hardwoods. The coefficients of Freundlich equilibrium model, k and n show that Cypress (*Cypressus lusitanica*) had the highest potential having k and n values of 0.40 and 1.79, respectively, followed Pine (*Pinus spp.*) with k and n values of 0.33 and 1.05, while Meru oak and Camphor had the two values being 0.23 and 0.823, and 0.0069 and 0.619, respectively.

The higher dye uptake by softwood sawdust is attributable to more pore spaces and high specific surface area for adsorption than hardwood. The softwoods had lower densities than hardwoods and thus the far more porous. The adsorption correlated positively with the hemicellulose extract of the sawdust, which was high in cypress, pine, Meru oak, and Camphor in that order. Cellulose and lignin content correlated negatively with the adsorption capacity and intensity.

CHAPTER 1 Introduction

1.0 Background.

Colour removal is a pertinent problem for all categories of textile effluents due to the variety of chemicals used in fabric dyeing and printing. Apart from the deterioration in the aesthetic value of the receiving water bodies, the presence of colour makes water reuse difficult (UNEP, 1993).

When colour removal is necessary, the following provides useful treatment technology:

- Segregation of all print wastes and disposal of each separately to landfill
- Reduction of colour shop losses by careful hand cleaning of all brushes, troughs, doctors' blades, cans, tanks, screens.
- In all weaving mills, reduce use of fugitive tints in weaving.
- Exhaustion of dye thoroughly in the dyeing process.
- Use of dye processes that can cause less colour losses e.g. solvent, pad and stream, microfoam, methanol and ammonia dyeing method.

Incase dye colour finds way into waste stream, removal may be achieved by techniques such as:

1. Chemical coagulation . It is generally applied to remove colour arising from dyes such as dispersed, vat, and sulphur dyes. Coagulants such as alum and ferric sulphate applied at a dose of 300 - 600 mg/l and lime at a dose approximately 300 - 600 mg/l will remove 75 -90% of colour (UNEP, 1993). These dosages are very high making chemical coagulation an expensive colour removal technique. Chemical coagulation cannot however achieve satisfactory removal of soluble dyes.
2. Adsorption. It is an efficient and popular method of colour removal . Several adsorbents are known to be capable of removing dyes from textile effluent. These include activated carbon, fullers earth, fly ash, fired clay, baggasse pith, wood, peat etc. (Poots et al. 1978). Techniques to regenerate adsorbents include the use of bouler water, organic solvents and catalytic oxidation. The pH must be adjusted to near neutral and suspended particulates must be removed for adsorption unit to function properly.

3. Colour removal in biological treatment. It can be improved by addition of powdered carbon (as a catalyst) to the aeration basin in activated sludge system (UNEP, 1993). This system will not remove colour as efficiently as adsorption. However, an additional 20-55% reduction in colour can be realised from this process.

Other promising techniques for colour removal are ozonation and hyperfiltration. (UNEP ,1993)

1.1 Problems associated with Dyes and Textile Industry

Dyes have been reported to be among the different pollutants of aquatic ecosystems with world production estimated at 640,000 tonnes in 1978(Clarke and Anliker, 1980). Dyes used contain many compounds whose environmental behaviour is largely unknown (Baughman and Perinich,1988). Although most dyes are considered inert or nontoxic, Some are not totally innocuous (Liang, 1991). Anliker et.al (1981) showed that dispersed dyes have high partition coefficient and solubility suggesting significant potential for bioconcentration.

In addition to this, it has been reported that the bulk of these are used in textile industry. Textile industries have the markets demanding better performance each year (Jones, 1974). Dyes have to be resistant to ozone, nitric oxides, light, hydrolysis and other degradative environments (Pagga and Taeger,1994). Studies on biological degradation of dyestuffs yields negative results as indicated above since the dyes themselves are designed to resist this type of treatment. The high colour value or absoptivity needed for a commercial dye is not an advantage when it ends up in a wastestream. Although some dyes are biologically degradable as noted by Pratt (1968), most that are present in wastewater are objectionable for their colouration. Dyes are too refractory to undergo degradation in the time required for conventional treatment. The auxiliary chemicals used in aqueous dyeing can also present a problem to biological processes. Carriers such as methyl naphthalene, chloro-benzenes, biphenols, orthophenyl phenol and benzyl alcohol are used to speed up the dyeing process. These chemicals may

eventually find their way into the receiving waters when the dyeing process is completed (Jones, 1974).

Also untreated effluents from dyestuff production and dyeing mills may be highly coloured and, thus, particularly objectionable if discharged into open waters. The concentration of the dye may be much less than 1 ppm, but the dye is visible even in small concentrations; the transparency of streams would also be reduced. Because dyes absorb sunlight, plants in the drainage stream may perish; thus, the ecosystem of the streams may be seriously affected. Possible chronic risks of colourants and their intermediaries are carcinogenicity and to a lesser extent sensitization and allergies (Huang and Jang, 1993).

In the past, Kenya has experienced serious pollution problems resulting from discharge of dye waste into municipal waste treatment works. Investigations carried out on industrial effluents in Eldoret by OMS-Klaranlagen in 1985 confirmed that damage had occurred to the Eldoret sewage stabilization ponds due to high pH of the influent, dye stuff from textile industries and lack of pretreatment of industrial wastewater, especially those from textile industries (Sewe, 1986). Presently, textile dyeing by industries in Kenya's Export Processing Zone (EPZ) present give rise to coloured effluent which is discharged untreated to open streams. This poses a real challenge to the ecological balance in the streams.

1.2 Research objectives.

The objectives of the research were-:

1. To establish the properties of Cypress (*Cypressus lusitanica*), Camphor (*Ocotea usambarebsis*), Pine (*Pinus spp.*), and Meru Oak (*Vitex keniensis*) wood sawdus: as adsorbents.
2. To assess the potential of sawdust in removal of Congo Red dye from simulated wastewater.

1.3 Research Justification

Coloured effluent especially from textile industries and dyestuff houses poses a great challenge both to the environment and the industry. Various techniques have been used in removal of colour from dyestuff wastes. These include chemical oxidation, froth floatation, photochemical degradation, activated carbon adsorption and coagulation.

Chemical degradation by oxidation with chlorine or ozone is effective, but the oxidant requirements are high and expensive. The effectiveness of decolourisation by oxidation process is reduced by impurities in the wastewater. It may increase the amount of exhausted chlorine or ozone in the water and hence the treatment cost. Chlorine treatment works well with monoazo and anthraquinone anionic dyes but unsatisfactorily with disperse and direct azo dyes (Zollinger,1987).

The coagulation process only decolourises insoluble dyes, such as dispersed, but does not work well with soluble dyes (Kuo, 1992).

Photochemical degradation in aqueous solution is likely to progress slowly as synthetic dyes are, in principle, designed to possess high stability in light.

Adsorption technique has been tried using activated carbon and is still the most popular and widely used adsorbent: however, there are certain problems with its use. Activated carbon is quite expensive and the higher the quality the greater the cost; furthermore, regeneration using solutions produces an additional effluent, although quite small. In addition, activated carbon is quite expensive and the higher the quality the greater the cost. On the other hand, a brief economic comparison made between different adsorbents under similar experimental conditions by Poots et al. (1978), showed that wood and peat are effectively the most economical adsorbents for basic dye removal. Activated carbon removes most of dye on a unit weight basis while activated alumina is the most expensive because of its high cost and poor ability to remove basic dyes (Poots et al., 1978).

Table 1.1 shows the economic evaluation of various adsorbents in dye removal (Poots et al., 1978).

Absorbent Material	Comparative cost per Kg Adsorbent	Comparative cost to remove 1g of Dye	Mass(g) Adsorbent to remove 1g Dye	Time (min.) to 90% Equilibrium.
Carbon	1.00	1.00	1.3	150
Peat	0.04	0.07	2.4	200
Wood	0.01	0.07	8.9	200
Alumina	1.82	550	400	500
Fuller's Earth	0.66	20.2	2.0	200

CHAPTER 2

LITERATURE REVIEW

2.0 PROPERTIES OF DYES.

2.1. Introduction.

With few exceptions all dyes are aromatic organic compounds. They are divide into three main groups: non-ionic, anionic and cationic. The molecules of ionic (anionic or cationic) dyes are composed of two main parts, one of which is a complex aryl radical. This is the colour-imparting ion. If the balance of the charge on the latter is negative then the dye is classed as anionic. On the other hand, if the balance of charge on the ion is positive then the dye is classed cationic.

The second part of an ionic dye molecule is an inorganic ion (an aliphatic organic ion or, in a few cases, an aryl ion). The former is called the gegen-ion, and the latter the dye ion. The function of the gegen-ion is to balance the charge on the dye-ion and to render the dye soluble in water. With few exceptions anionic dyes are manufactured as metallic salts. The vast majority of anionic dyes are sodium salts of carboxylic acids, uranine being the most notable. In case of cationic dyes, gegen ion is usually the chloride ion. In vast majority of cases the gegen-ion could be replaced by another of the same charge without seriously effecting the functioning of the dye. For example, a calcium salt might be less soluble in water than a sodium salt. Similarly a sulphate might be less soluble in water than a chloride. When dyes are used as reagents for the detection of certain ions, due consideration has to be given to the gegen-ion of the dyes. However, unless the gegen-ion itself is coloured, it has no influence whatever upon the colour of the dye ion in aqueous solution. For example, pararosanaline chloride or sulphate or acetate exhibits exactly the same colour in solution. On the other hand, the dye ion cannot be replaced by another ion without profound changes in the nature and the functioning of the dye molecule. The individual chemical, physical and tinctorial characteristics of a dye are due to its dye ion.

The simple gegen-ion of a dye could be replaced by another dye-ion of the same charge as the original gegen-ion and of opposite charge to that of the first dye-ion. This would result in the formation of a polychrome compound dye. Such dyes are prepared for special purposes and their molecules consists of an electro-positively charged dye-ion and a negatively charged dye-ion. Dyes of this kind are insoluble in water but soluble in absolute and aqueous alcohol. Partial dissociation takes place in the latter. Such dyes are used in biological micro-technique for differential staining of acidic and basic elements of cells and tissues.

The colour index gives the structures of about 2100 anionic dyes and classifies them variously as "acid", "basic", "direct" and "mordant" according to the manner of usage in the textile-dyeing industry. About 1400 of these anionic dyes are amino dyes or imino amino acids. The remainder are wholly acid in that they have no basic side-chains.

By definition an "acid" dye is one which dyes wool from a dye bath which contains acid. Such dyes now, however, find their application not only for wool but also for silk, polyamide, acrylic and regenerated protein fibres. They are applied from dye baths containing sulphuric or formic or acetic acid or ammonium sulphate; sometimes from a neutral and occasionally from a slightly alkaline bath.

According to colour index, "direct dyes" are originally designed and marketed for the primary purpose of dyeing cellulosic fibres, such dyes having being defined as 'Anionic dyes having affinity for cellulosic fibres when applied from an aqueous dyebath containing electrolyte. Direct dyes provide the simplest means of colouring cellulosic materials as they are normally applied in the textile dyeing industry from a neutral to a slightly alkaline dyebath, at or near boiling point, to which sodium chloride and sodium sulphate is added. Direct dyes are anionic- most are amphoteric since they possess side chains which are basic in reaction.

Mordant dyes are described as dyes having the property of combining with metallic oxides and salts to form metallic complexes. Dyes of this class are, however, very difficult to define. The colour Index states that the make-up of this class not as a matter of strict definition but of a convention which has grown up over the years and which has no logical basis. The majority of dyes are used with the acid of the mordants, in the textile industry, mainly for dyeing wool, the secondary application being for dyeing silk and nylon and for printing on cellulose, silk and wool fabrics. The major classification of dyes by colligators is shown in Figure 2.1.

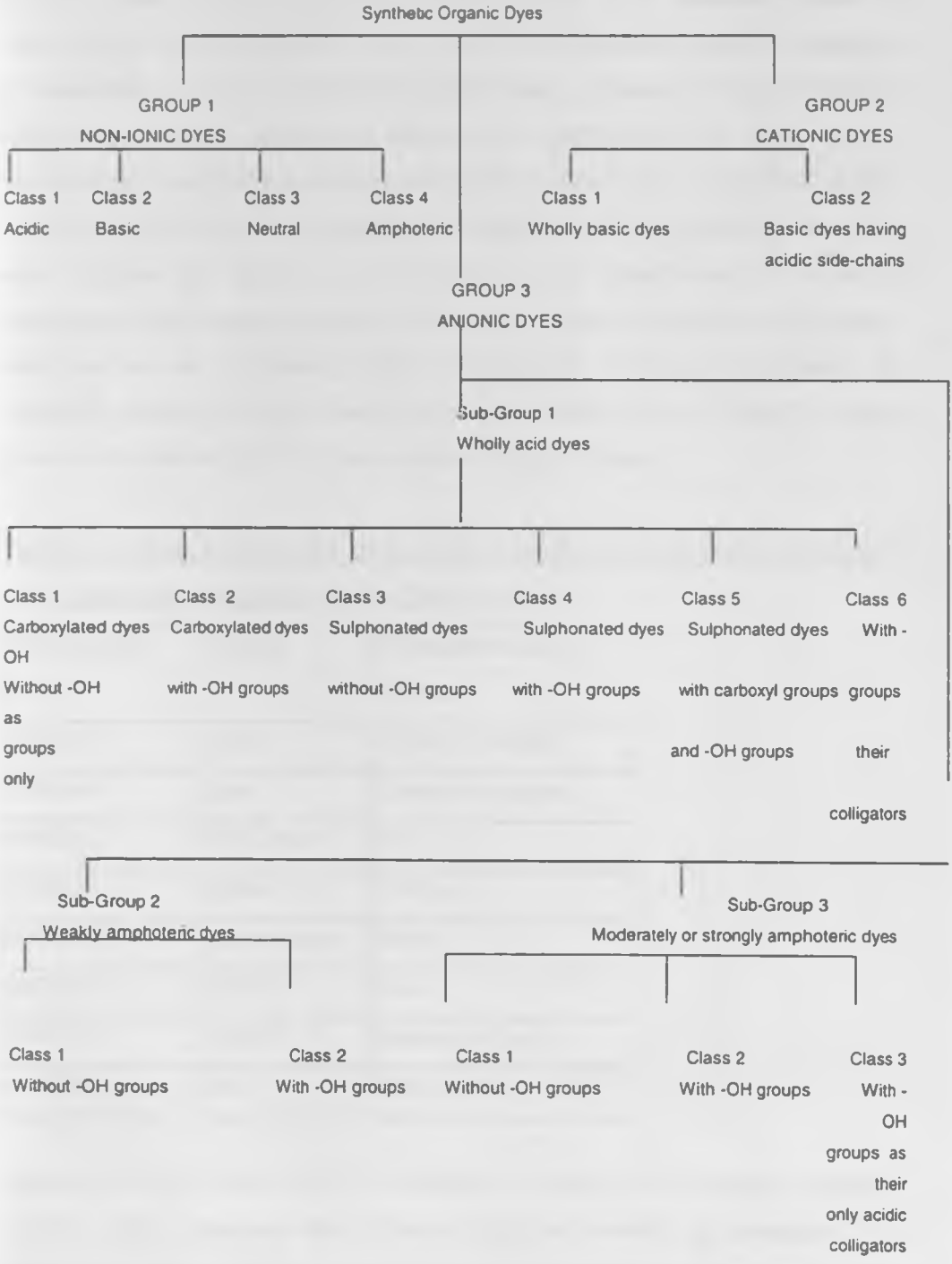


Figure 2.1 Classification of Dyes by Colligators.

2.2 Absorption Spectra of Dyes.

The wavelength of maximum absorption for each dye is given for the visible spectral region. White light is composed of light of the entire spectral range. And an object appears coloured in ordinary white light because it absorbs some of the spectral radiation but not all. The unabsorbed colour is reflected or transmitted and is the colour of the object as it appears to the eye. Objects which appear black absorb the whole of the visible spectral range without transmitting or reflecting any component of the white light. If a coloured object, illuminated by a source of white light, is examined with spectroscope it will be seen that the light reflected or transmitted by the object does not show the complete visible spectral range. On the other hand if the object is blue-green, then the red will be missing from the spectrum. Red and blue-green are therefore regarded in this respect as complementary colours. Table 2.1 shows colour in the visible light and their complimentary colours.

Table 2.1 shows wavelengths of the more important complimentary colours of the visible spectrum(adopted from Gurr 1971).

Wavelength (mm)	Colour	Complementary colour
400-430	violet	Greenish-yellow
430-490	blue	Greenish-orange
490-510	blue-green	Red
510-530	green	Purple
530-560	yellow-green	Violet
560-590	yellow	Blue
590-610	orange	Greenish-blue
610-750	red	blue-green

Absorption often takes place in more than one region of the visible spectrum and the colour observed also depends upon the intensity of absorption. The absorption spectra obtained by the spectrophotometer are characteristic of the individual dyes; they might be regarded as their fingerprints. However, variations in the wavelengths of maximum absorption of many dyes with

variations in the pH, temperature and concentration of the solution examined (Gurr, 1971).

2.2.1 Why are dyes Coloured?

Colour in dyes is explained as a consequence of the presence of a chromophore. By definition, chromophores are atomic configurations that contain delocalised electrons. They are usually represented as nitrogen, carbon, oxygen and suphur that have alternate single and double bonds. (*http://members.pgonline.com/*) Below are some chromophoric configuration:- -C=C-, -C=N-, -C=O-, -N=N-, $-NO_2$ and -Quinoid rings.

On the other hand, dyes are aromatic compounds and their structures include aryl rings which have delocalised electron systems. These are responsible for the absorption of electromagnetic radiation of varying wavelengths, depending on the energy of the electron clouds. For this reason, chromophores do not make dyes coloured in the sense that they confer on them the ability to absorb radiation. Rather, chromophores function by altering the energy in the delocalised electron in the dye, and this alteration results in the compound absorbing radiation from within the visible range instead of outside it. Our eyes detect that absorption, and respond to the lack of a complete range of wavelengths by seeing colour. (Fessenden and Fessnden,1990)

2.3 Classification of Dyes.

There are various methods of dyeing and many more types of dyes for each method. There are, however, six main classes of dyes for cotton fabric: vat, direct, developed, naphthol, sulphur and analine black.

Vat dyes, known as fast dyes are insoluble in water. An acid rinse (acetic acid) is used to neutralise the alkali present in the dye bath followed by detergent washing to produce brightness and wash resistance.

Direct dyes are so named because they are applied to the fibres without pre-application of chemicals required for retention. Some direct dyes are subject to post treatment with copper sulphate and acetic acid to increase light

fastness and potassium dichromate and acetic or formaldehyde to increase wash fastness.

Developed dyeing is a procedure whereby two different chemicals are employed. The first chemical (0.5 - 4%) is applied and absorbed into the fibres. The second chemical (developer) is then applied and reaction with the first takes place directly on the fibre for stable colour development.

Naphthol dyeing is developed dyeing in reverse. A cloth is first impregnated with developer and then the dye is formed on the fibre by saturation in the dye bath. In the actual process, the naphthol dye is dissolved by mixing either sodium hydroxide under heat or ethyl alcohol and cold solution of sodium hydroxide.

Sulphur dyes are principally used to dye heavy cottons in shades of blacks, dark blues , browns and other dark colours. The dyes are generally water insoluble and require dissolving in an alkaline solution before application. The manufacture and use of sulphur dyes results in the formation of a toxic and highly alkaline waste liquor which cannot be disposed of in a conventional manner, since it unduly pollutes and stagnates fresh water rivers and streams. These waste liquors are highly coloured and odiferous The sulphide or other alkali sulphides contained therein hydrolyses with water and forms hydrogen sulphide which is toxic to marine life and has foul, disagreable odour.

No wholly suitable means for the treatment or disposal of this liquors is known. Neutralization treatments of these alkaline liquors, such as with sulphuric acid , results in the formation of a highly turbid suspension and evolution of large quantities of hydrogen sulphide gas. Such acid treatment does not improve the colour of these waste liquors (Sittig,1973). It has now been found that sulphur dyes waste liquors can be deodorized, decolourized, neutralized and otherwise purified by treatment with an aqueous sulphurous acid. It is necessary that the liquor be mixed with sulphurous acid within a limited time and that the ratio of the liquor to acid or the initial pH be controlled within relatively close limits. Under such conditions, the sulphurous acid react

with the toxic, colour and odour producing components of the waste liquor, coagulating the undesirable components of there of and forming a stabilized clear solution phase . The coagulated fractions can then be removed from the clear solution by filtration, decantation, centrifugation and any separation technique and solution disposed of in a river or other waterway without danger of pollution or stagnation of the water.

Analine black dye is an insoluble pigment produced by oxidation of Analine. The cloth is passed through dye bath typically consisting of 42 kg of Analine hydrochloride, 16 kg of sodium Chlorate, and 6 kg of copper sulphate in 455 litres of water. After impregnation, the cloth is given a steam treatment to develop the black pigment. Alkaline sodium dichromate treatment completes the process.

2.4 Solubility of dyes.

Many water-soluble dyes owe their solubility to the presence of at least one sulphonic acid group, and they are usually applied as sodium salts. In most cases sulphonic groups are introduced into the intermediates from which the dye is made, but sometimes an insoluble dye is sulphonated. Water-soluble basic dyes contain no sulphonic acid group, but are prepared in the form of hypochlorides. Water-insoluble dyes of certain types can be rendered soluble in this form, and then converted on the fibre into the original insoluble form. The sulphur and vat dyes depend on this principle, which enables tint fastness onto wet treatments obtained. Insoluble azo dyes can be formed directly within the fibre.

Gurr 1971 used 17 symbols to describe the relative solubility of dyes in various solvents at 20^{o} C. These are as follows:

- = insoluble

s- = only very slightly soluble

s = slightly soluble ; the amount of dyestuff dissolved being insufficient to render the solution of practical use as a colourant

s+ = slightly soluble ; the amount of dyestuff dissolved might be sufficient to render the solution of use as a feeble colourant

P- = slightly more soluble than s+

P = slightly more soluble than p-

P+ = slightly more soluble than p

M- = moderately soluble (around 1 %)

M = slightly more soluble than m-

M+ = slightly more soluble than m

R- = slightly more soluble than M+

R = readily soluble

R+ = very readily soluble (to the extent of around 5- 7 %)

V- = slightly more soluble than R+

V = more soluble than V-

V+= more soluble than V

H = highly soluble (usually around 20 %)

s-, s, s+, P-, P, P+ denote varying degrees of low solubility

M-, M, M+ denote three different degrees of moderate solubility

R-, R, R+ denote varying degrees of good solubility

V-, V, V+ and H denote high solubility

In this regard, Congo Red was found to have good solubility in water and was classified as R-.

2.4.1 The Congo red dye.

Congo red is an example of a diazo dye. This is characterised by the presence of two azo groups (-N=N-) as a chromophore. This dye is made by coupling a diazonium salt with an amine. The structures are shown in Figures 2.2 and 2.3. Other characteristics of the dye are given in Table 2.2.

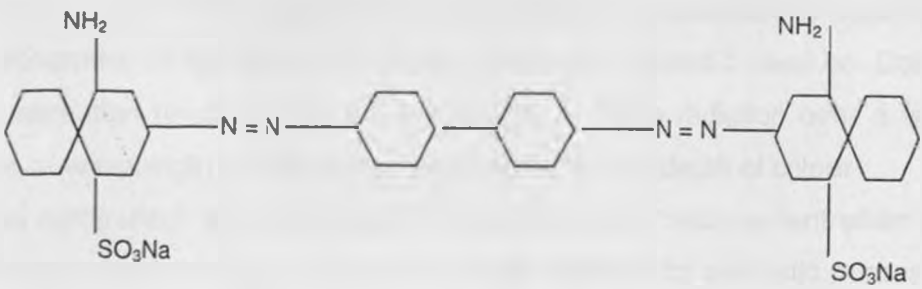


Fig 2.2 Structure of Congo Red dye Molecule

Table 2.2 Characteristics of Congo Red dye.

Common name	Congo red
Other names	Direct red, Cotton red
CI number	22120
CI name	Direct red
Class	Disazo
Ionisation	Acid
Solubility in water	Soluble
Solubility in ethanol	0.19%
Wavelength of Maximum Absorption	488(Merck) ,497 (Conn)
Colour	Red
Empirical Formula	$C_{32}H_{22}N_6O_6S_2Na_2$
Formula weight	696.696

As such, the dye being a strong electrolyte readily ionises to the dye ion containing the sulphonic acid group and the sodium ion, as shown below.

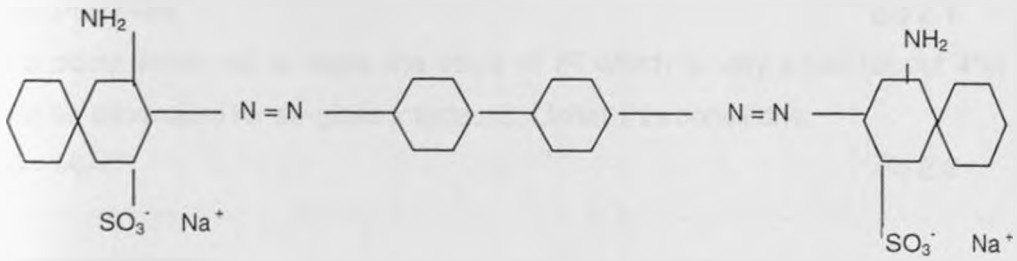


Fig 2.3 Structure of Congo Red Dye ion.

2.5 Measurement of dye concentration in a dye bath.

In order to obtain the concentration of a dye bath, it is necessary to determine the absorption of light through a portion of the bath, diluted if need be. Colour is a sensation resulting from the perception of visible radiation over a wide range of wavelength and embodies such factors as the depth of colour.

Visual comparison is the method of choice for colour measurement when the object is to assess the appearance of a water sample for aesthetic purposes. Instrumental methods, which determine only the absorption of light at limited

range of wavelength, are objective and provide accurate and precise measurements but do not measure the optical properties as visual comparison.

In the visual comparison technique the colour intensity of the sample is compared with that of a series of standard solutions or permanent glass standards to obtain a colour match. The instrumental method measures the absorption of light of a permanent set by sample. Both visual and photometric determination rely on the fact that the depth of colour (absorbance) is governed by the concentration of the material in the solution (Lamount, 1981). Colour is measured by optical density (D) on the spectrophotometer and the whole colour band should be scanned.

When light (monochromatic or heterogeneous is incident upon a homogenous medium a part of the incident light is reflected, a part is absorbed by the medium and the remainder is allowed to transmit.

If IO, denotes the incident light, IR the reflected light, IA the absorbed light and IT the transmitted light, then

$$IO = IA + IT + IR \qquad Eq\ 2.1$$

If a comparison cell is used, the value of IR which is very small (about 4%) can be eliminated for air-glass interfaces. Under this conditions,

$$IO = IA + IT \qquad Eq\ 2.2$$

Lambert's Law.

"When a beam of light is allowed to pass through a transparent medium, the rate of decrease of intensity with the thickness of medium is directly proportional to the intensity of the light.

Mathematically,

$$dI/dt = kt \qquad Eq\ 2.3$$

Where I_O = intensity of incident light

t denotes the thickness of the medium

k denotes the proportionality constant.

Integrating and putting $I=I_O$ when I=0,

we get

$ln\ I_O/I_T = Kt$ *Eq 2.4*

$I_T = I_O\ e^{-kt}$ *Eq 2.5*

$I_T = I_o exp(-kcl)$ *Eq 2.6*

Where

IT = the transmitted light

IO = the incident light

c = concentration of the absorbing species

l = cell length

k = extinction coefficient

The optical density D is by definition

$D = log_{10}\ (I_O/I_T) = 0.434kcl$ *Eq 2.7*

D is therefore proportional to the cell length and dependent on wavelength through coefficient k (Environmental Technology letters, 1986). The first step in photometric or spectrophotometric analysis involves the establishment of working conditions and the preparation of a calibration curve relating to the absorbance. Spectrophotometric absorbance measurements are ordinarily made at a wavelength corresponding to an absorption peak because the change in absorbance per unit concentration is greatest at this point; the maximum sensitivity is thus realised .In addition, the absorption curve is often flat in this region, under these circumstances, a good adherence to Beer's Law can be expected. Finally, measurements are less sensitive to uncertainties arising from failure to reproduce precisely the wavelength setting of the instrument. Variables that influence the absorption spectrum of a substance include the nature of the solvent, the pH of the solution, the temperature, high electrolyte concentration and the presence of interfering substances. The effect of these substances must be known; conditions for the analysis, it is necessary to prepare a calibration curve from a series of standard solutions. These standards should approximate the overall composition of the actual samples and should cover a reasonable concentration range of the analyte. It is safe to assume adherence to Beer's Law and use only a single standard to determine the molar absorptivity. The results of the analysis should never be based on a literature value for molar absorptivity.

2.6 Nature of Colour in Aquatic and Marine Environment

The observed colour in water is the result of light back scattered upward from a water body after it has passed through the water to various depths and undergone selective absorption. The colour of light (i.e. wavelength) and the turbidity of water determines the depth to which light penetrates in the water system (Canadian Council of Ministers of Environment, 2001). In pure water, light is highly absorbed in the infra-red region of the light spectrum and poorly absorbed in the blue region. Thus, blue light is refracted, reflected and/or re-emitted back causing the visible colour of the water to be blue (Jerome 1994).

The colour of water is characterised as true or apparent. True colour depends on dissolve fraction in water which can include natural minerals such as ferric hydroxide and dissolved substances such as humic or fulvic acid (Hongre and Akesson, 1996). Dyes (e.g. Acid blue toilet flush), wood preservatives, antisapstains, and various other dissolved organic substances from anthropogenic sources may also contribute to water colouration
(McCrum 1984; Brown, 1987; Boegeding and Hites, 1994). Colour also depends on factors that affect the solubility and stability of the dissolved and particulate fractions of water such as pH and temperature. True Colour is measured by comparator and calorimetric methods.

Apparent colour is a function of dissolved and suspended material, such as organic plant debris, phytoplanton and zooplanktons, and inorganic suspended sediments (Effler and Aver 1987, APHA 1992; Bennett and Drikas 1993). Apparent color is commonly estimated by light transmittance/absorbance through water.

2.7 Effects of Colour in Aquatic and Marine Environment.

Numerous studies have demonstrated a strong positive correlation between primary production and water colour in fresh water (Henebry and Cairns 1984; Arvola, 1986; Ilmarvia and Hutte 1989; Del Giorgio and Peters, 1994). The colour of water may affect algal species composition, as photosynthetic efficiency at various wavelengths differs markedly among algal groups

according to the amounts of accessory pigments accompanying chlorophyll a (Atlas and Bannister 1980; Arvola 1986; Sheath et al.1986; Vegas-Vilarrubia, 1995).

Wetzel (1975) and Juarez (1987) in the Canadian Water Quality Guidelines for protection of aquatic life: Colour state that many invertebrate species possess visual receptors and absorption spectrum peaks that correspond to the spectral quality of their preferred habitats (Canadian Council of Ministers of Environment, 2001). Thus changes in the spectral quality of water, therefore could have profound effects on the behavour of some invertabrates and fish species.

Mierle and Ingram (1991); Nilsson and Hakanson 1992; Haine et.al 1995 record that Mercury availability, bioaccumulation and hence toxicity increases as water colour increases. The reason for this relationship, in part, is that mercury brought from the surrounding environment is attached to coloured substances(op.cit).

2.8 ADSORPTION PHENOMENA.

Adsorption is the accumulation of a solute to a surface or interface between the solution and the adsorbent. Adsorption processes generally yield surface or interface concentrations of solute greater than those in the bulk phase. The driving forces for attainment of chemical equilibrium in the homogenous phases relate to the reduction of the free energies of the bulk system, whereas the driving force for a surface reaction is a reduction in surface energy (Weber et al., 1991).

There are two types of adsorption. Physical adsorption may be explained in terms of the energy per unit area of the solid. Molecules in the interior of any solid are subjected to equal forces in all directions whereas molecules on the surface of the solid are subjected to unbalanced forces as shown in Figure 2.4. Other molecules becoming attached to the surface can balance these forces. The attractive forces are relatively weak and are of Van der Waals type.

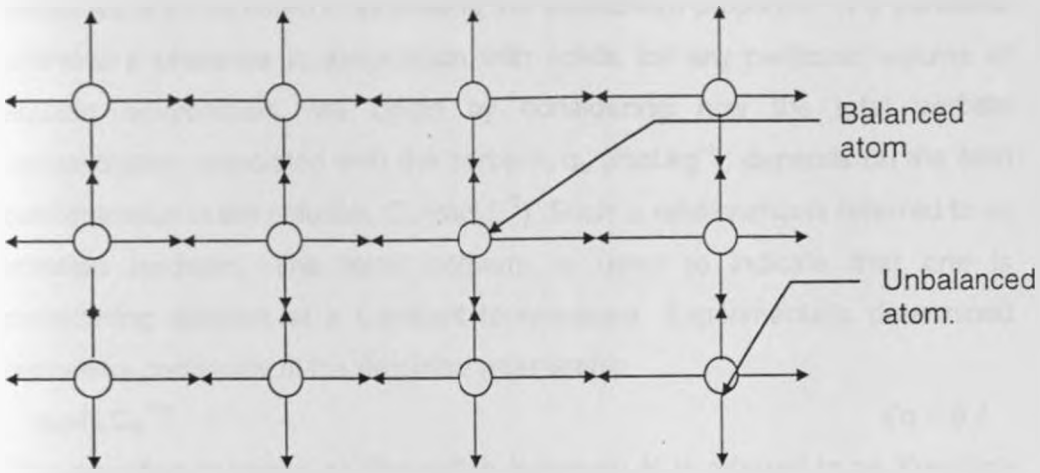


Fig 2.4 Balanced and unbalanced atoms

Chemical adsorption takes place by chemical interaction between the surface of the solid and the molecules of the liquid.

Absorption is a process in which solute transferred from one phase to another interpenetrates the sorbent phase by at least several nanometers. The differences in molecular environments of a contaminant in aqueous and sorbent phases, which manifest themselves in absorption processes, can be described using classical thermodynamics.

Sorption is the process by which chemicals become associated with solid phase. This term is general encompassing adsorption (adsorption onto a two dimensional surface) and absorption (into a three-dimensional matrix) (Schwarzenbach et al., 1993). Theories of sorption are based on the principle that the three main steps are involved in the process, any of which is the rate-controlling factor. The rate steps are:

- boundary layer mass transfer control across the liquid film surrounding each particle (Masumune, 1964).
- Particle diffusion control, due to diffusion in the liquid contained in the pores and the adsorbate along the pore walls (Rosen, 1954)
- surface adsorption control based on the rate of adsorption and desorption at some specified radius within the particles.

When we are interested in assessing the equilibrium proportion of a particular chemical's presence in association with solids for any particular volume of aquatic environment, we begin by considering how the total sorbate concentration associated with the sorbent, q_e ($mol.kg^{-1}$), depends on the total concentration in the solution, C_e ($mol.L^{-1}$). Such a relationship is referred to as sorption isotherm. The term isotherm is used to indicate that one is considering sorption at a constant temperature. Experimentally determined isotherms commonly fit the empirical relationship

$$q_e=K.C_e^{1/n} \qquad \textit{Eq 2.8.1}$$

This equation is known as Freundlich isotherm; K is referred to as Freudlich constant; and n is a measure of the nonlinearity involved. Case 1 in Figure 2.2 ($n<1$) reflects the situation in which at higher and higher sorbate concentration, it becomes more and more difficult to sorb more molecules. This may occur in the cases where specific binding sites become filled or remaining sites are less attractive to the sorbate molecules. Case 3 ($n>1$) describes the contrasting situation in which the previously sorbed molecules lead to a modification of the surface which favours further sorption. Case 2 ($n=1$) reflects those situations in which the attractiveness of the solid for the sorbate remains the same for all levels of q_e. This is so called linear isotherm case.

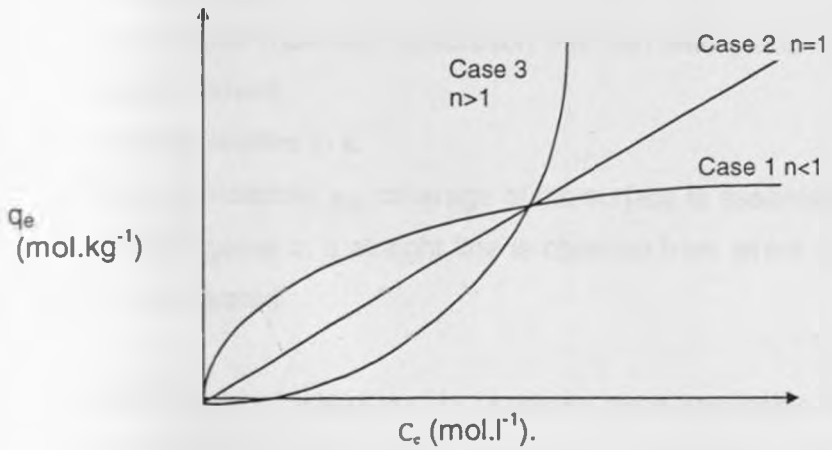


Fig 2.5 Freundlich Isotherms

The rate of adsorption of a molecule onto a surface can be expressed in the same manner as any kinetic expression : i.e.

$R_{ads} = kC^x$ *Eq 2.8.2*

Where R_{ads} -rate of adsorption

x- Kinetic order

k - rate constant

C - gas phase concentration

or

$R_{ads} = k'P^x$ *Eq 2.8.3*

Where x - kinetic order

k' - rate constant

P - partial pressure of the molecule

If the rate constant in either of the above expressions in an Arrhenius form, then we obtain kinetic equation of the form:

$R_{ads} = AC^x exp(-E_a/RT)$ *Eq 2.8.4*

Where E_a is the activation energy for adsorption, and A the pre-exponential (frequency) factor

Other equations which are used frequently used in describing adsorption isotherms and which can be derived from fundamental considerations are Langmuir and BET isotherm developed by Bruneur, Emmett and Teller.

The Langmuir isotherm is used to describe single layer adsorption and can be written as follows

$C/y = a/y_m + c/y_m$. Eq *2.8.5*

y_m -represents maximum adsorption that can take place in grams adsorbate per gram sorbent.

C - is large relative to a

When y approaches y_m, coverage of the surface is essentially complete. If C/y is plotted against c, a straight line is obtained from which constants a and y_m can be evaluated.

The BET type of adsorption is generally more applicable than the Langmuir isotherm and it corresponds to multi-layer adsorption. The model assumes

that a number of layers of adsorbate accumulate at the surface, and that the Langmuir isotherm applies to each layer. It takes the form

$$C_e/(q_e)[1/C_s-C_e)]=1/BQ_{max}+(B-1)/BQ_{max})(C_e/C_s) \quad \text{Eq2.8.6}$$

Where Q_{max} represents maximum adsorbate per mass of adsorbent, C_s is saturation concentration and B is a constant.

BET equation is represented in straight line form as in Figure 2.6.

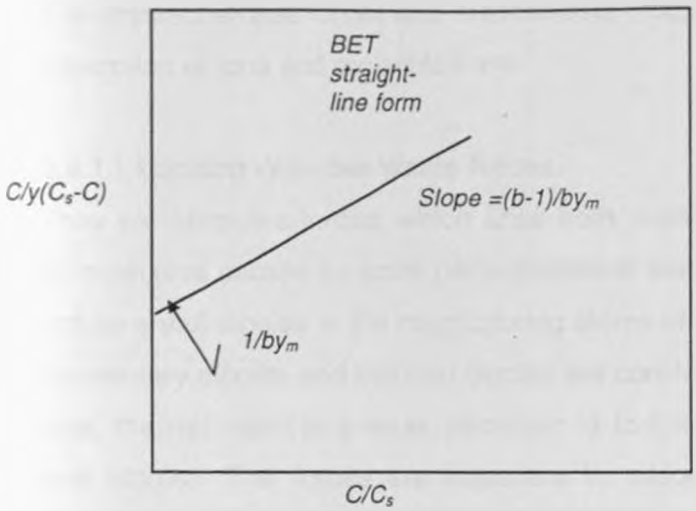


Figure 2.6 Linearized BET Isotherm

With this equation C_s and b can be obtained from the slope and the intercept of the straight-line best fitting of the plot of the left side versus c/c_s. The best isotherm equation to use in a particular instance can be determined by comparing the goodness of the fit of the data when plotted in the form for each isotherm, which yields a straight line.

In any practical process, the removal of a contaminant from a gas or liquid is determined by the rate at which the material is adsorbed onto the solid surface. Three major steps can be identified in the removal of a contaminant by adsorption-:

- It must move from the liquid or gaseous phase through a surface film to the exterior of the adsorbent.
- It must pass by diffusion into and through the pores of the adsorbent
- It must be attached to the adsorbent

2.8.1 Forces and Mechanisms of adsorption.

The physiochemical forces and mechanisms thought to be responsible for the adsorption of ions and molecules are:-

2.8.1.1 London -Van der Waals forces.

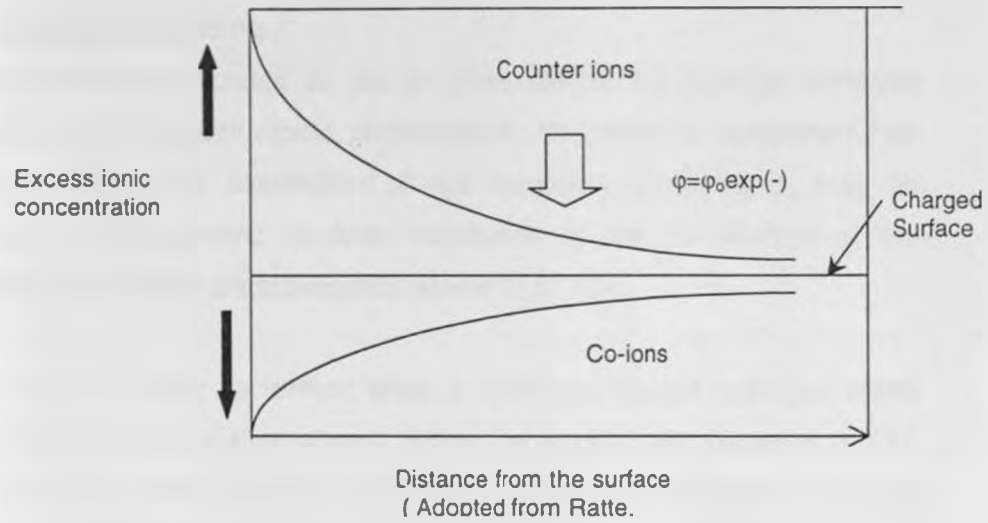
They are attractive forces, which arise from momentary dipoles about atoms or molecules caused by small perturbations of electronic motions. The dipoles induce small dipoles in the neighbouring atoms of opposite sign. Although the momentary dipoles and induced dipoles are constantly changing positions and sign, the net result is a weak attraction (4 to 8 kJ /mol) for small molecules and atoms). The forces are important in adsorption of organics and are generally attributed to non-ideal behaviour in gases(Roy et al., 1992).

2.8.1.2 Coulombic-electrostatic-chemical.

An electrostatic force results from a charged surface due to substitution in the mineral lattice (permanent charge) or protonation of surface oxygen and OH group (pH dependent charge) and an oppositely charged species, which maintains electro-neutrality of the surface. In layer silicates, substitution of octahedrally or tetrahedrally coordinated cations by cations of lower valence results in a net negative charge. This excess charge can bring about the formation of a diffuse layer of positively charged atoms or molecules about the colloid; the density of this layer is greater at the surface, and the decreases exponentially to the level of bulk solution. This type of reaction is important in adsorption of inorganic and ionized organic molecules.

When the adsorbent and the adsorbate bear a charge i.e. both are ionised, then attractive forces are inversely related to the distance between the charge centres. Dyes may be anionic or cationic and adsorbing substrates such as proteins, carbohydrates and polyamides may be charged also. Even if the adsorbent bears no formal charge before adsorption of a dye ion, the process of adsorption produces a surface charge and the surface potential is determined by the adsorbed dye ions. Coloumbic interactions can either favour or disfavour dye adsorption so that they may be regarded as binding or

anti-binding. The presence of a charge on the adsorbing surface confers upon it an electric potential, which simultaneously attracts oppositely charged (counter) ions and repels similarly charged ions (co-) ions. As the distance from the charged surface increases the effect of the surface potential becomes less. Thus the surface potential is only apparent over a limited distance in all practical sense and within this limited distance the entire imbalance of ionic concentrations near the surface is combined. This means that near to the surface exists a diffuse layer and since within it there will be a separation it is termed as an electrical double layer.



(Adopted from Ratte.

Fig 2.7 Distribution of ions near a charged surface

Three main coloumbic effects are encountered in dye adsorption.

- The presence of acid may determine the potentials of the adsorbing phase to make it more or less attractive to dye ions e.g. proteins contain positive (NH_3^+) and negative (COO^-) groups. In acid the carboxyl groups are back titrated giving the fibre a positive charge favourable to the uptake of dye anion. Cellulose contains hydroxyl groups which in the presence of an alkali may ionise giving the fibre a negative charge repelling the dye ions and preventing their absorption.
- Dye ions will be adsorbed by uncharged substrates to a very limited degree since the first few molecules taken up will confer on the fibre a charge repelling other similarly charged ions. This effect is most

marked in relatively hydrophobic fibres since the volume of water taken up broadly corresponds to the double layer volume and when this is small the charge effects will be concentrated.

- Dye ions will be taken up without hindrance by a substrate of opposite charge but in doing so they will reduce the potential of the substrate eventually to zero when the adsorbed ion concentration equals that of fixed charges. Since further absorption will meet constraints mentioned above, the substrate may appear to be saturated with dye ion at this point (Ratte, 1974).

2.8.1.3 Hydrogen Bonding .

A hydrogen atom is bonded to two or more atoms; the bond is generally conceived as an induced dipole phenomenon. No universal agreement has been reached on the description of the hydrogen bond, but it may be considered as asymmetric electron distribution of the 1s electron of the hydrogen atom by very electronegative atoms (F,O, Cl).

A hydrogen bond may be formed when a covalently bound hydrogen exists between two electronegative atoms. Since the appropriate groups e.g. OH, NHR, CF3 are fairly common in dye molecules and substrates, it is not surprising that hydrogen bonding should be postulated as a potential binding force for dyes in aggregates and with substrates. The hydrogen bond is relatively weak one, the bond energy lying in the range 2-10 Kcal/mole. Its formation involves also low activation energy. The strength of a hydrogen bond depends upon the Electro-negativity of the bound atoms so that fluorine forms much stronger hydrogen bonds than chlorine. The hydrogen bonding power of an atom can be enhanced by inductive effects and substitution so that RNH_3^+contains a more powerful hydrogen bonding than $R\text{-}NH_2$.

When we consider a dye molecule and substrate in aqueous medium, then if there is any possibility of the two becoming associated through a hydrogen bond then the relevant residues will be hydrogen bonded with water prior to the anticipated association. Hydrogen bonding between the dye and the substrate will then require breaking the water hydrogen bonds.

Alternatively hydrogen bonding groups in the substance may be associated with one another (intra-molecular hydrogen bonding) so that involvement with the dye molecule will again require two hydrogen bonds to be broken for each one formed in the adsorption. Where the two broken hydrogen bonds involves water it is possible for the two water molecules freed to bond together and with an intra-molecular hydrogen bond for the free group to bond with water so that there is no net charge in the number of bonds.

Another form of hydrogen bonding is one in which the delocalised electrons of a conjugated ring system provide an electronegative centre for involvement in a bond e.g. benzene will interact with proton donor substances, e.g. methanol, to form a hydrogen bond.

2.8.1.4 Ligand exchange -anion penetration-coordination.

Many atoms or molecules for coordinated complexes with ligands that range in complexity from simple molecules to extensive chelate complexes. The coordinated complexes may carry a net negative charge that may be localized on some part of the complex. These complexes may inturn be bonded to the surfaces by hydrogen bonding or by polyvalent cation linking the complex to a charged surface. The bonded coordinated complexes may be displaced by other coordinated complexes that better satisfy electro-neutrality requirements (i.e. are stronger complexing agents) while being restrand by steric limitations. The energy of ligand exchange reactions with inorganic ion ranges from 8 to 60 kJ/mol.

2.8.1.5 Chemisorption .

In this adsorption process an actual chemical bond, usually covalent, is formed between the molecules and surface atoms. A molecule undergoing chemisorption may loose its identity as the atoms are rearranged, forming new compounds at the demand of the unsatisfied valencies of the surface atoms. The enthalpy of chemisorption (h >29KJ/Mol) is much greater than for physical adsorption -ligand exchange reactions are forms of chemisorption.

2.8.1.6 Dipole-dipole or orientation Energy.

This interaction results from the attraction of a permanent dipole for another dipole. The resulting energy of attraction is less than 8 kJ/mole.

2.8.1.7 Induction or dipole induced dipole.

This type of interaction results from the attractions of an induced dipole about by either; - a permanent dipole or a charged site or species. The energy of attraction is less than 8 kJ/mol.

2.8.1.8 Hydrophobic effect.

The exact nature of adsorption mechanism is uncertain. Some investigators believe that hydrophobic adsorption is primarily an entropic driven mechanism brought about by the destruction of the physical cavity occupied by the solute in the solvent, and from the partial loss of structured water molecules about the solute, ordered by Van der-waals forces (Horvath et al 1976; Sinanoglu and Abdulnur, 1965). Other researchers postulate that the hydrophobic effect is the result of simple partitioning. Non polar organic solutes tend to migrate from the aqueous phase to hydrophobic surfaces on the adsorbent (Dzombak and Luthy, 1984; Chiou et al., 1979, 1983; Griffin and Roy, 1985).

2.8.2 Thermodynamics of adsorption Equilibra.

Adsorption equilibria can well be described in terms of thermodynamics.

Accordingly at equilibrium in a system

$\mu_s = \mu_s^o + RTlna_s$ *Eq 2.8.7*

$\mu_f = \mu_f^o + RTlna_f$ *Eq 2.8.8*

Where μ_s and μ_f are the chemical potentials of the adsorbate in the external and adsorbent surfaces respectively; a_s and a_f are the corresponding activities; μ_s^o and μ_f^o are the corresponding standard state chemical potentials. At equilibrium, the chemical potentials in the two phases must be equal so that

$\mu_s^o - \mu_f^o = -\Delta \mu^o = RTlna_f / a_s$ *Eq 2.8.9*

The term $-\Delta \mu^{o}$ represents the change in standard chemical potential or standard molal free energy in the transfer from the external to the adsorbant phase and is thus the affinity.

The free energy per mole, μ, is given by

$$\mu = H - T\Delta S = E + PV - TS \qquad Eq\ 2.9.0$$

Where

μ = is the free energy per mole

H =is the enthalpy

T= is the Absolute temperature

ΔS = Change in Entropy

P = Partial Pressure

V =Volume

E =Internal energy

2.8.3 PROPERTIES OF WOOD AS AN ADSORBENT.

A great variety of alternative low cost materials like fly ash, soil, wood chippings, tyre cuttings, coconut shell powder, hair, coal etc., are being tried in place of activated carbon for sorption of different pollutants like pesticides, detergents, heavy metals, dyes etc(Chu et.al., 1978; Emig, 1973; Huang and Liao, 1970; Aga, 1983; Mckay and Poots, 1980; Michelson et al., 1975).The chemical and physical characteristics of sorbent materials as well as those of sorbates vary widely.

Wood industry bi-products such as bark and sawdusts have been widely used for their property of metal adsorption and metal removal from contaminated effluents. Concerning the utilisation of sawdusts, many researchers have studied metal adsorption of materials from species such as red fir, mango, lime, pine, ceda, teak, Japanese redpine and Japanese beech. As regards wood barks, several species were studied in particular pine, oak and spruce (Fiset et.al 2000).

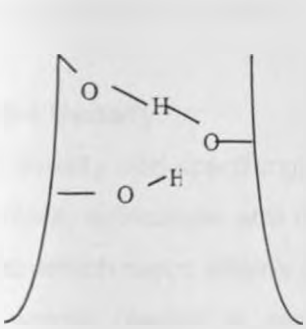
2.8.3.1 Hygroscopicity.

Hygroscopicity is the property of wood to attract moisture from the surrounding atmosphere and hold it in the form of liquid water or water vapour. This property originates from the chemical composition of wood: cellulose, hemicelluloses, pectins, lignin, and certain extractives are

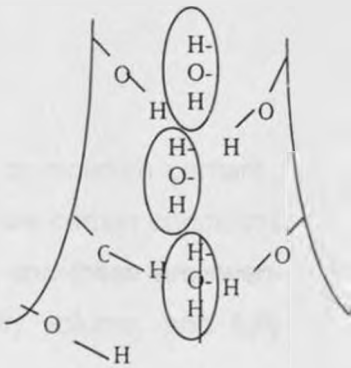
hygroscopic substances (Tsoumis, 1991). To understand the properties of wood as an adsorbent, it is first important to understand the mechanism of moisture adsorption onto wood.

2.8.3.2 How moisture is held in wood.

Moisture is found in wood in two forms: as liquid water in cell walls and as liquid and/or vapour in cell cavities. In saturated conditions there is only liquid water. The basic reason for moisture entering into the mass of wood is the attraction of water molecules by the hydroxyls of its chemical constituents, mainly cellulose. A monomolecular layer of water shown in Figure 2.8 is formed and held by these hydroxyls with strong hydrogen bonds. The formation of this layer results in pushing apart chains of cellulose molecules in the amorphous regions and between the chrystalites of microfibrils, so the wood starts to swell. Under the effect of secondary attractive forces, more water molecules enters and form a polymolecular layer.



I Gradual formation of monomolecular layer by breaking the hydrogen bonding between adjacent cellulose molecules.



II Polymolecular Layer

Fig 2.8 Formation of monomolecular and polymolecular water layers on wood surface.

An additional part may enter by capillarity condensation in the cell wall voids and pit features (pit membrane, small pit mouths).

2.8.3.3 Desorption and adsorption.

Loss of moisture is called desorption, and gain adsorption. Desorption begins by evaporation from an exposed surface of wood. If the walls are saturated, evaporation of water from the cavities need little more energy than that required to evaporate water from the free surface (Tsumois, 1991). Reduced relative vapour pressure in the atmosphere (lower than unity) represents an attractive force holding water in the walls and, depending on its magnitude, causing less desorption. To replace desorbed water, other water moves from the interior to the surface of the wood.

Adsorption is the process by which dry wood exposed to an atmosphere containing water vapour, is adsorbed through its surface. At the beginning, a monomolecular layer is formed, then polymolecular and if the relative pressure in the atmosphere is high (close to unity), capillary condensation may take place. Movement of moisture from the exterior to the interior of the wood is attained by diffusion. When dry wood is immersed in water, there is active movement of water through cell cavities. Long immersion results in near saturation of cavities.

2.8.3.4 Density.

The density and specific gravity of wood are influenced by moisture content , structure, extractives and chemical composition. There are certain conditions under which wood attains constant weight and volume, and these are oven-dry weight (weight at zero moisture content), oven-dry volume, and fully swollen volume.

Density is determined by measuring mass (weight) and volume, or by other methods. Dry (oven dry) mass is measured by placing the chosen specimen of wood in an oven at 103°C, until its weight becomes constant; 12-48 hours are needed for specimen about 100g in weight, volume is determined by measuring dimensions if the shape permits

2.8.4 Desorption process.

An adsorbed species present on a surface at low temperatures may almost remain indefinitey in that state. As the temperature of the substrate is increased, there will be a point at which thermal energy of the adsorbed species is such that one of the following may occur:

- A molecular species may decompose to yield either gas phase products or other species.
- An atomic adsorbate may react with the substrate to yield specific surface compound, or diffuse into the bulk of the underlying solid.
- The species may desorb from the surface and return into gas phase.

The last of these options is the desorption process.

2.8.5 Desorption Kinetics.

The rate of desorption of an adsorbate from a surface can be expressed in the general form:

$R_{des}=kN^{x}$ *Eq 2.9.1*

Where,

X - Kinetic order of desorption

k - rate constant for the desorption process

N - surface concentration.

The rate constant for the desorption process may be expressed in an Arrhenius form,

$K_{des} = A\ exp\ (-E_a^{des}/RT)$ *Eq 2.9.2*

Where,

$-E_a^{des}$ is the activation Energy for desorption, and *A* is the pre-exponential factor

This gives the following general expression for the rate of desorption

$R_{des} = -\ dN/dt\ = v.Nx.\ exp(-E_a^{des}/RT)$ *Eq 2.9.3*

R= Universal molar gas constant

T= absolute temperature

2.9 Characteristics of Wood.

Woods differ in colour, porosity, grain and figure. Porosity is mainly a function of dicotyledon woods. These term refers to how the vessels are distributed. Grains refers to the alignment of the xylem cells. Figure is determined by many factors: rays, porosity, grain, and arrangement of rings. The presence of knots or burls may also be involved. Density is the weight per unit size. Wood with higher density than water will sink in water.

2.9.1 Hardwoods

Hard wood is derived from dicotyledonous angiosperms. Most dicotyledonous plants have vessels or short water conducting cells that conduct water through openings in the ends of the cells. Hardwoods have tracheids, vessels, fibres, ray tracheids, and xylem parenchyma. The cell walls are about 70% cellulose and hemicellulose and about 20 – 35% lignin.

2.9.2 Soft woods.

Softwood is derived from gymnosperms. The xylem of gymnosperms is composed mostly of tracheids. Gymnosperms do not have vessels. Resin canals are common in gymnosperms. Softwoods are simpler than hard woods: they tend to be uniform. They have tracheids, resin canals, but no true fibres or vessels.

2.9.3 Chemical composition of Hardwood and softwood.

Inorganic compounds

Inorganic materials in plants depend on the type of the plant and the soil contamination in which the plant grows. On average wood contains 0.5% ash compounds. The ash is typically composed of the following components:-

CaO (±50%), K_2O(±20%).Na_2,O, MgO, SiO, Fe_2O_3, P_2O_5 and SO_3 (Baldwin 1987)

Organic materials

The inorganic compounds in wood are principally in the form of cellulose, hemicellulose lignin. A small proportion are solvent soluble extractives.

Cellulose

It is composed of D-glucopyranose units linked linearly with a b-(1-4) links. It is the main component of wood. Principal component of cellulose is a polymer of glucose (about 10,000) glucose units per cellulose molecule.

Hemicellulose

Acetyl-4-0-methylglucoronoxylan forms the main hemicellulose of hardwood. Glucomannan forms the main hemucellulose of softwoods. Hardwoods also have a greater proportion of methoxyl group than softwoods. In addition, hemicellulose contain several molecules of water $[C_6(H_20)_5]_n$ or $[C_5(H_20)_4]_n$. occurs in shorter chain of 150- 200 glucose units as compared to cellulose.

Lignin.

It has an approximate analysis of $C_{10}H_{11}O_2$ for both softwood and hardwoods (Shafizadeh,1981). In addition to the same compounds as hemicellulose, hardwoods have syringl propane units and softwoods contain guaiacyl propane units. It is a phenolic compound (benzene with attached methyl, propyl and hydroxyl groups) tightly bound to the cellulose.

In summary, the average chemical composition of softwoods and hardwoods is shown in the Table 2.3

Table 2.3 Average % chemical composition of softwoods and hardwoods (Irving,1977).

Chemical constituent	Softwood	Hardwood
Cellulose	42 ±2	45 ± 2
Hemicellulose	27 ± 2	30 ± 5
Lignin	28 ± 3	20 ± 2
Extractives	3 ± 2	5 ± 3

CHAPTER 3. EXPERIMENTAL SETUP

MATERIALS AND METHODS.

3.1 Introduction

To assess the potential of sawdust in dye colour removal from water, different materials and equipment were used at different stages of experimentation.

3.2 Materials.

The consumable materials used in the research included:

- Hardwood and Softwood Sawdust from 4 different tree species namely:- Cypress and Pine for the softwoods, Meru oak and Campor for the Hardwoods. The sawdust was obtained from Wood Makers Limited located in Nairobi's Industrial area.
- Congo Red dye powder obtained from Industrial Chemical supplier located in Nairobi's Industrial Area.
- 55mm Whatman Filter papers.
- Distilled water

3.3 Methods

3.3.1 Introduction

The performance of sawdust as an adsorbent was assessed on the basis of removal of a direct disazo dye (Congo red). The dye is widely used in direct dyeing of textile fabrics such as cotton, paper dyeing and in staining biological specimens in various microbiological techniques. Batch experiments were conducted in which dye samples with predetermined concentration were placed in 350ml-plastic tumblers and then different masses of sawdust added. The mixture was thoroughly mixed by means of a continuous shaker. On reaching equilibrium, the mixture was then separated by means of a filter funnel using a pre-soaked filter paper. The absorbance of the filtrate was then obtained by means of a spectrophotometer at the wavelength of maximum absorbance. Final concentration was determined from a predetermined equation of Congo red calibration showing the relationship between absorbance and concentration.

3.3.2 Sample Preparation

3.3.2.1 Congo red dye

The dye that used in this research was obtained from Industrial Chemical distributors, located in Nairobi's Industrial area. A stock solution of the dye with a concentration of 1000mg/l was prepared by dissolving 1 g of the dye in 1000cm^3 of distilled water. From this stock solution, different concentrations were prepared by diluting required volumes with tap water.

3.3.2.2 Sawdust.

Sawdust used in this research was obtained from a local timber dealer, Wood Makers Limited located in Nairobi's Industrial area. Different types of sawdust species were obtained. These included:-cypress, camphor, Meru Oak and African pine. These tree species were chosen since they were the most used hard and softwood in timber factories around Nairobi. The sawdust was oven-dried for 24 hrs. The other main preparation carried out for the sawdust involved sieving using different sieve sizes ranging from BS sieve No. 14 to No 100. This was meant to obtain different particle sizes for the determination of the effect of particle sizes on the contact time and overall dye removal.

Also included in this study was the determination of cellulose, lignin and Hemicellulose contents of the different sawdust species. This was done using the Van soest procedure. In addition, the specific gravities were determined.

3.3.3 Experimental Procedure.

3.3.3.1 Specific gravity of wood.

To obtain the specific gravity of wood, samples of oven dry timber specimen measuring 100 mm long were used. The samples were weighed (M) and then immersed in a cylinder of water (V_1) by pushing them below the water surface with a piece of wire. The new volume of water (V_2) was taken quickly as timber easily absorbs moisture. Two samples of each species were tested for each tree species and the average specific gravity obtained. The specific gravity was then obtained as follows

$$Gs = M/(V_2-V_1)) \qquad \text{Eq. 3.1}$$

The values obtained are recorded in Table 4.1

3.3.3.2 Determination of Chemical composition of Sawdust.

Wood can be analysed by breaking it down into structural components (called Proximate Analysis) or into chemical elements (Ultimate Analysis). In carrying out this research, Van Soest procedure, which is a form of proximate analysis was used (Van Soest and Goering, 1994)

a) Determination of Cellulose content (Neutral-Detergent Method)

The Neutral Detergent procedure for cell-wall was used to determine the cellulose content in the different sawdust species.

1 g of air-dried sample was weighed into a beaker of the refluxing apparatus and 100ml cold neutral detergent solution followed by 2ml decahydronaphthalene and 5g sodium sulphite were added in that order with a calibrated scoop. The mixture was heated to boiling in 5 to 10 minutes with the heat being reduced at the onset of boiling to avoid foaming. The boiling was adjusted to an even level and reflux continued for 60 minutes, timed from onset of boiling.

Tared Gooch crucibles were placed on filter manifold. The beaker was swirled to suspend the solids and content used to fill the crucibles. The sample was rinsed into crucible with minimum of hot (90-100°C) water. Vacuum was removed and mat broken up. The crucible was then filled with hot water. The liquid was filtered and washing procedure repeated. In a similar manner, the content was washed twice with acetone and sucked dry. The crucibles were dried at 100°C for 8 hrs and afterwards weighed. This procedure was repeated for four samples of the each sawdust type. Which were averaged to obtain overall NDF.

Neutral Detergent Fibre (NDF) was determined using Equation 3.2:-

NDF= Cell Wall Content(CWC) = Hemicellulose, Lignin, Cutin, Cellulose, Silica and firbre bound nitrogen.

$$(NDF)\ \% = \frac{[(\text{wt of crucible + cell contents}) - \text{wt of crucible}] \times 100}{\text{wt of sample}} \qquad Eq\text{-}3.2$$

b) Determination of Hemicellulose content.(Acid –Detergent Fibre)

The Acid-Detergent fibre procedure was used to determine the hemicellulose content in the sawdust.

1 g of air-dried sample consisting particles passing BS sieve 7 was weighed into a beaker for refluxing and100ml cold acid detergent solution and 2ml decahydronaphthalene added. The mixture was heated to boiling in 5 to 10 minutes with the heat being reduced at the onset of boiling to avoid foaming. The boiling was adjusted to an even level and reflux continued for 60minutes, timed from onset of boiling.The mixture was filtered on a previously tared Gooch crucible set on the filter manifold using light suction. The filtered mat was broken up with a rod and washed twice with hot water (90-100°C). The sides of the crucible were rinsed in a similar manner. In addition, the wash was repeated with acetone until no colour was removed. This procedure was repeated for four samples of the each sawdust type which were averaged to obtain overall ADF.

The Acid Detergent Fibre (ADF) was thus determined using Equation 3.3.

$$ADF\% = \% = \frac{[(\text{wt of crucible + fibre}) - \text{wt of crucible}] \times 100}{\text{wt of sample}} \qquad Eq\text{-}3.3$$

c) Determination of Lignin content.(Acid –Detergent Lignin)

In the acid –detergent lignin procedure, the acid detergent fibre procedure was used as a preparatory step. The detergent removes protein the proteins and other acid-soluble material that would interfere with lignin determination. The ADF residue consists of cellulose, lignin, cutin, and acid-soluble ash (mainly silica). To determine the lignin content in the sawdust, acid-detergent –fibre was prepared. Asbestos of volume equal to the volume of the fibre was added to the crucible containing the acid-detergent fibre. The contents of the crucible were covered with 72% H_2SO_4 at 15°C and stirred with a glass rod to a mooth paste, breaking all lumps. The crucible was half-filled with acid and stirred. It was then refilled with 72% H_2SO_4 and stirred at hourly intervals as the acid was draining away. After 3 hrs, the acid was filtered off with vacuum and the content washed with hot water until it was acid-free. The crucible was dried at 100°C and weighed. It was then ignited in a muffle furnace at 500°C

to 550°C for 3 hrs and then cooled off to 100°C and weighed. This procedure was repeated for four samples of the each sawdust type which were averaged to obtain overall ADL.

Acid Detergent Lignin(ADL) was then determined using Equation 3.4;

$$ADL\% = \frac{[(wt\ of\ crucible + Lignin) - wt\ of\ crucible + ash] \times 100}{wt\ of\ sample} \qquad Eq\text{-}3.4$$

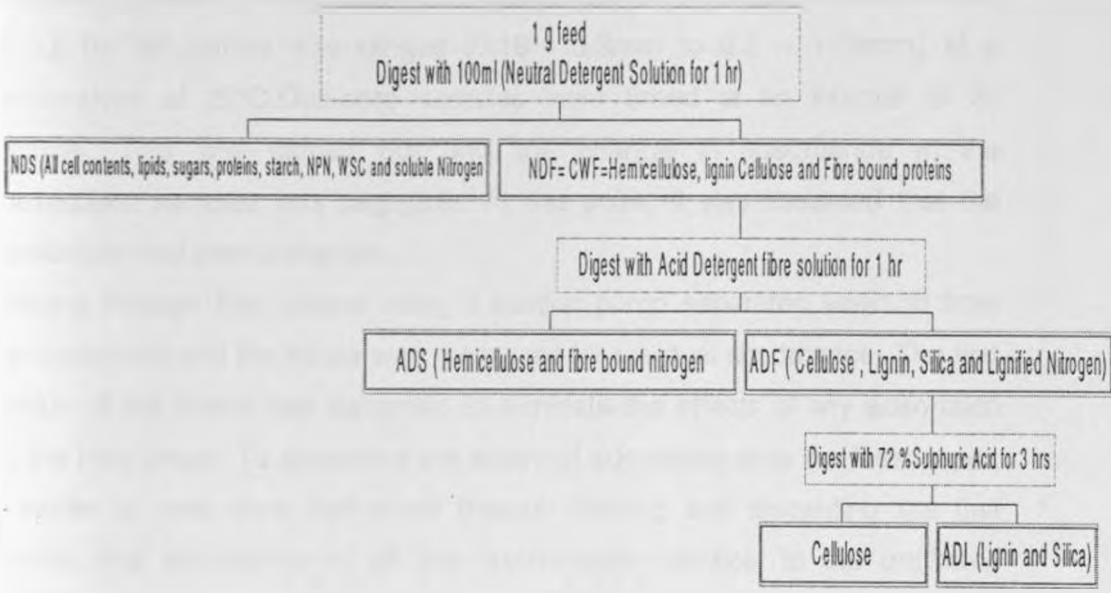


Figure 3.1 Schematic representation of Van Soest Procedures

3.3.3.3 Effect of Shaking Velocity on removal.

1 g sawdust of different particle sizes were added to plastic tumblers each containing 100ml of 10mg/l dye concentration. The samples were allowed to stand undisturbed for 30 minutes. Each sample was then filtered using pre-saturated 55mm Whatman filter paper. The absorbance of the resulting aliquot was measured using Ultra Spec II 4050 Spectrophotometer and the final concentration obtained from equation 4.1 of Congo red Calibration curve earlier prepared.

The above procedure was repeated for samples of each particle size at different rotation speed varied at an interval of 25 r.p.m upto 250 r.p.m at which point the shaking speed was too high to causing losses of the sawdust

and the dye through spillage. Removals were plotted against the speed of revolution as shown in Table 4.3 and Fig 4.3.

3.3.3.4 Equilibrium time.

Synthetic water samples (100 ml) of 10mg/l concentration of *Congo Red* dye were taken in separate set of containers and 1 g of sawdust was added. The sample containers were shaken on a continuous shaker at 150 rpm a speed obtained in section 3.4.3.3 above. The experiments were carried out at a pH of 8.9 for all particle size ranges (0.15 - 0.3mm to 0.6 – 1.18mm) at a temperature of 22°C.Duplicate samples were timed at an interval of 30 minutes. This was carried out until the change in absorbance in the subsequent samples was negligible. At this point, it was assumed that the equilibrium had been achieved.

Filtering through filter papers using a suction pump separated sawdust from the containers and the filtrate was measured for residual absorbance. The first portion of the filtrate was discarded to eliminate the effects of any adsorption on the filter paper. To determine the extent of adsorption onto the filter paper, a series of runs were performed through filtering and discarding the first portion; the absorbance of all the results were identical to the unfiltered sample.

3.3.3.5. Effect of pH on dye removal

For the investigation of the effect of pH, a pH range of 5 to 12 was selected. A sample solution of 10 mg/l was prepared. 100 ml samples were adjusted to the required pH using either 0.5 N NaOH to raise the pH or 0.5 N H_2SO_4 to lower the pH. 1 gram of sawdust (0.15 – 0.3mm) then added to the solutions. The samples were shaken at a speed of 150 r.p.m for 90 minutes (equilibrium time for the particles). The samples were filtered and the concentration of each determined.

3.3.3.6 Equilibrium Studies

Batch experiments were conducted for the development of adsorption isotherms using the particle sizes of 0.15 -0.3 mm which showed best removal and shorter equilibrium time (reported in the rate studies). Containers of

300ml capacities were used in all the experiments. Duplicate 100ml samples of 5, 10, 20,30, 40, 50 and 60mg/l concentration, were taken in different containers and 1 grams of each type of sawdust were added to it. The sample containers were shaken on the continuous shaker at 150 rpm. After an equilibrium time of 90 minutes, the samples were withdrawn from the shaker and the adsorbent from the sample containers was separated by filtration. The filtrate was then measured for the dye concentration. Dosages of 1.0, 2.0, 3.0, 5 and 6 grams of Sawdust were used. A room temperature of 22°C and constant pH of 8.9 were maintained in all the experiments.

Chapter 4

4.0 Results and Discussion

4.1 Physical and Chemical properties of Sawdust.

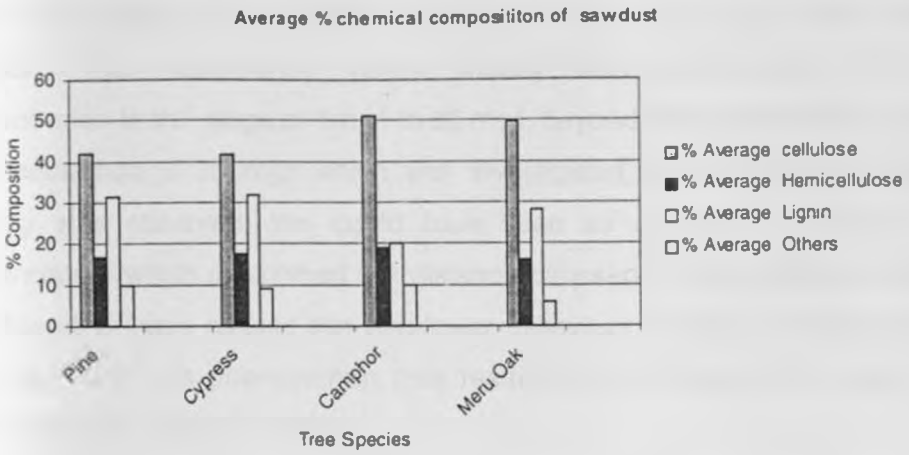
The laboratory tests were carried out to establish the characteristics of the 4 different sawdusts. The results, shown in Table 4.1 below summarise chemical and physical properties of the sawdusts studied. The percentage composition of cellulose was found to be within the range shown in Table 2.3 for softwood. Hard woods had values higher than those in the table. Other lignin content was lower in the test samples both for softwood and hardwood while hemicellulose content was within range. Extractives were high in both sawdust species tested.

Table 4.1 Chemical and Physical properties of sawdust.

Property	% composition for each Sawdust Species			
	Pine	Cypress	Camphor	Meru Oak
Cellulose	41.94	41.57	51.06	49.73
Lignin	16.97	17.52	18.86	16.00
Hemicellulose	31.37	31.82	20.28	28.3
Others	9.72	9.09	9.8	5.97
	Pine	Cypress	Camphor	Meru Oak
Specific Gravity	0.496	0.472	0.51	0.565

Figure 4.1 shows the major chemical components of the different sawdust species used in the research. Camphor and Meru oak were found to have higher amount of cellulose than Cypress and Pine this is inherent of hardwoods which have been reported elsewhere in literature by Irving (1977).

Fig 4.1 Chemical properties of Sawdust.



On the other hand, softwoods were found to have amount of hemicellulose than hardwood while both species were found to have varying amount extractives and other components. Irving (1977) and Shafizadeh (1981) have recorded similar values for both hard woods and softwoods. Specific gravity varied between 0.473-0.496 for the softwoods and 0.51 - 0.565 for the hardwoods.

4.2 Variation of Absorbance with Dye Concentration

To obtain the final dye concentration after adsorption has taken place. It is necessary to have a calibration curve.Table 4.2 shows absorbance values for different dye concentration.

Concentration	Mean Absorbance
0	0
1	0.042
2	0.066
5	0.162
10	0.322
20	0.606
30	0.885
40	1.200
50	1.363
60	1.587

Table 4.2 Concentration Versus Absorbance.

Fig 4.2 below shows the relationship between absorbance and concentration of the Congo Red dye. It was observed that in tap water, a linear relationship fitted to the data with correlation coefficient R^2 value being 0.9938. This indicated that absorbance varies linearly with concentration for a concentration in the range of 1mg/l to 60 mg/l. beyond this concentration up to a concentration of 500mg/l which was investigated, a high degree of non-linearity was observed. this could have been as a result of increase in concentration which diminished the distance between the dye molecule. This is believed to have caused the non-linear behaviuor of the curve (shown in Appendix A2). This phenomenon thus restricted the concentrations used in this research to 5mg/l and 60mg/l.

Thus, the equation of the treadline was adopted as the calibration curve to obtain final concentration of the samples used in the experiment by extrapolation.

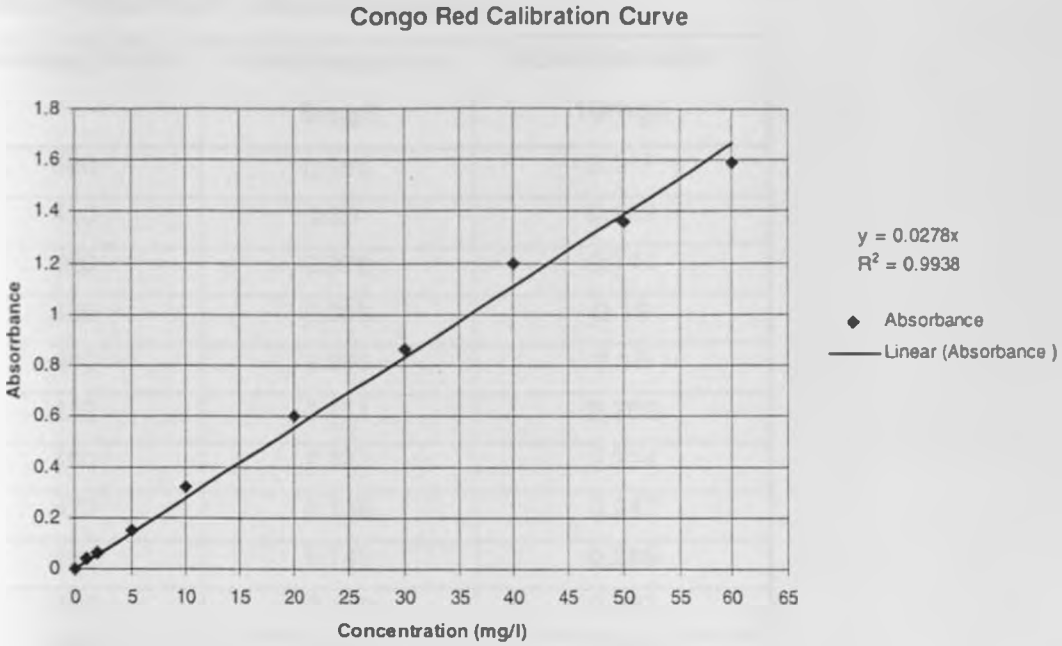
This took the form

$$Y=.0278X \qquad \text{Eq 4.1}$$

Where X is the dye concentration

Y is the absorbance (OD-optical density).

Fig 4.2 Congo Red Calibration curve.



4.3 Variation of Absorbance with Wavelength.

Wavelength of maximum absorption is an important parameter in any spectrophotometric studies within both the visible and the ultra-violet ranges. For dyes, it is the identification mark and acts as the fingerprint that specifically identifies them.

Figure 4.3 shows the relationship between the absorbance and wavelength for Congo Red concentrations of 5 and10mg/l. Within the visible spectra (400nm – 750nm), Congo red Dye was found to have a wavelength of maximum absorption as 495nm. This wavelength was used for all the measurements made using the spectrophotometer. This value is well in range with 497nm obtained by Lillie (1990) and 488nm obtained by Bundavari (1990). Gurr (1971) used a value of 487nm. In addition, Githere (MSc Thesis) used a value of 500nm for Congo Red. In light of this therefore, wavelength of 495nm lies well in range of the wavelengths used by other researcher dealing with Congo red dye i.e. between (487 – 500nm). The slight variations could have arisen as a result of solvent variations and different experimental conditions. For the same pH, dye concentration only amplifies the absorption peak but does not alter the wavelength of maximum absorption as shown by Figure 4.3.

Table 4.3 Wavelength versus Absorbance

Wavelength (nm)	Absorbance for 5mg/l	Absorbance for 10mg/l
400	0.065	0.117
410	0.07	0.126
420	0.078	0.141
430	0.088	0.16
440	0.099	0.18
450	0.111	0.202
460	0.123	0.224
470	0.136	0.247
480	0.149	0.269
490	0.159	0.287
500	0.16	0.289
510	0.152	0.275
520	0.139	0.25
530	0.118	0.213
540	0.094	0.173
550	0.07	0.13

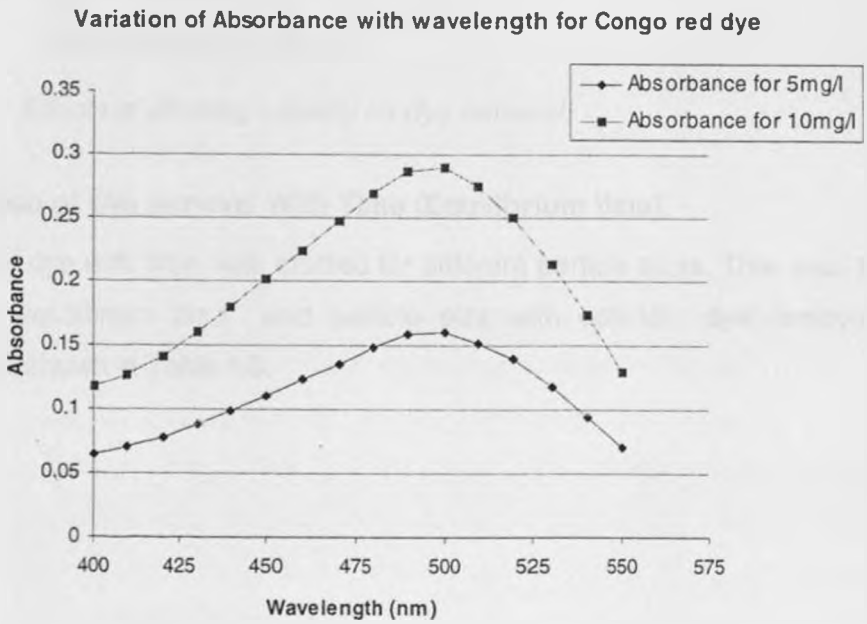


Figure 4.3 Variation of absorbance with wavelength

4.4 Effect of shaking on Dye removal.

The effect of shaking velocity on removal was investigated. It was observed that removal increased steadily from 0.5mg/g of dye at quiescent conditions of 0 r.p.m to a maximum of 0.91 mg/g at 150 r.p.m. for the composite sample. This was the the speed at which removals were best and beyond which point a steady declined to 0.72 mg/g at 250 r.p.m for all the particle sizes as shown in Figure 4.3 below. In this case therefore, a speed of 150 r.p.m was adopted for all the other investigations. From other sources this speed had been used by Alam et.al. (2000) in investigating the performance of low cost adsorbents in the removal of herbicides from aquatic environment.

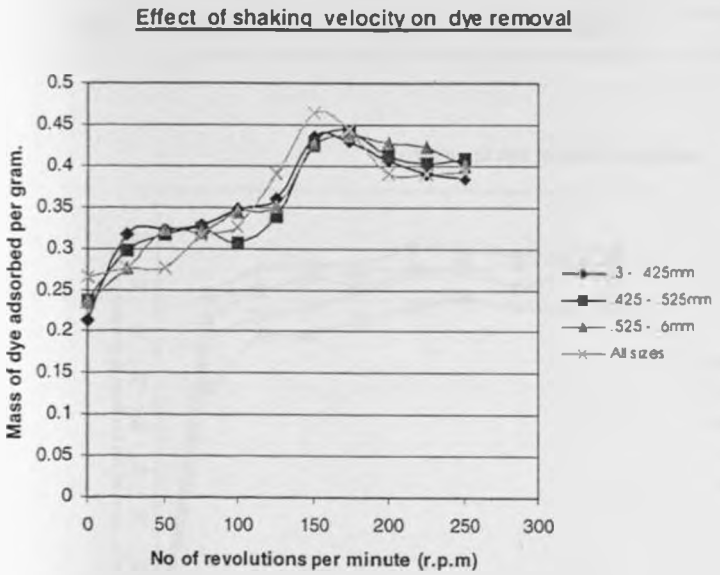


Figure 4.4 Effects of Shaking velocity on dye removal.

4.5 Variation of Dye removal With Time (Equilibrium time).

Removal of dye with time was studied for different particle sizes. This was to determine equilibrium time and particle size with optimal dye removal. Results are shown in Table 4.5.

Table 4.5 Removal Versus Time

Time (min)	Dye sorbed per gram of sawdust (mg/g)				
	0.15-0.3mm	0.3 - 0.425mm	0.425 - 0.525mm	0.525 - 0.6mm	0.6-01.18mm
0	0	0	0	0	0
30	0.78	0.78	0.72	0.69	0.575
60	0.833	0.78	0.79	0.73	0.69
90	0.84	0.82	0.805	0.745	0.69
120	0.84	0.79	0.83	0.78	0.72
150	0.88	0.83	0.83	0.8125	0.75
180	0.87	0.84	0.83	0.825	0.77
210	0.865	0.79	0.845	0.7875	0.75
240	0.865	0.83	0.845	0.8125	0.75
270	0.88	0.855	0.855	0.825	0.75

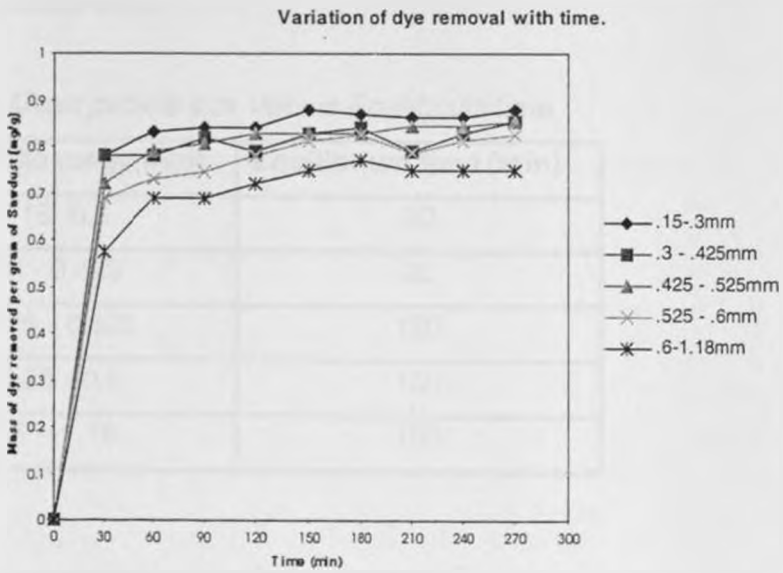


Fig 4.5 Variation of dye removal with time

The results shown in Fig 4.5 indicate that the amount of dye sorbed on sawdust increased steadily with time up to a certain time for each particle size range after which it remained almost constant. Also noted from the results was the fact that the rate of sorption was highest in the first 30 minutes for each particle size with particles in the range of 0.15mm - 0.3mm sorbing 79 % of the dye in the initial 30 minutes while particles in the range of .6mm – 1.18mm sorbed 58% of the dye from solution. The other particle sizes i.e. 0.3

–0.425mm, 0.425 - 0.525mm, and 0.525 - 0.6mm sorbed 78%, 72 % and 69% of dye respectively.

Equilibrium was attained after different contact times for the various particle sizes. It was observed to vary from 90 minutes for smallest 0.15 - 0.3mm particle sizes to 180 minutes for the biggest particle size 0.6 – 1.18mm. These variations can be associated to the ease with which dye molecules reach the adsorption site for the small particles. The particle being small in size present shorter travel routes as compared to the longer torturous route found in the larger particles. In addition, the available sorption area is higher for the small particle Sizes and less for the bigger sizes hence the rate of sorption is higher. Similar observation was made by Gupta (1990), in the study of removal chrome dye from wastewater. Table 4.6 shows the equilibrium time for the different particle sizes.

Table 4.6 Mean particle size Versus Equilibrium time

Particle size range(mm)	Equilibrium time (min)
0.15 -0.3	90
0.3 - 0.425	90
0.425 - 0.525	120
0.525 - 0.6	150
0.6 – 1.18	180

4.6 Effect of Particle size on dye removal.

From the graph, it was found that as the particle sizes of sawdust increase, there was a decrease in the amount of the dye adsorbed from 0.84mg/g for 0.15mm - 0.3mm particles to 0.75mg/g for 0.6 – 1.18mm particles for a dye concentration of 10mg/l. This can be explained on the basis of the available specific surface area for different particle size which is higher for the small particle sizes as compared to the bigger particles. The same was observed by Gupta et. al (1990) with mixed fly ash and coal adsorbents in the removal of chrome dye from aqueous solution where with the increase of adsorbent

particle size from 53 to 125 μm led to decrease in removal from 92.7% to 65.84% for 10mg/l dye concentration. The observed trend for both the soft woods and hardwoods was similar with soft wood particles removing more dye per gram than Hard wood particles. An explanation for this is that softwoods are lighter and have more pores hence higher specific surface area than hardwood. In addition, hardwoods were observed to impart some colour into the dye solution.

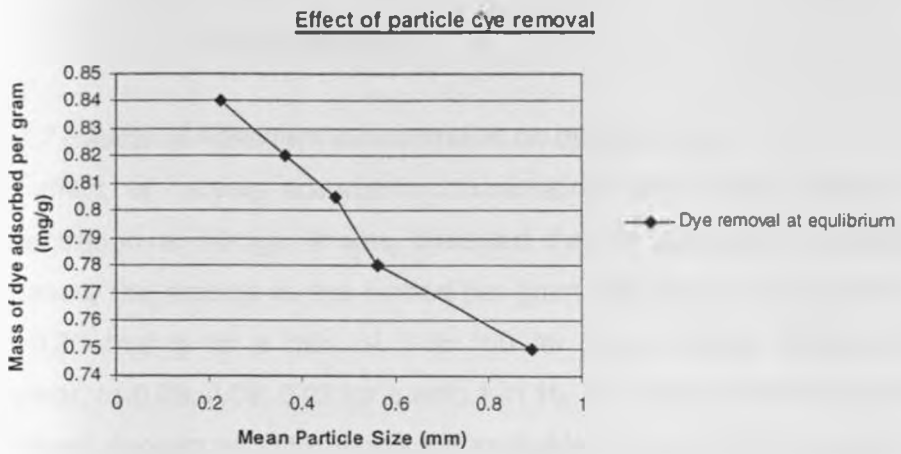


Fig 4.6 Above shows the effects of particle size on dye colour removal

4.7 Effect of Adsorbent concentration on removal.

Different masses of sawdust adsorbent were used to evaluate effect of change of adsorbent concentration on dye removal. Table 4.7 and Figure 4.7 show the results.

Table 4.7 Adsorbent concentration Versus Dye removal

Mass of Sawdust (g)	Mass of dye adsorbed by different Sawdusts (mg/g)			
	Cypress(mg/g)	Pine(mg/g)	Camphor(mg/g)	Meru Oak(mg/g)
1	0.51	0.62	0.35	0.5208
2	0.305	0.35	0.225	0.35
3	0.22	0.25	0.08	0.25
4	0.165	0.1875	0.085	0.2375
5	0.15	0.15	0.092	0.2
6	0.128	0.125	0.076	0.16
7	0.118	0.118	0.025	0.13
8	0.11	0.0975	0.03	0.125
9	0.096	0.0878	0.04	0.111
10	0.091	0.075	0.025	0.1

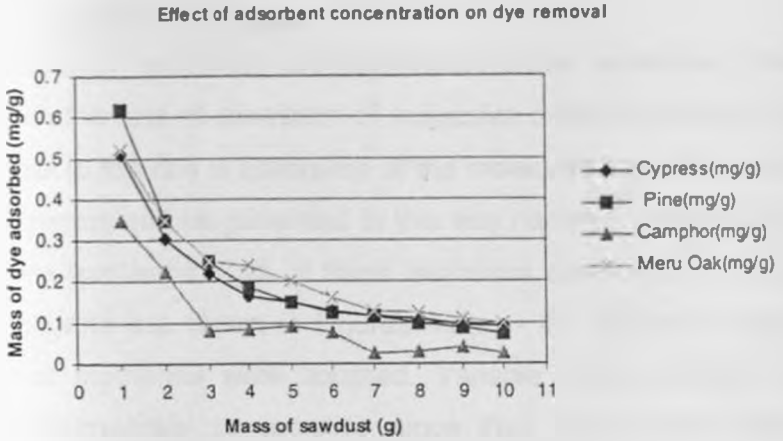


Fig 4.7 Effects of Adsorbent concentration on dye removal.

The effect of varying adsorbent concentration was studied using a dye concentration of 10mg/l. It was observed that as adsorbent concentration increased, the amount of dye sorbed per gram decreased varying from 0.63, 0.5, 0.35 mg/ g for a ratio of 1 in 100 for pine, cypress, Meru oak and camphor, to 0.08, 0.08, 0.03 for a ratio 1 in 10. This shows that an increase in adsorbent concentration increases the available surface area for sorption thus the reduction of in the amount of dye sorbed per gram. However, increase was not uniform as would be expected. This shows that there are other factors working against sorption process. Increase of the sorbent concentration can inhibit the movement of the dye molecules due to increased sorbent-sorbent interaction resulting to particle aggregation. This phenomenon was observed with high ratios such as 1:10 to about 1:12.5 the high masses also resulted in air being trapped in the absorbent hence resulting into dead capacity.

High masses were also found to increase the amount of colour imparted on the samples and reduced amount of aliquot available at the end of each set of experiment for measurement. Therefore, putting the above factors into consideration, masses of 1, 2, 3, 4, 5, and 6 g were used to develop both variable and constant mass sorption isotherms at equilibrium conditions.

4.8 Equilibrium Studies.

Adsorption isotherms are determined under equilibrium conditions, that is, when the rate of adsorption of molecules onto the surface of the adsorbent is equal to the rate of adsorption of the molecules from the surface. Two types of isotherms can be generated in this way namely:- Variable mass and constant mass isotherms. Both of these isotherms were used in this research. These isotherms are shown in Figures 4.8(a) - 4.8 (d) both variable and constant mass isotherms were adopted. Variable mass isotherms are considered environmentally conservative since they yield lower values of adsorption constants than constant mass isotherms. Environmentally conservative isotherms are thus used for prediction purposes.

In the data analysis, the equilibrium data was plotted on log – log scale and fitted to a power function which takes the form of the empirical Freundlich equilibrium model. The model yields values of k (constant) and 1/n (power of function) where k gives sorption capacity of the adsorbent for the equilibrium concentrations and n gives an idea about intensity of the capacity. Since all experiments were conducted under same experimental condition (pH 8.9, adsorbent size (0.15 -0.3 mm and temperature 23°C), the value of k is taken as a measure of maximum adsorption capacity for comparison purposes.

On considering variable mass isotherms, it was observed that the value of k for *Cypressus lusitanica* indicated that the amount of dye sorbed at equilibrium by sawdust decreased with increase in dye concentration in the liquid. The value of n was also found to be greater than 1, which indicates unlimited sorption for the dye. The other sawdusts showed poor adherence to Freundlich model at low concentrations (5-30mg/l), however, for higher concentrations (40 -60mg/l) it was observed that the k values were greater than 1 for Meru oak *(Vitex keniesis)* and Pine *(Pinus spp.)* giving rise to a scenario of unlimited sorption capacity. Camphor *(Ocotea usambarebsis)* sawdust was observed to values of n less than 1 giving an indication of saturation and low values of k.

These isotherms had very low correlation coefficients indicating poor adherence to the model proposed. A number of reasons can be associated with this behaviour, but the mainly, experimental artifacts such as the variations of both concentration and the adsorbent masses (with the attendant air trapping tendencies) could have contributed to these data skews. For the hardwoods, colour impartation on the samples could have resulted to increase of the competing species in the bulk solution and hence alter the measurements of absorbance of the aliquot.

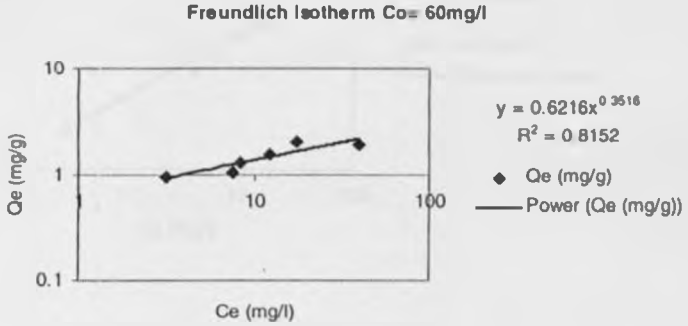
Constant mass isotherms showed fitted well into the data with high correlation values and hence good fit. For *Cypressus lusitanica* R^2 values range between 0.87 - 0.987 with K value being 0.40 mg/g and n value of 1.79. *Pinus spp* had R^2 values of 0.6 – 0.94 and k value of 0.45 and n value of 1.18.

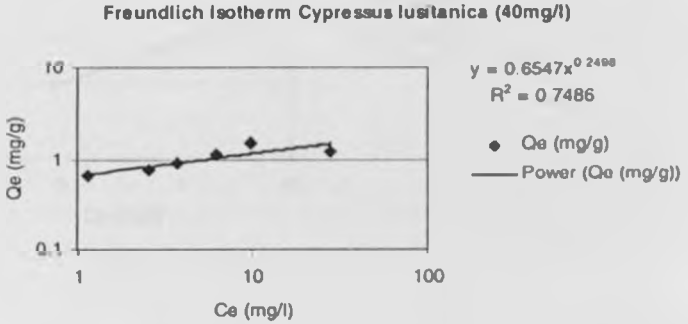
Camphor (*Ocotea usambarebsis*) had R^2 values of 0.6 – 0.99, k value of 0.006 and n value of 0.69. Meru Oak (*Vitex keniensis*) on the other had R^2 values in the range of 0.1 – 0.9, k value of 0.24 and n value of 0.823.
The above figures of k and n show distinctly that both softwoods have a high intensity of sorption and they show a possibility of unlimited sorption capacity. It can also be deduced that the hardwoods have low sorption capacity as evidenced by the low values of k. The values of n indicate that these two hardwoods have the possibility of experiencing dye saturation after sometime. For the hardwoods, this can be attributed to limitation in the number of sites on the adsorbent or from the fact that hardwood produce colour which could give rise to a false situation of saturation. The latter was also attributed to the great variabillity of R^2.

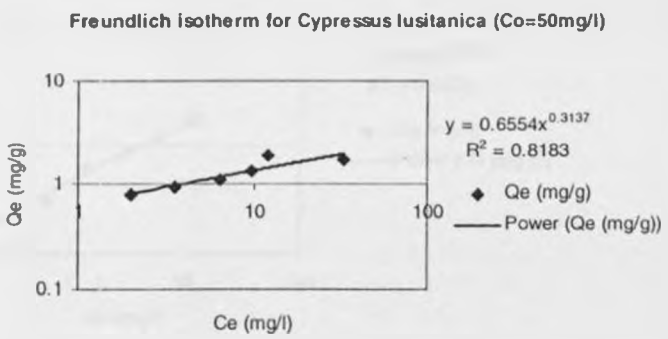
The softwoods show a high sorption capacity than the hard wood due to the high number of sites available. This can be deduced from the low densities, which indicate more pores and hence a larger surface area for the softwood than the hardwoods. The values of n show the possibility of unlimited sorption capacity. This is a feasible explanation as shown by Tsoumis (1990) that wood is able to adsorb moisture by way of formation of a mono molecular

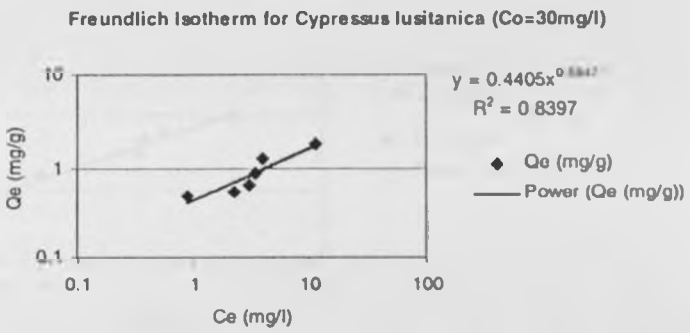
layer and then eventually polymolecular layers which cause wood to expand. This same scenario can be said to be true for the softwoods.

4.8 (a)Adsorption Isotherms for Cypressus lusitanica (Variable mass)

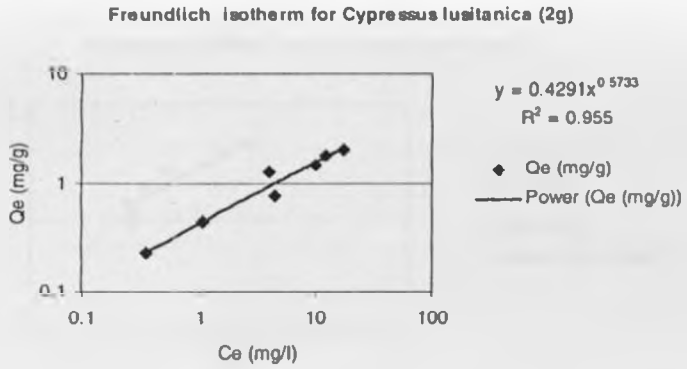


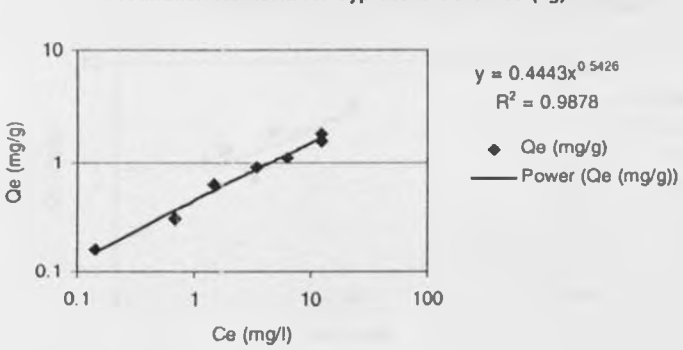




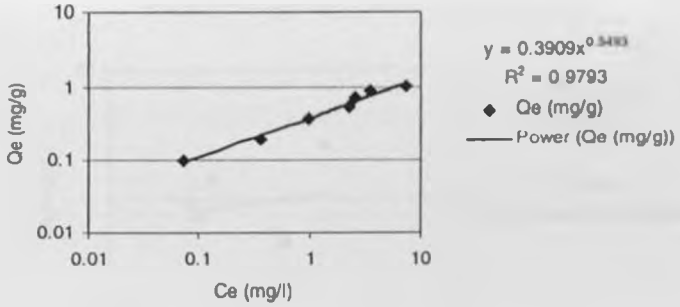


Cypressus lusitanica (Constant mass)

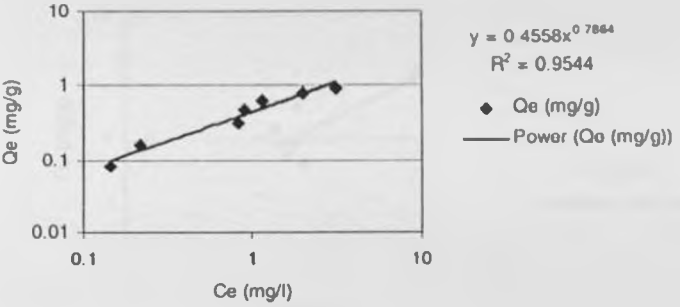




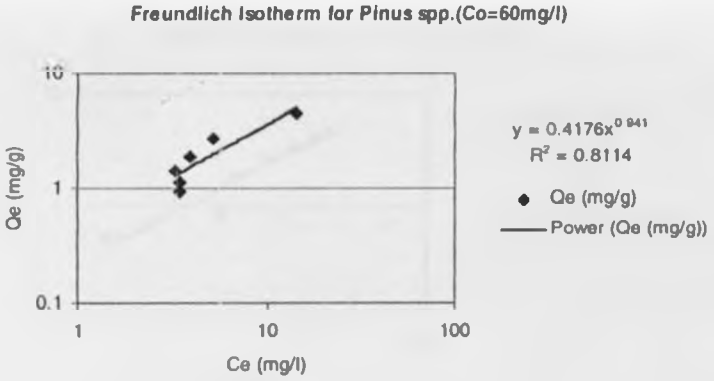
Freundlich isotherm for Cypressus lusitanica (5g)

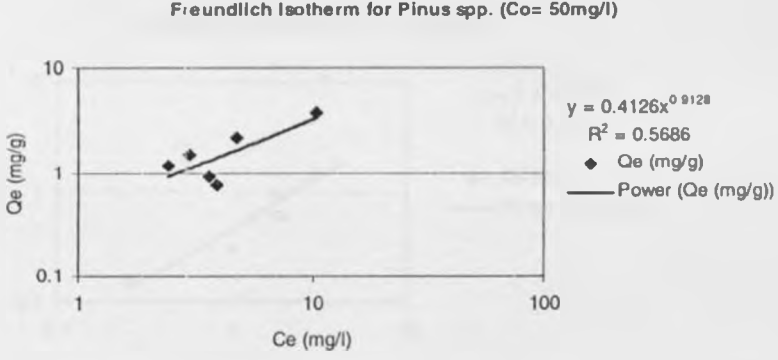


Freundlich isotherm for Cypressus lusitanica

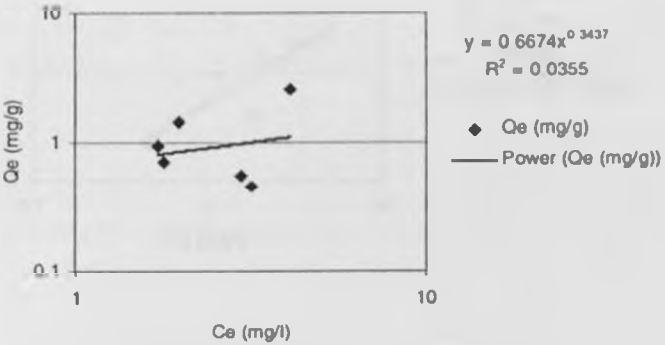


4.8 (b) Adsorption isoherms for Pinus spp. (Variable mass)

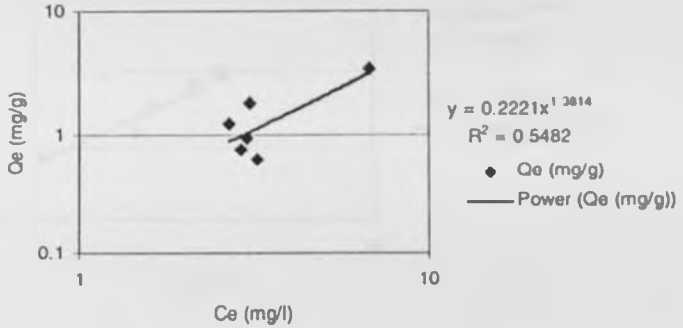




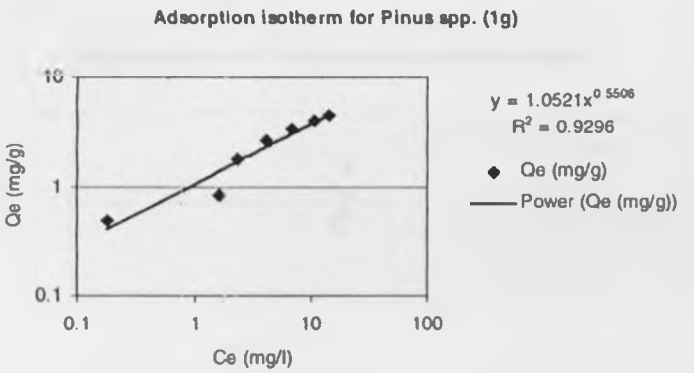
Freundlich isotherm for Pinus spp. (Co=30mg/l)

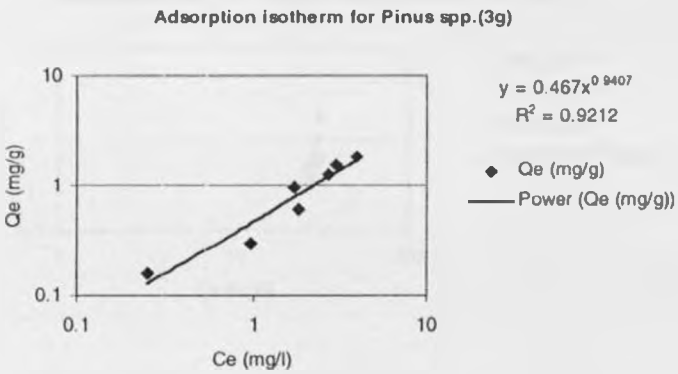


Freundlich Isotherm for Pinus spp. (40mg/l)

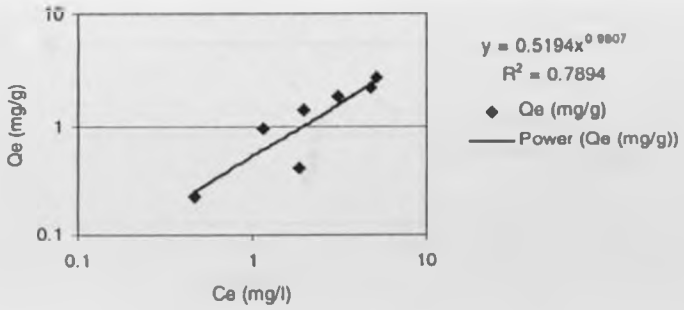


Pinus spp. (constant mass)

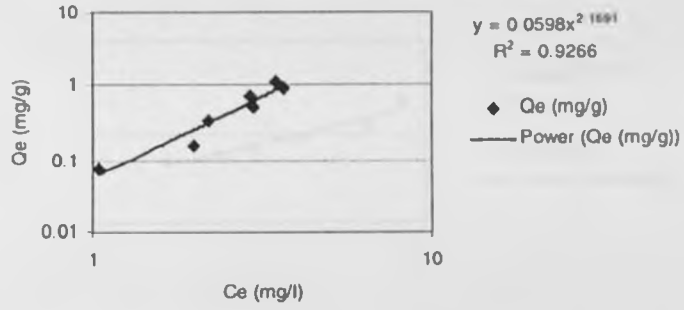




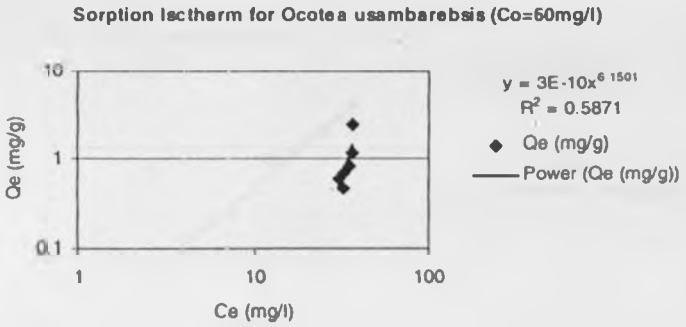
Adsorption isotherm for Pinus spp. (2g)

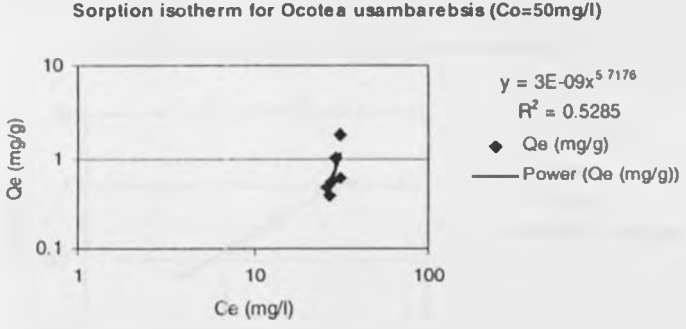


Adsorption isotherm for Pinus spp. (5g)

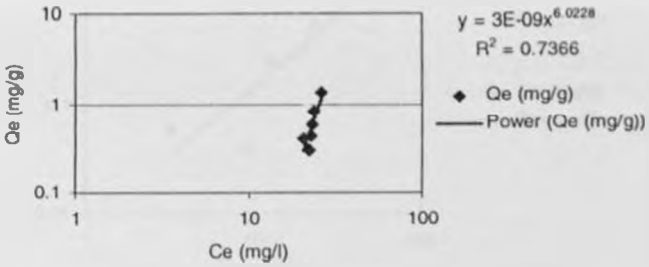


4.8 (c) Adsorption Isotherms for Ocotea Usambarebsis (Variable mass)

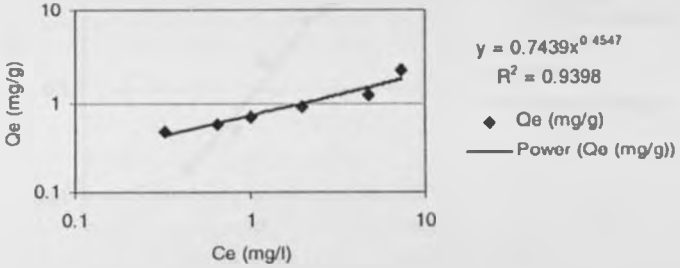




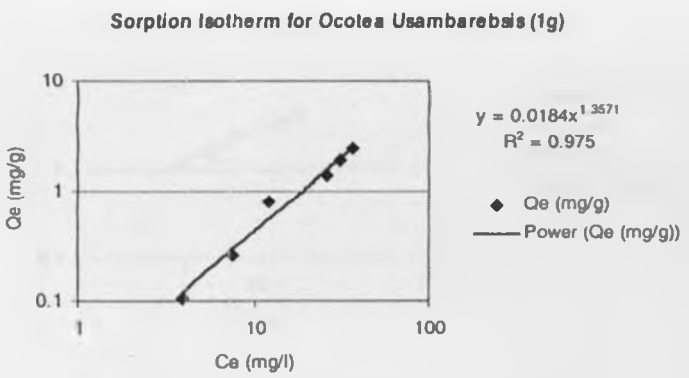
Freundlich Isotherm for Octea usambrensis (Co=40mg/l)

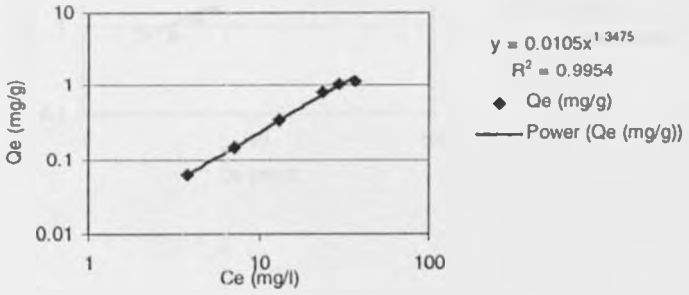


Sorption Isotherm for Octea Usambrensis (Co=30mg/l)

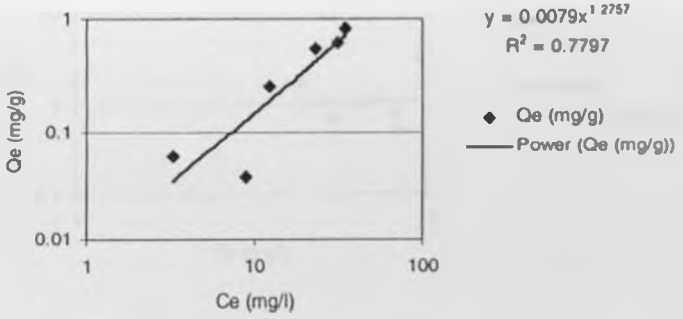


Ocotea usambarebsis (Constant mass)

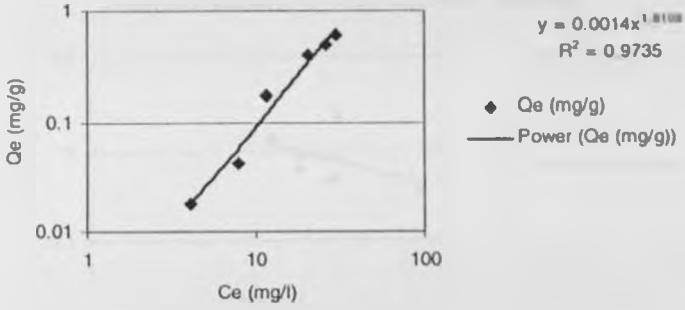




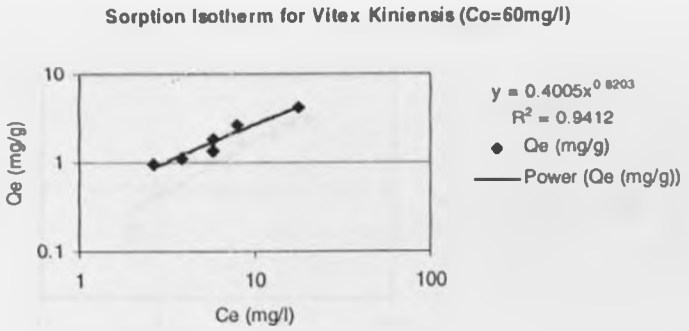
Sorption isotherm for Ocotea usambrebsis (3g)

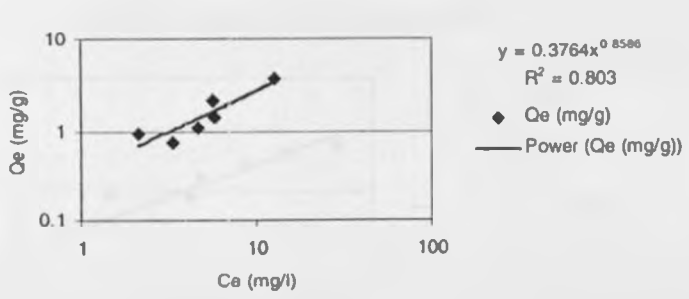


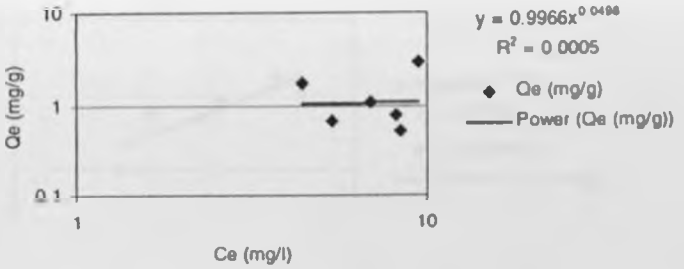
Sorption Isotherm for Ocotea usambrebsis(5g)

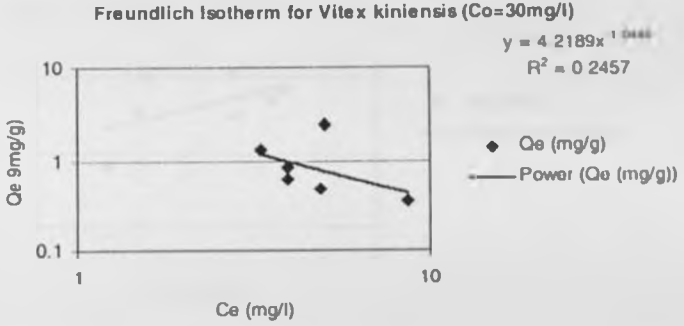


4.8 (d) Adsorption isotherms for Vitex Keniensis (Variable mass)

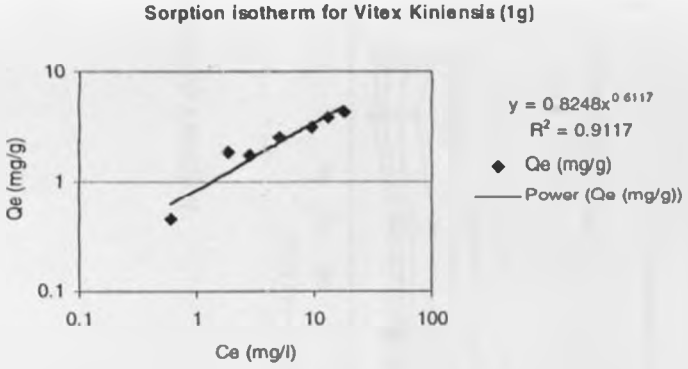


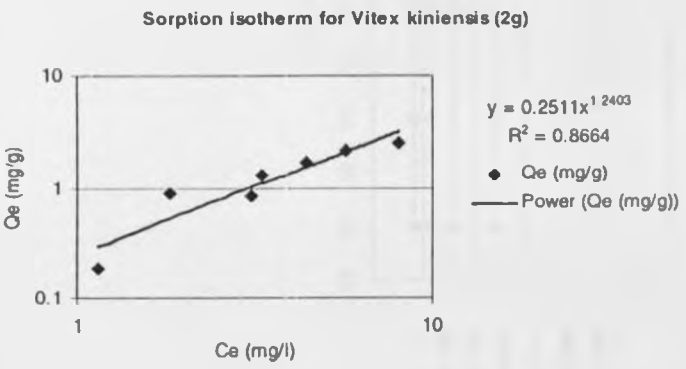



Sorption isotherm for Vitex kiniensis (Co=40mg/l)
10
1
0.1
Qe (mg/g)
1
10
Ce (mg/l)
y = 0.9966x^0.0498
R² = 0.0005
Qe (mg/g)
Power (Qe (mg/g))

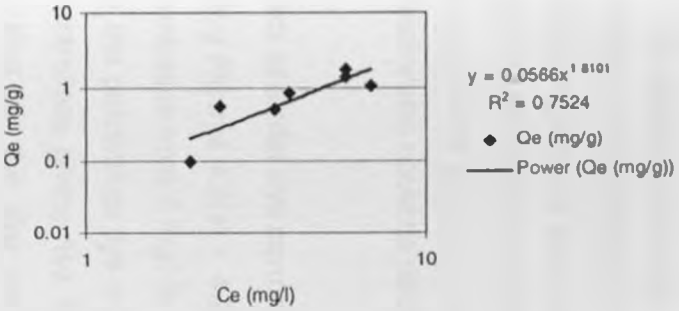

Freundlich Isotherm for Vitex kiniensis (Co=30mg/l)
10
1
0.1
Qe 9mg/g)
1
10
Ce (mg/l)
y = 4.2189x^1.0446
R² = 0.2457
Qe (mg/g)
Power (Qe (mg/g))

Vitex keniensis (Constant mass)

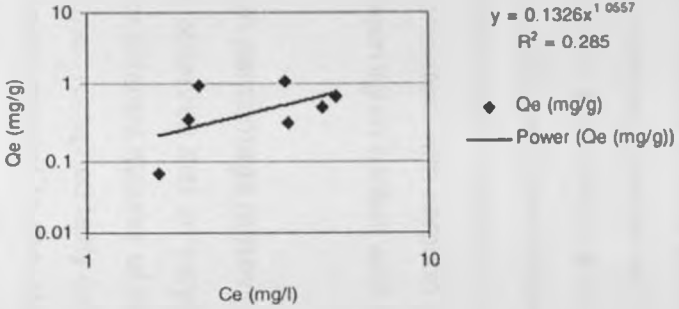




Sorption isotherm for Vitex Kiniensis (3g)



Sorption isotherm for Vitex Kiniensis (5g)

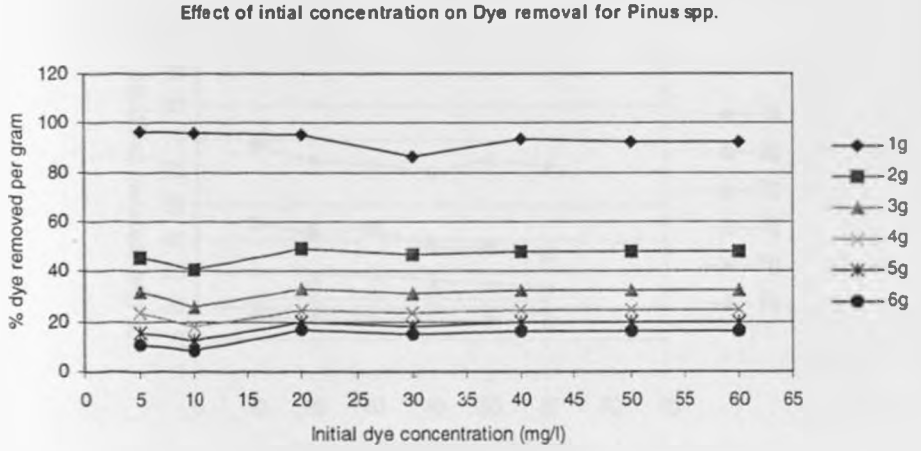


4.9 Relationship between sawdust properties and Sorption data.

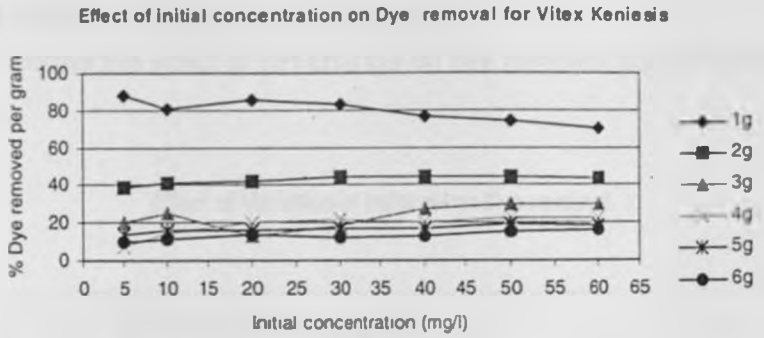
The softwoods were found to be less dense than the hardwoods which implies the possibility more pore spaces and higher specific surface area for sorption process. The latter were found to impart coloured species on the samples thus interfering with absorbance measurement and yielded low values of k and n. Sorption capacity was found to increase with hemicellulose content which was high in cypress, pine, Meru oak and Camphor in that order. Cellulose was found to have a negative correlation with sorption capacity. No definite relationship could be deduced between lignin content and sorption.

4.10 Effect of initial dye concentration on percentage removal.

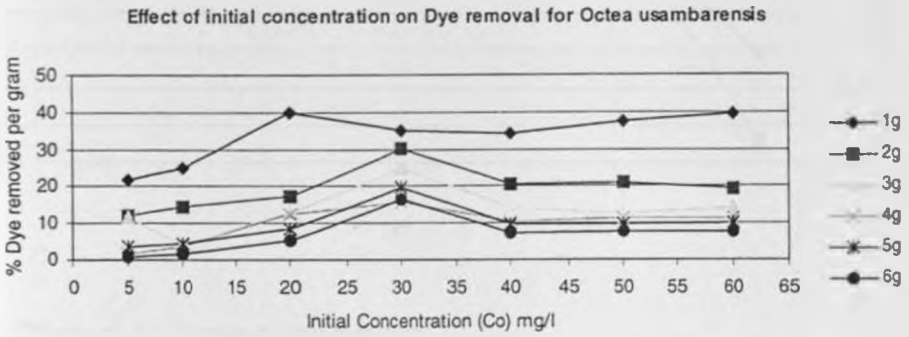
Considering Figures 4.9(a) – 4.9(d) it was observed that on varying the initial dye concentration from 5 mg/l to 60 mg/l for different masses of the 4 different sawdusts, the percentage dye sorbed per gram remained fairly constant for all the concentrations giving rise to graphs near parallel to the abscissa. This indicates that for the dye concentrations considered, the mechanism of sorption remain the same and an increase in the initial dye concentration only alters the magnitude adsorbed per gram of sawdust for all tree species tested.



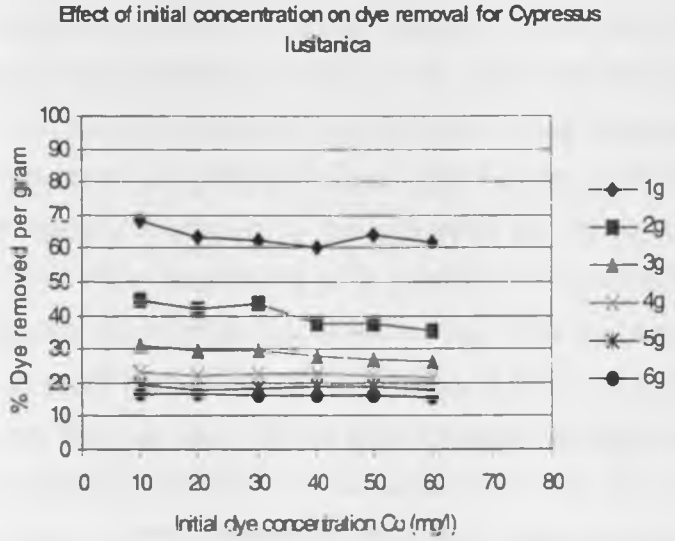
4.9 (a) Pinus spp sawdust.



4.9(b) Vitex keniensis sawdust



4.9(c) Ocotea Usambarebsis



4.9(d) Cypressus lusitanica sawdust.

4.11 Effect of pH Variation on dye removal

Figure 4.11 shows the effect of pH change on dye removal from synthetic wastewater.

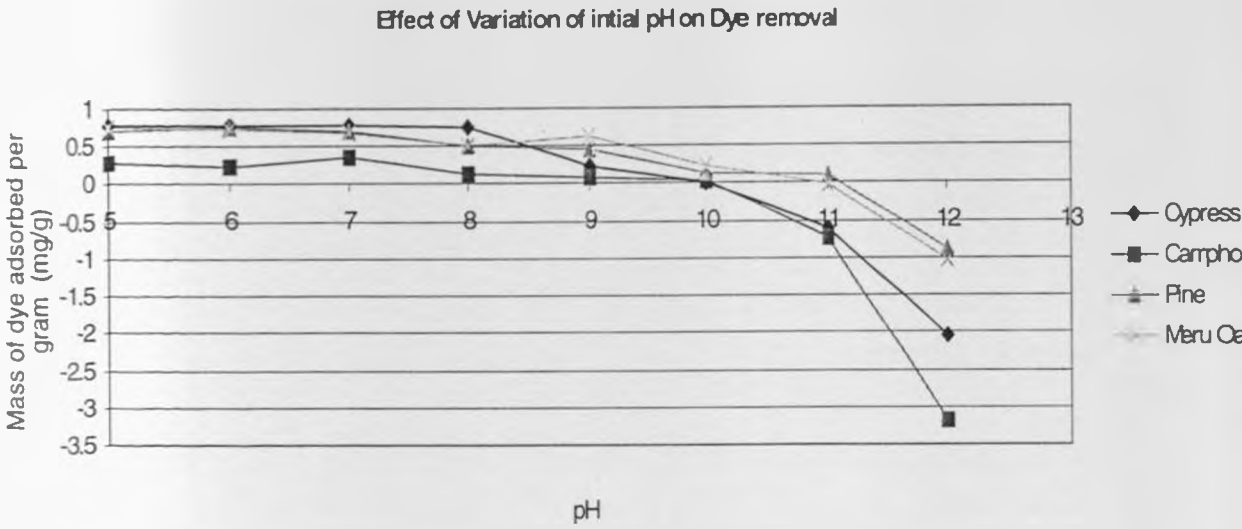


Fig 4.10 Effect of pH change on Sorption

In tap water, Congo Red dye ionizes to a pH of 8.9. It was observed that when the initial pH of the dye solution was varied from 8.9 to 12 by addition of Sodium hydroxide dye removal declined steadily to zero at pH 10 for both Camphor and Cypress Sawdust and pH 11 for Meru Oak and Pine Sawdust respectively. This can be explained from the point of view that an increase in -OH ions from the base competed favourably with the dye ions for the available sites thus reducing the amount of dye adsorbed by the sawdust. Another factor which may have contributed to a decline in the amount of the dye sorbed is the polar nature of the adsorbent surface. This could preferably sorb the -OH ions in preference to the dye ions. Beyond this point of zero removal, it was observed that the colour of the dye increased abruptly to absorbance value exceeding that of the initial concentration of 10 mg/l dye solution. Thus as shown in Figure 4.10, dye removal in this case takes negative values. This could possibly have resulted from side reactions favoured by the high pH.

On lowering the pH using 0.5N H_2SO_4, the amount of dye sorbed remained fairly constant with only slight increase at pH 8 and thereafter remained

constant for all the species tested. A similar phenomenon was observed by Gupta (1991) where an increase in the pH resulted in a decrease of the amount of chrome dye adsorbed on a mixture of fly ash and coal.

Chapter 5

Conclusions and Recommendations

5.1 Conclusions.

From the research findings, it may be concluded that:-

- The tested softwoods' sawdust have potential of removing direct dyes from water as indicated by the high value of k (a constant obtained from the Freundlich equilibrium model) yielded sorption capacity of the adsorbent ranging from 0.33- 0.4
- Hardwoods were found to have low potential of colour removal with low k values ranging from 0.0069 – 0.23. They also had a problem of colour impartation.
- Initial pH of effluent stream affects the amount of direct dye removed from he waste. High pH was found to reduce the amount of dye adsorbed and promoted side reactions with increase the absorbance of the water.

5.2 Recommendations

- Further investigations should be carried to investigate the effects of different methods of adsorbent preparation such as washing and air drying on dye removal using sawdust from the various tree species.
- Investigations should also be carried out on an actual dye waste stream containing different dyes and other dyeing chemicals.
- Further research should be carried out on the possibility of regeneration and proper disposal of the adsorbent.

Appendix A1. Reagents and Equipment.

- Disodium ethylenediaminetetra-acetate (EDTA, dihydrate crystal reagent grade)
- Sodium borate decahydrate reagent grade
- Disodium hydrogen phosphate,anhydrous ,reagent grade
- 2-ethoxyethanol purified grade
- Decahydronaphthalene reagent grade
- Acetone
- Sodium Sulfite anhydrous, reagent grade
- Sulphuric acid,(reagent grade)
- Cetyl trimethylammonium bromide, technical grade
- n-Hexane , technical grade
- Asbestos
- Saturated potasium permanganate
- Lignin buffer solution
- Ferric nitrate nonhydrate
- Silver nitrate
- Acetic Acid, glacial
- Potassium acetate
- Tertiary butyl alcohol
- Combined permanganate solution
- Oxalic acid dihydrate
- 95.5% ethanol
- Concentrated (12 N hydrochloric acid)
- Hydro bromic acid , reagent grade.

Equipment

- Ultra-spec II 4050 spectrophotometer
- XL- 3100D Electronic balance
- Measuring cylinders of different sizes
- 1000 Ml Volumetric flasks
- Model C-33 Continuous shaker
- 100ml beakers

- 350ml plastic tumblers
- Millipore 3500 filter.
- BS Sieves No7 to No. 100
- 50ml density bottle
- A vacuum Dissector
- A drying oven.
- Glass rod
- Vacuum Pump
- Refluxing apparatus-

Beakers, Berzelius without spout, 600ml capacity

Crucibles, Gooch type, high-form Pyrex fritted glass, 50 ml capacity, course porosity. Type sold by scientific, Silver spring,Md, Cat No.8-237

Scimatco rubber tubing, black, thick-wall, 5/16 in.-(80mmm) bore, 3/22-(35mm) wall

Hot plate, Thermolyne 9HP-A8805B), blue porcelain, steel-flattop, 120v, 3.3-a, 400-w., 3 ¾-in.-(9.5-cm) diameter

Multi electric receptacle box, 20-a., 115-v.

Condensers, reflux, crude-fiber, Pyrex. E.H. Sargent and Company, Philadelphia, Pa., Cat No.S-22742

Flexa frame hook connectors

Rings, cast-iron

Flexa frame rods

- Filter manifold

Polyethylene pipe

Funnels

Flasks

Clamps

Rubber Adopter

Rubber tubing

Glass tubing

Polyethylene tubing

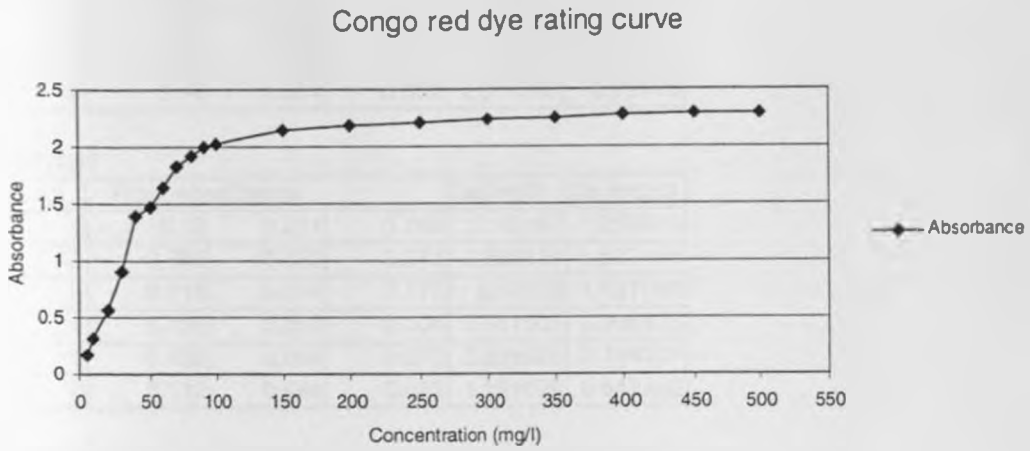
Screw Clamp

- Water heater

Appendix A2 Chemical composition of Sawdust

	Pine		Cypress		Camphor		Meru Oak	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample1	Sample 2
Crucible Number	293	963	927	877	237	253	480	31
Crucible wt (g)	31.4105	30.7969	31.6161	30.1758	31.8517	30.7956	29.5801	30.8274
Sample Weight (g)	1	1	1	1	1	1	1	1
Dry matter	94.59	94.59	94.77	94.77	94.75	94.75	95.11	95.11
Crucible +NDF Residue	32.2857	31.682	32.4934	31.0732	31.0423	31.6055	30.4961	31.7199
NDF Residue	0.8752	0.8851	0.8773	0.8974	0.8094	0.8099	0.916	0.8925
Crucible + ADF	32.1379	31.5087	32.3456	30.8889	31.7702	31.4268	30.3386	31.573
% Celluose	42.700372	41.17637763	43.52542589	39.61162466	154.10868	51.055284	49.061675	50.399296
% Hemicellulose	15.62533	18.3211756	15.59565263	19.44708241	-76.95317	18.860158	16.559773	15.445274
Crucible +ADL	31.7125	31.0975	31.9057	30.4776	31.3057	30.9767	29.856	31.0902
Crucible + Ash	31.4145	30.802	31.613	30.1672	31.1288	30.7845	29.5861	30.8218
% Lignin	31.504387	31.2400888	30.88530126	32.7529809	18.701766	20.28496	28.377668	28.219956
% Average cellulose	41.93837502		41.56852527		51.05528366		49.73048544	
% Average Hemicellulose	16.97325299		17.52136752		18.86015831		16.00252339	
% Average Lignin	31.37223808		31.81914108		20.28496042		28.2988119	
% Average Others	9.716133911		9.090966128		9.799597608		5.968179262	

Appendix A3 Variation of Absorbance with concentration



Appendix A4 Specific Gravity of Sawdust. (G_s)

Tree Species	Sample	Mass (g)	Initial Volm (cm^3)	Final Volm(cm^3)	Density (g/cm^3)
Pine	1	54	700	810	0.490909091
	2	55.7	700	800	0.557
	3	55.1	700	820	0.459166667
	4	60.9	700	810	0.553636364
Cypress	1	47.6	700	800	0.476
	2	48.2	700	810	0.438181818
	3	50.4	700	800	0.504
	4	47.2	700	800	0.472
Camphor	1	52.8	700	800	0.528
	2	45.8	700	800	0.458
	3	49.5	700	800	0.495
	4	55.7	700	800	0.557
Meru Oak	1	39.7	700	770	0.567142857
	2	40.69	700	770	0.581285714
	3	41.1	700	770	0.587142857
	4	41.9	700	780	0.52375

Appendix A5 Variable mass Isotherm data.

Cypressus lusitanica

Co = 60mg/l

Mass (g)	Final Absorbance			Ce(mg/l)	Qe (mg/g)
1	1.13	0.021	1.109	39.89209	2.010791
2	0.516	0.032	0.484	17.41007	2.129496
3	0.382	0.044	0.338	12.15827	1.594724
4	0.281	0.052	0.229	8.23741	1.294065
5	0.271	0.064	0.207	7.446043	1.051079
6	0.171	0.084	0.087	3.129496	0.947842

Co=50 mg/l

Mass (g)	Final Absorbance			Ce(mg/l)	Qe (mg/g)
1	0.937	0.021	0.916	32.94964	1.705036
2	0.369	0.032	0.337	12.1223	1.893885
3	0.315	0.044	0.271	9.748201	1.341727
4	0.23	0.052	0.178	6.402878	1.089928
5	0.162	0.064	0.098	3.52518	0.929496
6	0.14	0.084	0.056	2.014388	0.79976

Co=40 mg/l

Mass (g)	Final Absorbance			Ce(mg/l)	Qe (mg/g)
1	0.79	0.021	0.769	27.66187	1.233813
2	0.306	0.032	0.274	9.856115	1.507194
3	0.216	0.044	0.172	6.18705	1.127098
4	0.156	0.052	0.104	3.741007	0.906475
5	0.136	0.064	0.072	2.589928	0.748201
6	0.116	0.084	0.032	1.151079	0.647482

Co=30 mg/l

Mass (g)	Final Absorbance			Ce(mg/l)	Qe (mg/g)
1	0.333	0.021	0.312	11.22302	1.877698
2	0.141	0.032	0.109	3.920863	1.303957
3	0.138	0.044	0.094	3.381295	0.88729
4	0.136	0.052	0.084	3.021583	0.67446
5	0.127	0.064	0.063	2.266187	0.554676
6	0.109	0.084	0.025	0.899281	0.485012

Co=20 mg/l

Mass (g)	Final Absorbance			Ce(mg/l)	Qe (mg/g)
1	0.457	0.021	0.436	15.68345	0.431655
2	0.155	0.032	0.123	4.42446	0.778777
3	0.085	0.044	0.041	1.47482	0.617506
4	0.074	0.052	0.022	0.791367	0.480216
5	0.091	0.064	0.027	0.971223	0.380576
6	0.107	0.084	0.023	0.827338	0.319544

Co=10 mg/l

Mass (g)	Final Absorbance			Ce(mg/l)	Qe (mg/g)
1	0.108	0.021	0.087	3.129496	0.68705
2	0.062	0.032	0.03	1.079137	0.446043
3	0.063	0.044	0.019	0.683453	0.310552
4	0.073	0.052	0.021	0.755396	0.231115
5	0.074	0.064	0.01	0.359712	0.192806
6	0.09	0.084	0.006	0.215827	0.16307

Co=5 mg/l

Mass (g)	Final Absorbance			Ce(mg/l)	Qe (mg/g)
1	0.049	0.021	0.028	1.007194	0.399281
2	0.042	0.032	0.01	0.359712	0.232014
3	0.048	0.044	0.004	0.143885	0.161871
4	0.065	0.052	0.013	0.467626	0.113309
5	0.066	0.064	0.002	0.071942	0.098561
6	0.088	0.084	0.004	0.143885	0.080935

Vitex Keniensis.

Co=60 mg/l

Mass (g)	Final Absorbance			Ce(mg/l)	Qe (mg/g)
1	0.567	0.068	0.499	17.94964	4.205036
2	0.327	0.105	0.222	7.985612	2.600719
3	0.288	0.126	0.162	5.827338	1.805755
4	0.3	0.139	0.161	5.791367	1.355216
5	0.35	0.244	0.106	3.81295	1.123741
6	0.32	0.247	0.073	2.625899	0.956235

Co=50 mg/l

Mass (g)	Final Absorbance			Ce(mg/l)	Qe (mg/g)
1	0.425	0.068	0.357	12.84173	3.715827
2	0.263	0.105	0.158	5.683453	2.215827
3	0.287	0.126	0.161	5.791367	1.473621
4	0.269	0.139	0.13	4.676259	1.133094
5	0.303	0.244	0.059	2.122302	0.957554
6	0.339	0.247	0.092	3.309353	0.778177

Co=40 mg/l

Mass (g)	Final Absorbance			Ce(mg/l)	Qe (mg/g)
1	0.331	0.068	0.263	9.460432	3.053957
2	0.227	0.105	0.122	4.388489	1.780576
3	0.318	0.126	0.192	6.906475	1.103118
4	0.365	0.139	0.226	8.129496	0.796763
5	0.393	0.244	0.149	5.359712	0.692806
6	0.481	0.247	0.234	8.417266	0.526379

Co=30 mg/l

Mass (g)	Final Absorbance			Ce(mg/l)	Qe (mg/g)
1	0.209	0.068	0.141	5.071942	2.492806
2	0.197	0.105	0.092	3.309353	1.334532
3	0.236	0 126	0 11	3.956835	0.868106
4	0.249	0.139	0.11	3.956835	0.651079
5	0.38	0.244	0.136	4.892086	0.502158
6	0.486	0.247	0.239	8.597122	0.356715

Co=20 mg/l

Mass (g)	Final Absorbance			Ce(mg/l)	Qe (mg/g)
1	1.03	0.068	0.962	2.87	1.713
2	1.051	0.105	0.946	3.09	0.8455
3	1.025	0.126	0.899	3.59	0.547
4	0.97	0.139	0.831	3.72	0.407
5	0.919	0.244	0.675	3.88	0.3224
6	0.993	0.247	0.746	3.92	0.268

Co=10 mg/l

Mass (g)	Final Absorbance			Ce(mg/l)	Qe (mg/g)
1	0.121	0.068	0.053	1.906475	1.809353
2	0.156	0.105	0.051	1.834532	0.908273
3	0.195	0.126	0.069	2.482014	0.583933
4	0.26	0.139	0.121	4.352518	0.391187
5	0.299	0.244	0.055	1.978417	0.360432
6	0.336	0.247	0.089	3.201439	0.279976

Co=5 mg/l

Mass (g)	Final Absorbance			Ce(mg/l)	Qe (mg/g)
1	0.085	0.068	0.017	0.611511	0.438849
2	0.137	0.105	0.032	1.151079	0.192446
3	0.182	0.126	0.056	2.014388	0.09952
4	0.236	0.139	0.097	3.489209	0.03777
5	0.289	0.244	0.045	1.618705	0.067626
6	0.307	0.247	0.06	2.158273	0.047362

Octea usambarebsis

Co=60 mg/l

Mass (g)	Final Absorbance			Ce(mg/l)	Qe (mg/g)
1	1.03	0.022	1.008	36.25899	2.374101
2	1.051	0.034	1.017	36.58273	1.170863
3	1.025	0.056	0.969	34.85612	0.838129
4	0.97	0.063	0.907	32.6259	0.684353
5	0.919	0.078	0.841	30.2518	0.594964
6	0.993	0.083	0.91	32.73381	0.454436

Co=50 mg/l

Mass (g)	Final Absorbance			Ce(mg/l)	Qe (mg/g)
1	0.89	0.022	0.868	31.22302	1.877698
2	0.845	0.034	0.811	29.17266	1.041367
3	0.925	0.056	0.869	31.25899	0.6247
4	0.829	0.063	0.766	27.55396	0.561151
5	0.807	0.078	0.729	26.22302	0.47554
6	0.837	0.083	0.754	27.1223	0.381295

Co=40 mg/l

Mass (g)	Final Absorbance			Ce(mg/l)	Qe (mg/g)
1	0.751	0.022	0.729	26.22302	1.377698
2	0.69	0.034	0.656	23.59712	0.820144
3	0.698	0.056	0.642	23.09353	0.563549
4	0.7	0.063	0.637	22.91367	0.427158
5	0.649	0.078	0.571	20.53957	0.389209
6	0.701	0.083	0.618	22.23022	0.296163

Co=30 mg/l

Mass (g)	Final Absorbance			Ce(mg/l)	Qe (mg/g)
1	0.225	0.022	0.203	7.302158	2.269784
2	0.165	0.034	0.131	4.71223	1.264388
3	0.11	0.056	0.054	1.942446	0.935252
4	0.091	0.063	0.028	1.007194	0.72482
5	0.07	0.078	0.018	0.647482	0.58705
6	0.05	0.083	0.009	0.323741	0.494604

Co=20 mg/l

Mass (g)	Final Absorbance			Ce(mg/l)	Qe (mg/g)
1	0.357	0.022	0.335	12.05036	0.794964
2	0.398	0.034	0.364	13.09353	0.345324
3	0.394	0.056	0.338	12.15827	0.261391
4	0.403	0.063	0.34	12.23022	0.194245
5	0.397	0.078	0.319	11.47482	0.170504
6	0.458	0.083	0.375	13.48921	0.108513

Co=10 mg/l

Mass (g)	Final Absorbance			Ce(mg/l)	Qe (mg/g)
1	0.23	0.022	0.208	7.482014	0.251799
2	0.231	0.034	0.197	7.086331	0.145683
3	0.302	0.056	0.246	8.848921	0.038369
4	0.302	0.063	0.239	8.597122	0.035072
5	0.295	0.078	0.217	7.805755	0.043885
6	0.336	0.083	0.253	9.100719	0.014988

Co=5mg/l

Mass (g)	Final Absorbance			Ce(mg/l)	Qe (mg/g)
1	0.131	0.022	0.109	3.920863	0.107914
2	0.139	0.034	0.105	3.776978	0.061151
3	0.146	0.056	0.09	3.23741	0.058753
4	0.193	0.063	0.13	4.676259	0.008094
5	0.192	0.078	0.114	4.100719	0.017986
6	0.21	0.083	0.127	4.568345	0.007194

Pinus spp.

Co=60 mg/l

Mass (g)	Final Absorbance			Ce(mg/l)	Qe (mg/g)
1	0.419	0.021	0.398	14.316547	4.5683453
2	0.176	0.032	0.144	5.1798561	2.7410072
3	0.154	0.044	0.11	3.9568345	1.8681055
4	0.144	0.052	0.092	3.3093525	1.4172662
5	0.16	0.064	0.096	3.4532374	1.1309353
6	0.18	0.084	0.096	3.4532374	0.942446

Co=50 mg/l

Mass (g)	Final Absorbance			Ce(mg/l)	Qe (mg/g)
1	0.309	0.021	0.288	10.359712	3.9640288
2	0.163	0.032	0.131	4.7122302	2.2643885
3	0.127	0.044	0.083	2.9856115	1.5671463
4	0.12	0.052	0.068	2.4460432	1.1888489
5	0.165	0.064	0.101	3.6330935	0.9273381
6	0.193	0.084	0.109	3.9208633	0.7679856

Co=40 mg/l

Mass (g)	Final Absorbance			Ce(mg/l)	Qe (mg/g)
1	0.208	0.021	0.187	6.7266187	3.3273381
2	0.118	0.032	0.086	3.0935252	1.8453237
3	0.119	0.044	0.075	2.6978417	1.2434053
4	0.136	0.052	0.084	3.0215827	0.9244604
5	0.145	0.064	0.081	2.9136691	0.7417266
6	0.174	0.084	0.09	3.2374101	0.6127098

Co=30 mg/l

Mass (g)	Final Absorbance			Ce(mg/l)	Qe (mg/g)
1	0.135	0.021	0.114	4.1007194	2.5899281
2	0.087	0.032	0.055	1.9784173	1.4010791
3	0.092	0.044	0.048	1.7266187	0.942446
4	0.102	0.052	0.05	1.7985612	0.705036
5	0.147	0.064	0.083	2.9856115	0.5402878
6	0.173	0.084	0.089	3.2014388	0.4466427

Co=20 mg/l

Mass (g)	Final Absorbance			Ce(mg/l)	Qe (mg/g)
1	0.085	0.021	0.064	2.3021583	1.7697842
2	0.064	0.032	0.032	1.1510791	0.942446
3	0.095	0.044	0.051	1.8345324	0.6055156
4	0.099	0.052	0.047	1.6906475	0.4577338
5	0.125	0.064	0.061	2.1942446	0.3561151
6	0.148	0.084	0.064	2.3021583	0.294964

Co=10 mg/l

Mass (g)	Final Absorbance			Ce(mg/l)	Qe (mg/g)
1	0.045	0.034	0.011	0.3956835	0.9604317
2	0.052	0.052	0.052	1.8705036	0.4064748
3	0.061	0.082	0.061	2.1942446	0.2601918
4	0.0777	0.106	0.0777	2.794964	0.1801259
5	0.107	0.132	0.107	3.8489209	0.1230216
6	0.142	0.155	0.142	5.1079137	0.0815348

Co=5 mg/l

Mass (g)	Final Absorbance			Ce(mg/l)	Qe (mg/g)
1	0.039	0.034	0.005	0.1798561	0.4820144
2	0.065	0.052	0.013	0.4676259	0.2266187
3	0.089	0.082	0.007	0.2517986	0.1582734
4	0.116	0.106	0.01	0.3597122	0.1160072
5	0.161	0.132	0.029	1.0431655	0.0791367
6	0.202	0.155	0.047	1.6906475	0.0551559

Constant mass isotherm data

Cypressus lusitanica

Constant Mass of 1g

Initial Concentration (mg/l)	Ce (mg/l)	Qe (mg/g)
5	1.007194	0.399281
10	3.129496	0.68705
20	11.22302	1.877698
30	15.68345	0.431655
40	27.66187	1.233813
50	32.94964	1.705036
60	39.89209	2.010791

Constant Mass of 2g

Initial Concentration (mg/l)	Ce (mg/l)	Qe (mg/g)
5	0.359712	0.232014
10	1.079137	0.446043
20	3.920863	1.303957
30	4.42446	0.778777
40	9.856115	1.507194
50	12.1223	1.893885
60	17.41007	2.129496

Constant mass of 3g

Initial Concentration (mg/l)	Ce (mg/l)	Qe (mg/g)
5	0.143885	0.161871
10	0.683453	0.310552
20	1.47482	0.617506
30	3.381295	0.88729
40	6.18705	1.127098
50	12.1223	1.893885
60	12.15827	1.594724

Constant mass of 5g

Initial Concentration (mg/l)	Ce (mg/l)	Qe (mg/g)
5	0.071942	0.098561
10	0.359712	0.192806
20	0.971223	0.380576
30	2.266187	0.554676
40	2.589928	0.748201
50	3.52518	0.929496
60	7.446043	1.051079

Constant mass of 6g

Initial Concentration (mg/l)	Ce (mg/l)	Qe (mg/g)
5	0.143885	0.080935
10	0.215827	0.16307
20	0.827338	0.319544
30	0.899281	0.485012
40	1.151079	0.647482
50	2.014388	0.79976
60	3.129496	0.947842

Pinus spp.

Constant mass of 1g

Initial Concentration (mg/l)	Ce(mg/l)	Qe (mg/g)
5	0.179856	0.482014
10	0.395683	0.960432
20	2.302158	1.769784
30	4.100719	2.589928
40	6.726619	3.327338
50	10.35971	3.964029
60	14.31655	4.568345

Constant mass of 2g

Initial Concentration (mg/l)	Ce(mg/l)	Qe (mg/g)
5	0.467626	0.226619
10	1.151079	0.942446
20	1.870504	0.406475
30	1.978417	1.401079
40	3.093525	1.845324
50	4.71223	2.264388
60	5.179856	2.741007

Constant mass of 3g

Initial Concentration (mg/l)	Ce(mg/l)	Qe (mg/g)
5	0.251799	0.158273
10	1.726619	0.942446
20	1.834532	0.605516
30	2.194245	0.260192
40	2.697842	1.243405
50	2.985612	1.567146
60	3.956835	1.868106

Constant mass of 4g

Initial Concentration (mg/l)	Ce(mg/l)	Qe (mg/g)
5	0.359712	0.116007
10	1.690647	0.457734
20	1.798561	0.705036
30	2.446043	1.188849
40	2.794964	0.180126
50	3.021583	0.92446
60	3.309353	1.417266

Constant mass of 5g

Initial Concentration (mg/l)	Ce(mg/l)	Qe (mg/g)
5	1.043165	0.079137
10	2.194245	0.356115
20	2.913669	0.741727
30	2.985612	0.540288
40	3.453237	1.130935
50	3.633094	0.927338
60	3.848921	0.123022

Constant mass of 6g

Initial Concentration (mg/l)	Ce(mg/l)	Qe (mg/g)
5	3.453237	0.942446
10	3.920863	0.767986
20	3.23741	0.61271
30	3.201439	0.446643
40	2.302158	0.294964
50	5.107914	0.081535
60	1.690647	0.055156

Vitex keniensis

Constant mass of 1g

Initial Concentration (mg/l)	Ce(mg/l)	Qe (mg/g)
5	0.611511	0.438849
10	1.906475	1.809353
20	2.87	1.713
30	5.071942	2.492806
40	9.460432	3.053957
50	12.84173	3.715827
60	17.94964	4.205036

Constant mass of 2g

Initial Concentration (mg/l)	Ce(mg/l)	Qe (mg/g)
5	1.151079	0.192446
10	1.834532	0.908273
20	3.09	0.8455
30	3.309353	1.334532
40	4.388489	1.780576
50	5.683453	2.215827
60	7.985612	2.600719

Constant mass of 3g

Initial Concentration (mg/l)	Ce(mg/l)	Qe (mg/g)
5	2.014388	0.09952
10	2.482014	0.583933
20	3.59	0.547
30	3.956835	0.868106
40	5.791367	1.473621
50	5.827338	1.805755
60	6.906475	1.103118

Constant mass of 4g

Initial Concentration (mg/l)	Ce(mg/l)	Qe (mg/g)
5	3.489209	0.03777
10	3.72	0.407
20	3.956835	0.651079
30	4.352518	0.391187
40	4.676259	1.133094
50	5.791367	1.355216
60	8.129496	0.796763

Constant mass of 5g

Initial Concentration (mg/l)	Ce(mg/l)	Qe (mg/g)
5	1.618705	0.067626
10	1.978417	0.360432
20	2.122302	0.957554
30	3.81295	1.123741
40	3.88	0.3224
50	4.892086	0.502158
60	5.359712	0.692806

Constant mass of 6g

Initial Concentration (mg/l)	Ce(mg/l)	Qe (mg/g)
5	2.158273	0.047362
10	2.625899	0.956235
20	3.201439	0.279976
30	3.309353	0.778177
40	3.92	0.268
50	8.417266	0.526379
60	8.597122	0.356715

Ocotea usambarebsis

Constant mass of 1g

Initial Concentration (mg/l)	Ce(mg/l)	Qe (mg/g)
5	36.25899	2.374101
10	31.22302	1.877698
20	26.22302	1.377698
40	12.05036	0.794964
50	7.482014	0.251799
60	3.920863	0.107914

Constant mass of 2g

Initial Concentration (mg/l)	Ce(mg/l)	Qe (mg/g)
5	3.776978	0.061151
10	7.086331	0.145683
20	13.09353	0.345324
40	23.59712	0.820144
50	29.17266	1.041367
60	36.58273	1.170863

Constant mass of 3g

Initial Concentration (mg/l)	Ce(mg/l)	Qe (mg/g)
5	3.23741	0.058753
10	8.848921	0.038369
20	12.15827	0.261391
40	23.09353	0.563549
50	31.25899	0.6247
60	34.85612	0.838129

Constant mass of 4g

Initial Concentration (mg/l)	Ce(mg/l)	Qe (mg/g)
5	4.676259	0.008094
10	8.597122	0.035072
20	12.23022	0.194245
40	22.91367	0.427158
50	27.55396	0.561151
60	32.6259	0.684353

Constant mass of 5g

Initial Concentration (mg/l)	Ce(mg/l)	Qe (mg/g)
5	4.100719	0.017986
10	7.805755	0.043885
20	11.47482	0.170504
40	20.53957	0.389209
50	26.22302	0.47554
60	30.2518	0.594964

Constant mass of 6g

Initial Concentration (mg/l)	Ce(mg/l)	Qe (mg/g)
5	4.568345	0.007194
10	9.100719	0.014988
20	12.05036	0.794964
40	22.23022	0.296163
50	27.1223	0.381295
60	32.73381	0.454436

Appendix A6 pH versus amount of dye sorbed.

Variation of dye removal with pH

pH	Final absorbance					Mass of dye removed (mg/g)			
	Cypress	Camphor	Pine	Meru Oak	pH	Cypress	Camphor	Pine	Meru Oak
5	0.062	0.177	0.07	0.066	5	0.7769784	0.2841727	0.6978417	0.7625899
6	0.063	0.199	0.084	0.074	6	0.7733813	0.2338129	0.7482014	0.7338129
7	0.064	0.213	0.09	0.087	7	0.7697842	0.3633094	0.6978417	0.6870504
8	0.069	0.242	0.14	0.136	8	0.7517986	0.1294964	0.4964029	0.5107914
9	0.212	0.252	0.148	0.101	9	0.2374101	0.0935252	0.4676259	0.6366906
10	0.277	0.269	0.238	0.213	10	0.0035971	0.0323741	0.1438849	0.2338129
11	0.45	0.478	0.246	0.28	11	-0.618705	-0.719424	0.1151079	-0.007194
12	0.845	1.162	0.523	0.561	12	-2.039568	-3.179856	-0.881295	-1.017986

Appendix A7 Mean Particle size Versus dye removal at equilibrium

Effect of particle Size on Dye removal.

Mean particle size(mm)	Dye removal at equlibrium(mg/g)
0.225	0.84
0.3625	0.82
0.475	0.805
0.5625	0.78
0.89	0.75

Appendix A8 Number of revolutions per minute versus Dye removal

Effect of Shaking velocity on Dye removal.

Speed	Final Absorbance			
r.p.m	.3 - .425mm	.425 - .525mm	.525 - .6mm	All sizes
0	0.187	0.172	0.173	0.153
25	0.119	0.132	0.147	0.147
50	0.116	0.12	0.116	0.146
75	0.112	0.115	0.118	0.121
100	0.1	0.11	0.102	0.114
125	0.091	0.105	0.097	0.072
150	0.042	0.047	0.049	0.024
175	0.046	0.05	0.041	0.036
200	0.061	0.057	0.047	0.072
225	0.072	0.063	0.05	0.072
250	0.075	0.06	0.066	0.07

Speed	Mass of Dye adsorbed per gram of Sawdust (mg/g)			
r.p.m	.3 - .425mm	.425 - .525mm	.525 - .6mm	All sizes
0	0.314	0.383	0.371	0.45
25	0.561	0.524	0.477	0.477
50	0.593	0.574	0.593	0.47
75	0.6	0.589	0.575	0.57
100	0.642	0.61	0.62	0.63
125	0.66	0.625	0.65	0.746
150	0.85	0.825	0.825	0.912
175	0.8375	0.82	0.8375	0.875
200	0.786	0.8	0.825	0.746
225	0.746	0.782	0.82	0.746
250	0.738	0.7875	0.78	0.75

Appendix A9 Freundlich constants

	Values of K				Values of n			
Mass (g)	Camphor	Meru Oak	Cypress	Pine	Camphor	Meru Oak	Cypress	Pine
1	0.0184	0.8248	0.4127	0.5396	0.736	1.634	2.74	1.246572
2	0.0105	0.2511	0.4291	0.5194	0.742	0.806	1.744	1.02
3	0.0079	0.0566	0.4443	0.4359	0.7838	0.552	1.84	1.199
4	0.003	0.0117	0.3083	0.302	0.435	0.4186	1.378	1.128
5	0.0014	0.1326	0.3909	0.0998	0.552	0.9472	1.82	0.7156
6	0.0004	0.1504	0.4558	0.1028	0.466	0.5803	1.27	1.008
Average	0.006933	0.2378667	0.40685	0.33325	0.619133	0.823017	1.798667	1.052862

Appendix A10 .Initial concentration versus % dye removal for Pinus spp. Vitex kiniensis, Octea usambrensis and Cypressus lusitanica.

Pinus spp.

Co (mg/l)	% dye removal different masses					
	1g	2g	3g	4g	5g	6g
5	96.402878	45.323741	31.654676	23.201439	15.827338	11.031175
10	96.043165	40.647482	26.019185	18.01259	12.302158	8.1534772
20	95.197842	48.983813	32.89968	24.774843	19.876978	16.598721
30	86.330935	46.702638	31.414868	23.501199	18.009592	14.88809
40	93.52518	48.248651	32.547962	24.559353	19.729856	16.480566
50	92.517986	48.070054	32.465388	24.508813	19.684322	16.446926
60	92.290168	47.997081	32.431517	24.4894	19.671928	16.438237

Vitex keniensis

Co (mg/l)	% dye removal different masses					
	1g	2g	3g	4g	5g	6g
5	87.76978	38.48921	19.90408	7.553957	13.52518	9.472422
10	80.93525	40.82734	25.05995	14.11871	16.04317	11.33094
20	85.65	42.275	12.52998	20.35	16.12	13.4
30	83.09353	44.48441	18.23333	21.70264	16.73861	11.89049
40	76.34892	44.51439	27.57794	19.91906	17.32014	13.15947
50	74.31655	44.31655	29.47242	22.66187	19.15108	15.56355
60	70.08393	43.34532	30.09592	22.58693	18.72902	15.93725

Ocotea usambarebsis

Co (mg/l)	% dye removal different masses					
	1g	2g	3g	4g	5g	6g
5	21.58273	12.23022	11.7506	1.618705	3.597122	0.719424
10	25.17986	14.56835	3.83693	3.507194	4.388489	1.498801
20	39.7482	17.26619	13.06954	12.43165	8.52518	5.425659
30	35.2518	30.15588	24.94005	15.82734	19.56835	16.48681
40	34.44245	20.5036	14.08873	10.67896	9.730216	7.404077
50	37.55396	20.82734	12.494	11.22302	9.510791	7.625899
60	39.56835	19.51439	13.96882	11.40588	9.916067	7.573941

Cypressus lusitanica

Co (mg/l)	% dye removal for different masses					
	1g	2g	3g	4g	5g	6g
10	68.5	44.7	31.03333	23.125	19.3	16.46667
20	63.45	42.125	29.48333	21.95	18	16.40833
30	62.6	43.465	29.53333	22.4825	18.54	16.18
40	60	37.65	28.2	22.675	18.72	16.19833
50	64.24	37.75	26.86	21.78	18.576	16
60	62	35.4	26.53333	21.5375	17.52	15.80833

Bibliography

1. **Alam J.B. , Dikshit, A.K. and M. Bandyopadhyay,** (2000). Efficacy of adsorbents for removal 2,4-D and Atrazine removal from Water Environment. Global Nest: the Intl. Journal. Vol. 2. No 2 .pp.139-148.
2. **APHA (American Public Health Association).**(1992). Standard Methods for examination of water and Wastewater. 18th Edition. APHA, Washington D.C.
3. **Anliker, R., Clarke, E.A. and Moser**,P (1981), Use of the partition coefficient as an indicator of bioaccumulation tendency of dyestuffs in fish. Chemosphere Vol. 10, pp.263 - 274
4. **Arvola, L (1986**). Spring phytoplankton of 54 small lakes in Southern Finland. Hydrobilogia Vol. 137.pp.125 – 134.
5. **Atlas,G., and T.T. Bannister.** (1980). Depedence on mean spectral extinction coefficient of phytoplankton depth, water colour, and species. Limnol Oceanography. Vol. 25 pp. 157-159.
6. **Baldwin,S.** (1987) Biomass stoves: Engineering Design, Development and Dissemination. Volunteers in Technical assistance, Arlington, Virginia
7. **Baughmann,G and Perenich, T.A** (1988). Fate of Dyes in aqueous systems: Solubility and partition of hydrophobic dyes and related compounds. Environ.Toxic. Chemical. Vol. 7 pp. 188-199.
8. **Bennett, L.E, and M. Drikas** (1993). The evaluation of colour in natural waters. Water Res. Volume 27.pp.1209-1208.
9. **Boegerding, A.J., and R.A Hites** (1994). Identification and measurement of food and cosmetic dyes in a municipal wastewater treatment plant. Environment Science Technology. Vol. 28.pp.1278-1284
10. **Canadian Council of Ministers of Environment** (2001). Canadian water quality guidelines for the protection of aquatic life: Colour. Winnipeg.
11. **Chiou, C.T., L.J. Peters, and V.H Freed,** (1979). A physical concept of soil-water equilibria for nonionic organic compounds: Science, Vol..206, pp. 831-832.
12. **Chiou, C.T., P.E. Porter, and D.W. Schmeddling,** (1983), Partition equilibria of nonionic organic compounds between soil organic matter and water: Environmental Science and Technology.

13.**Clarke, E.A. and Anliker, R.** (1980). Organic Dyes and pigments in: *The Handbook of Environmental Chemistry Vol 3. Part A . Anthropogenic Compounds*. Hutzinger , O. (Ed), Springer-Verlag, Hiedelberg pp.181- 215.

14.**Del Giorgio, P.A., and R.H. Peters** (1994). Patterns in Planktonic P:R ratios in lakes: Influence of lake trophy and dissolved organic carbon. Limnol. Oceanography. Volume 39 pp. 772-787

15.**Dzombak, D.A., and R. G. Luthy**, (1984), Estimating adsorption of polyacyclic aromatic hydrocarbons on soils: Soil science, Vol. 137, p 292-308.

16.**Effler,S.W., and M.T. Auer** (1987). Optical heterogenisity in Green Bay. Water Resource Bulletin Vol. 23.pp. 937-942.

17.**Emig, D.K.** (1973) Removal of Heavy metals from acid bath plating by soil. Phd Thesis, Perdue University.

18.**Fessenden, R.J and Fessenden J.S**, (1990), Organic Chemistry, 4th Edition, Brooks/ Cole Publishing Company, Pacific Grove, California.

19.**Fiset,J.F, Blais J.F,Ben Cheikh R. and R.D.Tyagi** (2000).Review on metal removal from effluents by adsorption and wood barks. Rev. Sci. Eau Vol.13 pp.325- 349

20.Environmental technology Letters. (1986) Vol. 7, No.8, pp., 415.

21.**Githere P.G.** (MSc Thesis) Potential of ground Charcoal In removal of synthetic dye from water .MSc Thesis . University of Nairobi

22.**Griffin, R.A. and W.R. Roy**, (1985). Interaction of organic solvents with saturated soil-water systems: Environmental Institute for waste management Studies, Open File Report 3, University of Alabama, pp.86

23.**Gupta,G.S, Prasad,G. and Singh, V.N** (1990) Removal of Chrome dye from aqueous solutions by mixed adsorbents: Fly ash and coal. Wat. Res. Vol. 24, No 1,pp.45-50

24.**Gurr, E.** (1971) Synthetic Dyes in Biology, Medicine and Chemistry. Academic Press, London & New York.

25.**Haines, T.A, T.V.Komov, V.E, Matey, and C.H. Jagoe** (1995). Perch Mercury content is related to acidity and colour in 26 Russian Lakes. Water Air Soil Pollution. Vol. 85 pp.823-828.

26.**Henebry, M.S., ad J. Cairns,Jr**.(1984). Protozoan colonization rates in trophic status of some freshwater wetlands lakes. Journal of Protozool. Vol. 31. pp.456-467.

27.**Horvart C., Melander W. and Molnar I.** (1976) Solvophobic interactions in Liquid Chromatography with nonpolar stationary phases: Journal of chromatography, Vol. 125, pp. 129 - 156.

28. **http://:www.pgonline.com/**

29.**Huang J.C and Liao C.S** (1970) Adsorption of pesticides by clay minerals. Journal of Sanitation Eng. Div. American. Society of Civil Eng. Vol. 96, pp. 1057 - 1078.

30.**Irving S. Goldstein**,(1977) Wood Technology. Chemical Aspect. ACS Symposium series 43. American Chemical Society. Washington.

31.**Ilmavirta, V., and P. Huttunen**. (1989). Water chemistry and phytoplankton communities acidic clear and brown-water lakes in eastern Finland. Water Air Soil Pollution. Vol. 46.pp.415-432.

32.**Jang-Yeun Horng and Shang-Da Huang.** (1993). Removal of organic dye (Direct Blue) from synthetic Wastewater by adsorptive bubble techniques Environmental science Technology ,Vol. 27, pp.1169-1175

33.**Jerome, J.H, R. P Bukata, P.H Whitfield, and N. Rousseau**. (1994). Colour in natural Waters: 2 Observations of Spectral variations in British Columbia Rivers. Northwest Science Volume 68.pp.53 –64

34.**Jerome, J.H, R. P Bukata, P.H Whitfield, and N. Rousseau**. (1994). Colour in natural Waters:1 Factors controlling the dominant wavelength. Northwest Science .Volume 68.pp.43 –52 .

35.**Jones H.R.**, (1974). Pollution Control in the Textile Industry.

36.**Juarez, L.M, K.H. Holtschmit, J.J. Salmeron, and M.K. Smith** (1987). The effects of chemical and visual communication, space availability, and substratum colour on growth of juvenile fresh water prawn Macrobrachium rosebergii . Journal of marine Biology and ecology. Vol. 110 pp.285- 295.

37.**Kuo, W. G**. (1992) Decolorizing Dye Waste-water with Fenton Reagent Water resources, Vol.26, pp. 881

38.**Lamount I.M** (1981) Water Research topics, Ellis Horwood, London, Vol. 1, pp. 222.

39.**Liang I.G** (1991) The impact of effluent regulations on dyeing industry. Rev. Pro. Colouration. Vol 21,pp.56-71

40.**Lillie R.** Conn's Biological stains. Williams & Wilkins, Baltimore, MD USA.

41.**Masumune, S and Smith J.M.** (1976) Adsorption Rate Studies - significance of pore diffusion. America. Institute of Chemical Engineers Journal , Vol. 10,No. 2 pp.246.

42.**McCrum, W.A.,** (1984). The use of second-order derivative spectroscopy in investigation of sources of coloured pollutants in water. Water Res. Vol. 18.pp. 1249-1252.

43.**Mierle, G., and R. Ingram** (1991). The role of Humic substances in mobilization of Mercury from watersheds. Water Air Soil Pollution. Vol. 56 pp.349-357.

44. **Michelson D.L** (1975), Removal of soluble mercury from water by complexing techniques. US. D.1. Office of water Research and Technology, Bulletin No. 74, Virginia Polytechnique Institute , Blackburg, Va.

45.**Nilsson, A., and I. Hakanson** (1992). Relationship between Mercury in lake water, water colour and mercury in fish. Hydrobiologia. Vol. 235/236.pp.675-683.

46.**Pagga,U.M,and Taeger,K.**(1994), Development of a method for adsorption of dyestuffs on activated sludge. Water Resources, Vol. 28,pp.1051-1057.

47.**Poots,V.J.P., Healy J.J. and Mckay G.,** (1976), Removal of basic dye from effluent using wood as an adsorbent ,Water Pollution Control Federation Journal, pp. 926-934.

48.**Ratte, I.D and Bruener, M.M,** (1974), The physical chemistry of Dye adsorption. Academic Press, New York and London

49.**Rosen J.B.** (1954) General Numerical Solution for Solid diffusion in Fixed Beds. Ind. Eng. Chem. Vol. 46, 1590.

50.**Roy W.R., Krapac I.G, Chou S.F.J, and Griffin R.A** (1992) Batch-Type Procedures for Estimating Soil adsorption of chemicals. Illinois State Geological Survey Chapaign, Illinois 61820.

51 **Sawyer C N and McCarty, P.L** (1978) Chemistry for Environmental Engineering. McGraw-Hill book Company.

52 **Schwarzenbach R.P, Gsechwald,P.M and Imboden, D.M** (1993) Environmental Organic Chemistry John Wiley and Son Inc, New York.

53 **Sewe, P.O, 1986**,(MSc Thesis) Textile wastewater Treatment and management in Eldoret, Kenya.

54 **Shafizadeh, (1981)** Thermal deterioration of wood ACS Synposium Vol. 43 pp.57 – 81

55 **Sheath, R.G., M.O. Morison, J.E. Korch, D. Kaczmarczyk, and K.M. Cole. (1986).** Distribution of macroalgae in South-central Alaska USA. Hydrobiologia vol.135. pp.259-270.

56 **Sinanoglu O and Abdulnur S.** (1965). Effect of water and other solvents on the structure of biopolymers: Federation Proceedings, Vol 29 Part II, pp. 512-523

57 **Sittig, M.**, (1973). Pollutant Removal Handbook Noyes Patal Corporation , London England

58 **Susan Budavari, (1990)** The Merck Index, 12th Edition Merck & Company, NJ, USA.

59 **Tsoumis, G.**, (1991), Science and Technology of wood. Structure, Properties, Utilization. Chapman and Hall.

60 **UNEP,** (1993) The Textile Industry and The Environment. Technical Report No.16 pp. 65-66.

61 **UNEP,** (1996). Cleaner Production in textile wet processing. A Workbook for trainers. 1st Edition. Paris.

62 **Van Soest, P.J and Goering H.K.** (1994). Forage fibre Analysis. Handbook on Animal husbandry. Research Division Beltsville, Maryland 20705.

63 **Weber W.J, McGinley P.M and Katz L.E** (1991) Sorption Phenomena in subsurface Systems: Concepts, Models and effects of contaminant fate and Transport. Water Res. Volm 25, No. 5 pp. 499-528.

64 **Wetzel, R.G. (1975).** Limnology. W.B. Saunders Company, Philadelphia.

65 **Zollinger, H** (1987). Colour Chemistry - Syntheses, Properties and Application of Organic Dyes and Pigments; VCH New York, 92 - 102