

UNIVERSITY OF NAIROBI



**POTENTIAL FOR GROUND CHARCOAL FOR
SYNTHETIC DYE REMOVAL**

BY

PAULGAGI GITHERE

October 2003

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DEPARTMENT OF CIVIL ENGINEERING

Potential for ground charcoal for synthetic dye removal

POTENTIAL FOR GROUND CHARCOAL FOR SYNTHETIC DYE REMOVAL

PAULGAGI GITHERE

**A thesis submitted in part fulfillment for the degree of
Master of science in Civil Engineering (Environmental Health Engineering)
University of Nairobi.**

October 2003

DECLARATION

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

PAUL GAGI GITHERE

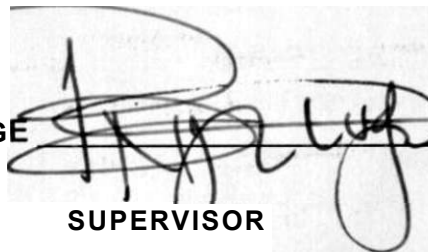
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CANDIDATE

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

Prof. B.N.K. NJORGE

 Date 28/12

SUPERVISOR

DEDICATION

This thesis is dedicated to my wife, Wanjiku. and son, Githere, whom I have not had time for because of it

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ACKNOWLEDGMENTS

I feel highly indebted to my wife, family members relatives colleagues and friends for the patience and moral support they all offered me

I am highly indebted to my supervisor Prof B N K Njoroge through whose keen supervision and constant constructive criticism made this research work a success

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Abstract

The potential for ground charcoal for synthetic dye removal was investigated in a series of batch experiments. Ground charcoal from black wattle tree was used to remove a synthetic dye, Congo red from water through sorption. Equilibrium time, rate studies, effect of pH on the dye removal, percentage removals and sorption isotherms were investigated.

The Equilibrium time for the particle size studied was found to be 18 hours. The long Equilibrium time obtained indicated that adsorption was a slow process. Possible causes of slow attainment to equilibrium could be due to slow molecular diffusion into the adsorbing sites in the micropores, formation of new bonds between the dye molecules and the charcoal, and slow reaction at the surface between the dye and the charcoal.

The percentage dye removals decreased with increase in concentration. The removal was predominant in the low concentrations, below 20mg/l.

The pH in the range of 4-9 had no any effect on the removal of the dye. Increase in pH beyond pH 9, however, resulted in decreased dye removal. The data analyzed was found to correspond to Freundlich's isotherm model with correlation coefficients ranging between 0.9014 and 0.9798. This indicated that the isotherm represented the data well. The constants in the model, k and n ranged between 0.8481-1.915 and 0.5357-0.4298, respectively. The mechanism through which the dye was adsorbed could be through coverage of the active sites in the charcoal and once covered, the adsorption capacity of the charcoal diminished.

A similar trend for the effect of mass of ground charcoal on the removal of the dye was observed indicated that the mechanism of removal predominant is most effective for low dye concentrations, below 20mg/l.

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Chapter One

INTRODUCTION

1.1 General

Industrial development is connected with production of large volumes of wastewater the disposal of a large number of various pollutants that are harmful to the environment, hazardous to human health and difficult to degrade by natural means. These pollutants may be in the form of solids, liquids or gases. Ultimately some of these pollutants pass into streams and other water bodies. The disposal of pollutants to natural water bodies should be done in such a way as to minimise pollution or contamination of the environment.

The amount of treatment required for wastewater from textile manufacturing processes depends largely on the water quality objectives for the receiving water and also the dilution available. It is important to identify which contaminants in the wastewater are to be removed so as to protect the environment from adverse pollution effects.

Organic dyes from textile industries are some of the most problematic pollutants. Textile industries are the largest users of dyes, and it is estimated that 10-15% of the dye is lost during the dyeing process and is released as effluent [Vaidya, 1982],

The major environmental problem with wastewater from textile manufacturing processes is the removal of dyes from effluents [Zollinger, 1987], Untreated effluent from dyestuff production and dyeing mills may be highly coloured and thus particularly objectionable if discharged into open water. The concentration of dye may be much less than 1mg/l but since the dye is visible even at small concentrations, the transparency of the streams would be reduced. Because dyes absorb sunlight, there are concerns of reduced light transmittance and organic productivity as well as toxic effects [Rosehart, 1985],

The coloured dye waste is likely to act as heavy metal carrier, either due to the structure in certain cases or due to the tendency to chelate with metals

A number of successful systems have been developed using adsorption techniques. Almost all the work has been based on studies using activated carbon and existing commercial systems use activated carbon exclusively [Healy, et al 1978], However, there are certain problems with its use as it is quite expensive and the higher the quality the greater the cost. Furthermore, regeneration using solutions produces an additional effluent although quite small.

For this reason the need to investigate the potential for use of locally available material instead of the activated carbon is warranted. Ground charcoal is investigated in this study with a view of establishing its potential for organic dyes removal from wastewater.

1.2 Objective

The study objective is to evaluate the removal of a synthetic dye, *Congo red*, using ground charcoal.

The tasks in the study are:

1. To evaluate the potential for the ground charcoal for the removal of *Congo red* dye
2. To investigate the effects of the dye concentration and pH on the dye removal.

Chapter Two

LITERATURE REVIEW

2.1 Dyes

2.1.1 General

A dye may be roughly defined, according to Imperial Chemical Industries Ltd [1968], as a coloured substance capable of application in aqueous or non-aqueous solution or in aqueous dispersion to a substrate so that the substrate acquires a coloured appearance. The substrate is usually a textile fibre, but may be paper, leather, hair, fur, plastic, wax, a cosmetic base or a foodstuff.

With a few exceptions, all synthetic dyes are aromatic (any system that is stabilised by a ring of delocalized π -electrons) organic compounds. Dyes may be divided into three main groups: non-ionic, anionic and cationic [Gurr, 1971]. The molecules of ionic (anionic and cationic) dyes are composed of two main parts, one of which is a complex aryl radicle. This is the colour-imparting ion. If the balance of the charge in the aryl radicle is negative then the dye is classified as anionic. On the other hand, if the balance of the charge on this ion is positive then the dye is classified as cationic. The second part of an ionic dye molecule is an inorganic ion (or an aliphatic organic ion or, in a few cases, an aryl ion) of opposite charge to that of the colour-imparting aryl ion. The inorganic ion is sometimes called the gegen-ion. and the aryl radicle 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 sulphonic acids. Some, however, are sodium salts of carboxylic acids, uranine being a notable example [Gurr, 1971]. In the case of cationic dyes, the gegen-ion is usually the chloride.

In the vast majority of cases the gegen-ion could be replaced by another of the same charge without seriously affecting the functioning of the dye. There might, however, be differences in solubility. For example a calcium salt might be less soluble in water than a sodium salt. Similarly, a sulphate salt might be less soluble in water than a chloride. And obviously, when dyes are used as reagents for the detection of certain ions, due considerations has to be given to the gegen-ion of the dyes. However, unless the gegen itself is coloured it has no influence whatsoever upon the colour of the dye in aqueous solution. For example, pararosaniline chloride or sulphate or acetate exhibit exactly the same colour in solution [Gurr, 1971]

On the other hand, the dye-ion cannot be replaced by another one without profound changes in the nature and functioning of the dye molecule. The individual chemical and physical characteristics of a dye are due to its dye ion.

The simple gegen of a dye could be replaced by another dye ion of the same charge as the original gegen ion and, of course, of opposite charge to that of the first dye ion. This could result in the formation of a polychrome (if the reacting ions were of contrasting colours) compound dye. Such dyes are prepared for special purposes. Their molecules consist 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.

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

2.1.2 Classification of dyes

Dyes were and still are classified in two ways. One of these is based upon their manners of usage in the textile industry while the other is upon

l'olcnliajar groundcharcoal Jar synlhclu dye removal

chromophores The chart below summarises the classification of dyes by colligators.

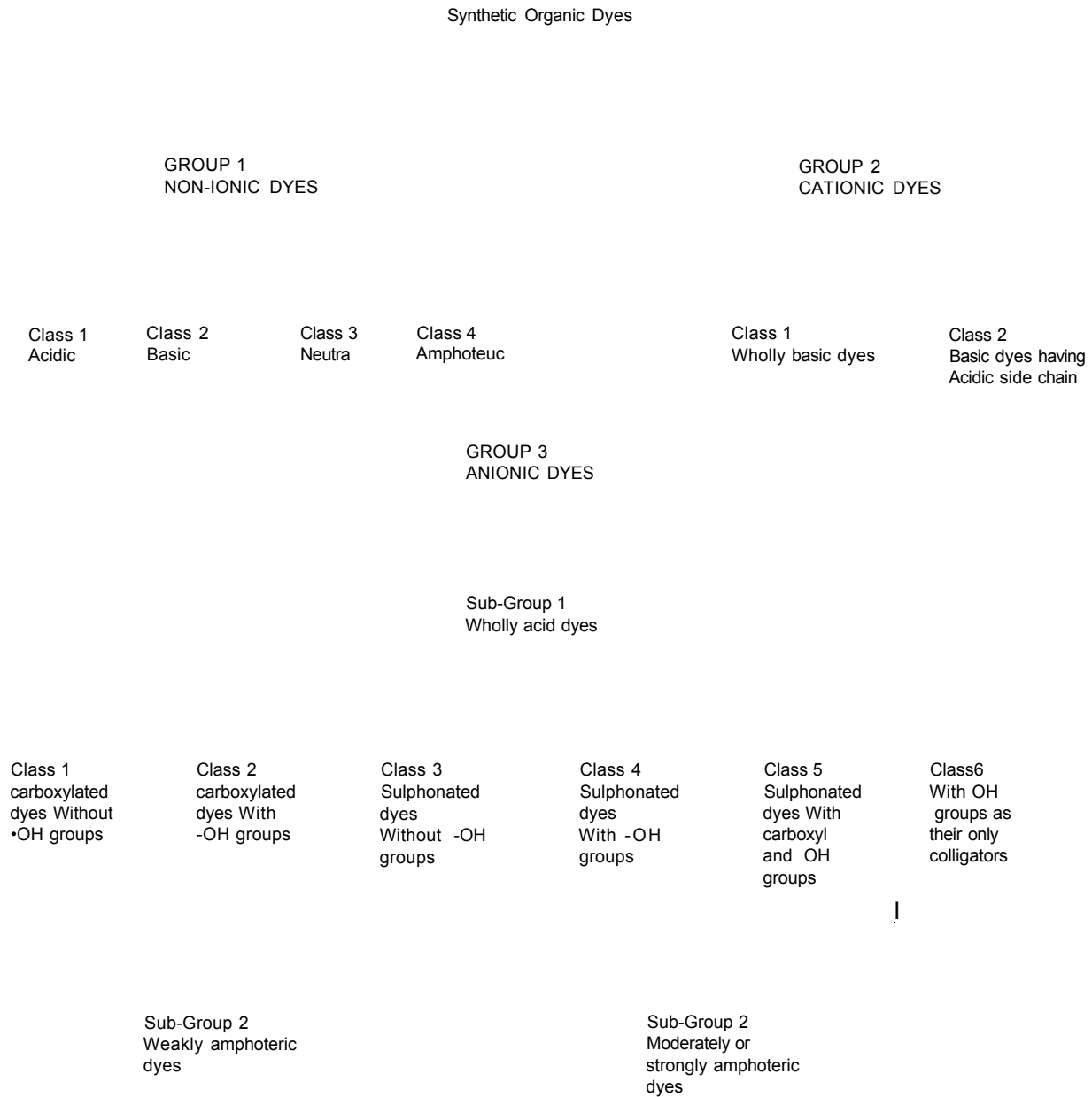


Figure 2 1 Classification of Dyes by Colligators [Gurr, 1971]

2.1.3 Types of dyes

There are six main classes of dyes for cotton fabric vat, direct, developed, naphthol, sulphur and aniline 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 may be applied to fibres without pre-application of chemicals required for retention They are usually negatively charged In other words, the coloured part of the molecule is the anion Some direct dyes are subject to post treatment with copper sulphate and acetic acid to increase light fastness and with potassium dichromate and acetic or formadehyde to increase wash fastness

Developed dyeing is a procedure whereby two different chemicals are employed The first chemical (0.5- 4% dye) is applied and absorbed into 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 with either sodium hydroxide under heat or ethyl alcohol and a 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

Aniline black dye is an insoluble pigment produced by the oxidation of aniline The cloth is passed through dye bath typically consisting of 41 kg of aniline 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 [Cockett, 1964]

2.1.4 Absorption spectra of dyes

White light is composed of the total spectral range. When an object appears coloured in ordinary white light it is 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 that appear black absorb the whole of the visible spectral range without transmitting or reflecting any component of the white light. If a colour object, illuminated by a source of white light, is examined with a spectroscope it will be seen that the light transmitted or reflected by the object does not show the complete visible spectral range. Some of the colours of the spectrum will be missing from the spectrum. On the other hand if the object is blue-green, red will be missing from the spectrum. Red and blue-green are, therefore, regarded in this respect as complementary colours. The wavelengths of the more important colours of the visible spectrum are given in Table 2.1.

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 in fact be regarded as their fingerprints. However, variations in the wavelengths of maximum absorption of many dyes occur with variations in the pH, temperature and concentration of the solutions examined.

Table 2 1 Wavelength of different ColoursftGurr, 1971] J

Wavelengths (m)	Colour	Complementary colour
400-430	Violet	Greenish-yellow
430-490	Blue	Yellowish-orange
490-510	Blue-green	Red
510-530	Green	Purple
530-560	Yellowish-green	Violet
560-590	Yellow	Blue
590-610	Orange	Greenish-blue
610-750	Red	Blue green

2.1.5 Solubility of dyes

The question of dyestuff solubility is a practical one and in certain cases one of theoretical importance. In the case of research studies, dyes are used in solution. In practice this is frequently not the case and solubility is an important factor. Disperse dyes, which are applied from a suspension, i.e. a saturated solution, have solubility characteristics of both practical and theoretical importance since the upper limit of concentration in the external phase determines the upper limit of fibre saturation.

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 hydrochlorides.

Water-insoluble dyes of certain types can be rendered soluble by chemical modification, dyed in this form, and then reconverted on the fibre into the original insoluble form. The sulphur and vat dyes depend on this principle, which enables high fastness to wet treatments to be attained. Insoluble azo dyes can be formed directly within the fibre.

2.1.6 Measurement of dye concentration in a dye bath

In order to obtain the concentration of a dye in 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 brightness and hue as well 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 a 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 pre-set by the sample. Both visual and photoelectric determination rely on the fact that the depth of colour (absorbance) is governed by the concentration of a material in solution [Lamount, 1981]. Colour is measured by optical density (D) on a spectrophotometer and the whole colour band should be scanned. Beer's and Lambert's laws combined gives for a monochromatic light: -

$$I_T = I_0 \exp(-kcl)$$

I_T = the transmitted light

I_0 = the incident light

c = concentration of absorbing species

l = cell length

k = extinction coefficient

The optical density D is by definition

$$D = \log_{10} (I_0/W) = 0.434kcl$$

D is therefore proportional to the cell length and dependent on wavelength through coefficient k [Environmental Technology Letters, 1986]

The first steps in a photometric or spectrophotometric analysis involve the establishment of working conditions and the preparation of a calibration curve relating to absorbance. Spectrophotometric absorbance measurements are ordinarily made at a wavelength corresponding to an absorption peak because the change in absorbance per unit of 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 must be chosen such that the absorbance will not be materially influenced by uncontrolled variations in their magnitude. After deciding upon the conditions for the analysis, it is necessary to prepare a calibration curve from a series of standard solution. These standards should approximate the overall composition of the actual samples and should cover a reasonable concentration range of the analyte. Seldom, if ever, it is safe to assume adherence to Beer's law and use only a single standard to determine the molar absorptivity. The results of analysis should never be based on a literature value for molar absorptivity [Skoog, 1971]

2.1.7 Congo red Dye

Congo red is a direct dye of the disazo series. It is a sodium salt of sulphonic acid. Particulars of the dye are given in Table 2.2

Table 2.2 Particulars of Congo red [R. D. Lillie, Susan Budavari]

Common name	Congo red
Suggested name	Congo red
Other names	Direct red Cotton red
C.I. number	22120
C.I. name	Direct red 28
Class	Disazo
Ionisation	Acid
Solubility in water	Soluble
Solubility in ethanol	0.19%
Absorption maximum	488 (Merck), 497 (Conn)
Colour	Red
Empirical formula	C ₃₂ H ₂₂ N ₆ O ₆ S ₂ Na ₂
molecular weight	696.696

The structure of congo red dye is as shown below

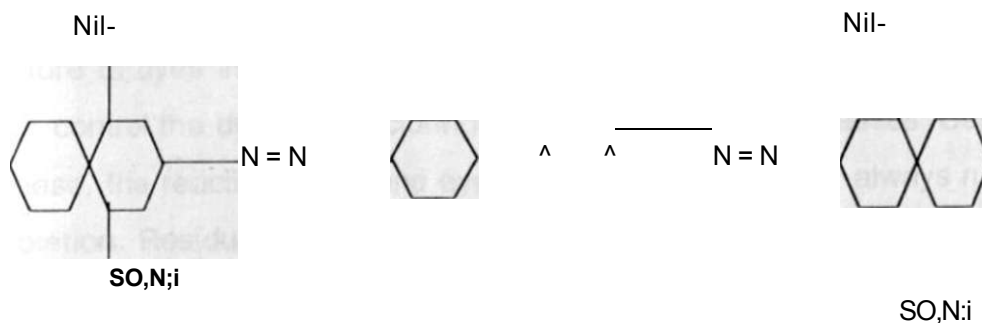


Fig. 2.2 Structure of Congo red C.I. 22120 [R. D. Lillie, Susan Budavari]

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

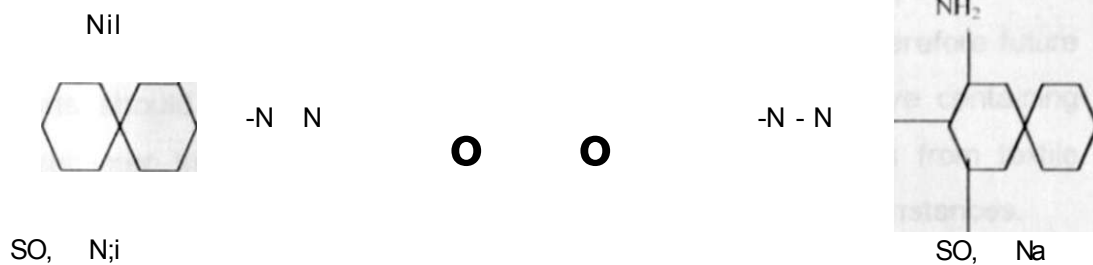


Fig 2.3 Structure of Congo red ion [R. D. Lillie, Susan Budavari]

Its industrial use includes the dyeing of paper. It has affinity for both cellulose and protein materials. It is used for staining a great variety of microscopic specimens of biological tissues, bacteria etc.; as a pH indicator (range 3.0 to 5.2 blue-red).

2.2 Problems related with dyeing industries

Dyes are required to exhibit a high degree of chemical, photolytic and microbiological stability in order to fulfil the fastness requirements of consumers. Consequently, dyes do not readily degrade under typical usage conditions, even under aerobic conditions prevailing in the conventional biological treatment processes. The producers' interests is to improve the fixation of certain dyes on specific substrates, to change the chemical structure of dyes in order to obtain more biodegradable alternatives and to better control the dye-manufacturing and dye-consuming processes. Despite all these, the reactions that bind dyes into a substrate do not always run to completion. Residual dyes, auxiliaries, and chemicals are often left in the process water and discharged with a wastewater. These effluents are discharged either to sewers, which are then treated by a municipal sewage treatment plant, or directly to rivers. The inability of these systems to function effectively makes dye related industries incapable of responding to the current stringent legislation. If an effort is not made to remove the visible

pollution of the colour, the public assumes that little effort has been expended in removing other pollutants [Rao et al 1987, McKay, 1986] Although biological treatment has been utilised generally as a method for purification of waste waters from dye factories, most synthetic dyes show not only low degradability but also high toxicity to microbes. These properties have prevented practical biological treatment [Idako et al 1981]. Therefore future efforts should focus on developing new and more efficient dye containing wastewater treatment processes. To effectively remove dyes from textile wastewater, non-biological processes have been used in many instances.

2.2.1 Possible methods of colour removal

Popular treatment methods for eliminating dyes from waste streams include coagulation, froth flotation, biodegradation, chemical degradation, photochemical degradation and adsorption.

- The coagulation process effectively decolorizes insoluble dyes, such as disperse dyes, but does not work well for soluble dyes [Kuo, 1992].
- The biological process does not effectively decolorize commercial dyes, because most commercial dyes are toxic to organisms used in the biological processes [Kuo, 1992].
- Chemical destruction by oxidation with chlorine or ozone is effective, but the oxidant requirements are high and also expensive. The effectiveness of decolorisation by the oxidation process is reduced by the impurities in the wastewater.
- Photochemical degradation in aqueous solution is likely to progress slowly as synthetic dyes are, in principle, designed to possess high stability to light.
- Other techniques that have been applied include Adsorptive bubble separation techniques [Jang-Yeun et al, 1993].

For adsorption, activated carbon, silica gel, bauxite, peat, wood, cellulose derivatives, and ion-exchange resins have been used [Zollinger, 1987]

Of all these methods, adsorption currently appears to offer the best potential for overall treatment, and it can be expected to be useful for a wide range of compounds, more so than any of the other listed processes. In addition, because adsorption is generally reversible, the regeneration of the adsorbent with resultant economy of operation may be possible.

A number of successful systems have been developed using adsorption techniques. Almost all the work has been based on studies using activated carbon and existing commercial systems use activated carbon exclusively [Healy, et al 1978]. However, there are certain problems with its use as it is quite expensive and the higher the quality the greater the cost. Furthermore, regeneration using solutions produces an additional effluent although quite small.

2.2.2 Adsorption phenomena

2.2.2.1 Adsorption Forces and Mechanisms

Adsorption process involves an array of phenomena, which can alter the distribution of contaminants between and among the constituents' phases and interfaces of systems. Solutes that undergo adsorption are commonly termed as adsorbates, the sorbing phase adsorbent, and the primary phase from which adsorption occurs solution or solvent.

Two broad categories of sorption phenomena, adsorption and absorption, can be differentiated by the degree to which the sorbate molecule interacts with and is free to migrate between the sorbent phase. In adsorption solute accumulation is generally restricted to a surface or interface between the solution and sorbent. In contrast absorption is a process in which solute transferred from one phase to another interpenetrates the sorbent phase by at least several nanometers [Schwarzenbach et al , 1993]

Adsorption results from a variety of different types of attractive forces between solute molecules, solvent molecules and molecules of an adsorbent. These physicochemical forces and mechanisms responsible for the adsorption of ions and molecules can be broken down into eight categories;

- **London-van der waals** attractive forces arise from momentary dipoles about atoms or molecules caused by small perturbations of electronic motions. These dipoles induce small dipoles in neighboring atoms of opposite sign. Although the momentary dipoles and induced dipoles are constantly changing position and sign, the net result is a weak attraction. These forces are important in adsorption of organic and are generally attributed to the non-ideal behavior in gasses.
- **Coulombic-electrostatic-chemical:** - An electrostatic force results from a charged surface due to isomorphous substitution in the mineral lattice (permanent charge) or protonation of surface oxygen and OH groups (pH-dependent charge) and an oppositely charged species, which maintains the electroneutrality 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 then 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 ionized, then attractive forces are inversely related to the distance between the charge centres. Adsorbates 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 an adsorbate ion, the process of adsorption produces a surface charge and the surface potential is determined by the adsorbed ions. Coulombic interactions can either favour or disfavour adsorption of

adsorbates 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.

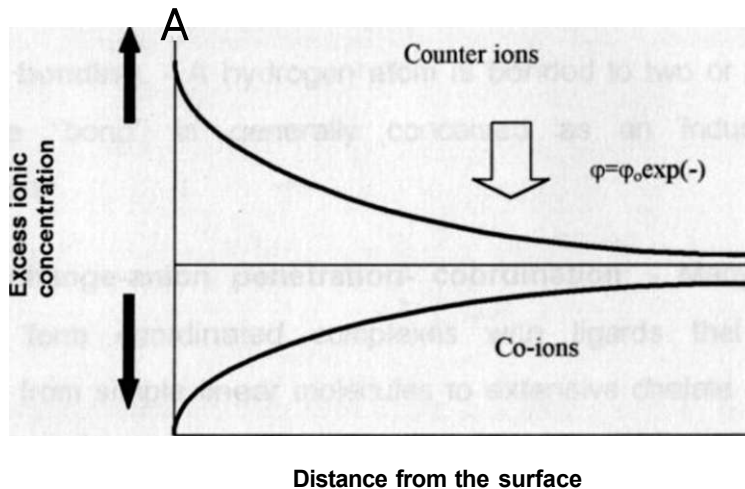


Fig 2.4 Distribution of ions near a charged surface[Ratte, 1974]

Three main coulombic effects are encountered in 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 favorable to the uptake of dye anion. Cellulose contains hydroxyl groups, which in the presence of an alkali may ionize giving the fibre a negative charge repelling the adsorbate ions and preventing their absorption.

- Adsorbate ions will be adsorbed by uncharged substrates to a very limited degree since the first few molecules taken up will confer on the fiber a charge repelling other similarly charged ions. This effect is most marked in relatively hydrophobic fibers 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.
- Adsorbate 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.
- **Hydrogen bonding:** - A hydrogen atom is bonded to two or more other atoms; the "bond" is generally conceived as an induced dipole phenomenon.
- **Ligand exchange-anion penetration- coordination** - Many atoms or molecules form coordinated complexes with ligands that range in complexity from simple linear molecules to extensive chelate complexes. The coordinated complexes may carry a net charge that may be localized on some part of the complex.
- **Chemisorption** - In this adsorption process an actual chemical bond, usually covalent, is formed between the molecule and surface atoms. A molecule undergoing chemisorption may lose its identity as the atoms are rearranged, forming new compounds at the demand of the unsatisfied valences of the surface atoms. The enthalpy of chemisorption is much greater than physical adsorption.
- **Dipole-Dipole or Orientation energy**

This interaction results from the attraction of a permanent dipole for another permanent dipole.

- **Induction or Dipole-induced Dipole**

This type of interaction results from the attraction of an induced dipole brought about by (1) a permanent dipole or (2) a charged site or species

- **Hydrophobic effect**

Occurs when the combination of mutual attraction between hydrophobic groups of the organic molecules and their tendency to escape from an aqueous environment become large enough to permit them to adsorb onto the solid adsorbent. Adsorption of organic molecules from the liquid phase onto or adjacent to other organic molecules already adsorbed on the solid adsorbent may also occur by this mechanism aggregating their chains.

All of these attraction mechanisms will operate simultaneously and the combination that dominates the overall solution-solid distribution will depend on the structural properties of the organic chemical and solid medium of interest.

2.2.2.2 Adsorption of Ionizable Organic Chemicals from Aqueous Solutions

Ionizable organic chemicals exhibit at least one ionic group in their structure (e.g., $-\text{COO}^-$, $-\text{NH}_3^+$, $-\text{SO}_3^-$). When organic chemicals include structural components that are ionized, a variety of effects become important insofar as the interactions of these adsorbates with solid surfaces are concerned [Schwarzenbach et al., 1993], This is largely due to two phenomena:

- (1) the electrostatic interactions of charged molecules with charged sites on the adsorbent, and
- (2) exchange reaction with ligands previously bound to the solid

First, owing to the ubiquitous phenomenon of ionizable surface groups on wet particles, virtually every solid presents a charged surface to the aqueous solution. If this surface charge is of opposite sign (e.g., positive) to that exhibited by an organic functional group (e.g., negative), then there will be an

electrostatic attraction between the organic adsorbate in the bulk solution and the particle surface. Such organic ions will accumulate in the thin film of water surrounding the particle as part of the population of the charges in the solution balancing the charges on the solid surface. Conversely, organic molecules of like sign as the surface will be repulsed from the near surface water. These electrostatic effects act similarly for all charged adsorbates.

The second interaction involves chemical bonding of the organic compound to the surface or to some component of the solid phase. This may involve displacing some ligand previously bound to the surface. Alternatively, such a reaction could look more like a condensation reaction. Such a surface reaction involves a free energy change. A surface reaction forms a second sorbed species which is distinct from like-structured organic ions dissolved in the near surface water [Schwarzenbach ET al , 1993]

Some charged organic compounds include a sufficiently large hydrophobic portion in their structure that transfer onto the solid surface is favoured even in the absence of surface charges or reactive surface sites. Such adsorption requires the co-transfer of a counterion to maintain local electro-neutrality [Schwarzenbach ET al.. 1993]

2.2.2.3 Adsorption Kinetics

The two important physiochemical aspects for parameter evaluation of the adsorption process as a unit operation are the kinetics and the equilibrium of adsorption. Kinetics adsorption refers to the movement of the solute molecules from the bulk phase of the solvent to the adsorbing sites of the adsorbent. It is necessary to study the kinetics of adsorption in batch systems in order to determine the rate-limiting step in adsorption process, which in turn governs the residence time of adsorption reaction. Equilibrium of adsorption is reached when the rate of adsorption of molecules onto the surface of the adsorbent is the same as the rate of de-sorption of the molecules from the surface. The rate at which adsorption proceeds, then, is proportional to the driving force, which is the difference between the amount

adsorbed at a particular concentration and the amount that can be adsorbed at that concentration. This difference is zero at equilibrium.

In a liquid phase application, transfer of the adsorbate from the bulk solution to the carbon particle (adsorbent) must proceed through at least two stages:

1. Transfer of the adsorbate molecule from the bulk liquid to the surface of the adsorbent, i.e. through the film that surrounds the adsorbent; and
2. Migration of the adsorbate from the surface of the adsorbent to the adsorption site within the particle.

Kinetic experiments demonstrate that step 1 is appreciably more rapid than step 2, so the latter is normally the primary rate determining step [Cheremisinoff ET al, 1978]. The rate of adsorption, then, will vary with the diameter of the carbon particle used in the test. To increase the rate of adsorption, and thus decrease the time necessary to complete the isotherm, it is recommended that the adsorbent be pulverized to a smaller size [Cheremisinoff et al. 1978].

2.2.2.4 Adsorption equilibrium.

The eventual equilibrium distribution of contaminants between solution phase and an adsorbent or interface is dictated by a corresponding energy balance and thus may be categorized. Thermodynamically, this characterization is somewhat more obvious for absorption than for adsorption, in that the former relates more to issues of classical chemistry and energy balances within and between discrete phases, whereas the latter often involves ill-defined surfaces and interfaces [Schwarzenbach et al., 1993].

2.2.2.5 Equilibrium models (Adsorption Isotherms).

The equilibrium adsorption isotherms are of fundamental importance in the design of adsorption systems. Models for characterizing the equilibrium distribution of a solute among the phases and interfaces of an environmental system typically relate the amount of solute, sorbed per unit of sorbing

phase or interface to the amount of solute, C_s , retained in the solvent phase. An expression of this type evaluated at a fixed system temperature constitutes what is termed an adsorption isotherm.

Examples of different phenomenological equilibrium adsorption isotherms are illustrated graphically in the Figure 2.5.

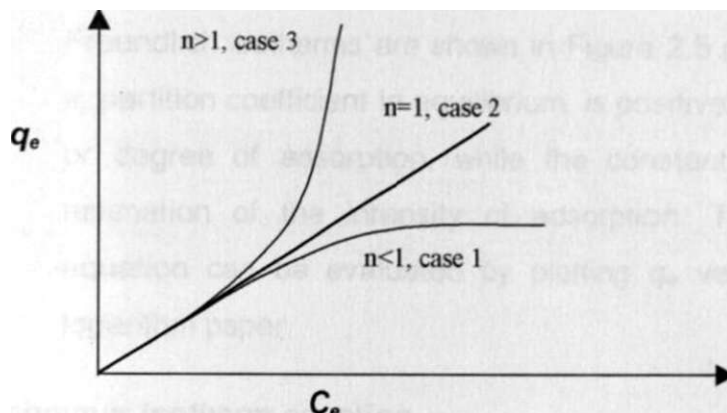


Figure 2.5: Phenomenological equilibrium adsorption isotherms

- Case 1-Specific binding sites become filled or remaining sites are less attractive
- Case 2-Attractiveness of the solid for the adsorbates remains the same for all levels of C_e .
- Case 3-Previously sorbed molecules lead to a modification of the surface, which favours further adsorption. Such effects have been seen for surface active compounds like alkyl benzene sulfonates where the adsorbent becomes coated and increasingly exhibit a non-polar nature [Schwarzenbach et al., 1993].

A number of conceptual and empirical models have been developed to describe these various adsorption patterns. Equations that are often used to describe the experimental isotherm data were developed by Freundlich, by Langmuir, and by Brunauer, Emmet, and Teller (BET isotherm)[Schroeder, 1977].

i. Freundlich Isotherm model

Derived from empirical considerations, the Freundlich isotherm is -

$$q_e = k.C_e^n \dots (1)$$

k = Freundlich constant

n = measure of the non-linearity involved

Freundlich isotherms are shown in Figure 2 5 page 21 The constant k , partition coefficient in equilibrium, is positively related to the extent or degree of adsorption, while the constant n provides a rough estimation of the intensity of adsorption The constants in this equation can be evaluated by plotting q_e versus C_e on a double logarithm paper

ii. Langmuir isotherm equation

Derived from rational considerations, the Langmuir adsorption isotherm is given by:

$$q_e = \frac{abC_p}{1+ bC_e} \quad (1)$$

a, b = empirical constants

This equation was developed on the basis of the assumptions that,

- A fixed number of accessible sites are available on the adsorbent surface, all of which have the same energy and that,
- Adsorption is reversible

A Langmuir isotherm is same as case 1 in the Freundlich isotherm

The linearized form of Langmuir isotherm is:

$$\frac{q_e}{q_c} = \frac{1}{ab} + \frac{1}{a} C_p \quad (2)$$

The effect of isotherm shape has been discussed with a view to predicting whether an adsorption system is "favorable" or "unfavorable" [Weber et al 1974] The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R which is defined by the following relationship

$$R = \frac{1}{1 + aC_0}$$

The parameter indicates the shape of the isotherm accordingly:

Table 2.3 Relationship between R values and type of isotherm

R Value	Type of Isotherm
$R > 1$	Unfavorable
$R = 1$	Linear
$0 < R < 1$	Favorable
$R = 0$	Irreversible

2.2.3 Batch-Adsorption

The batch-adsorption or static-equilibrium technique has been used in laboratory studies to assess the capacity of adsorbents to remove chemical constituents from solutions. Batch procedures vary considerably from one another in terms of experimental conditions and research objectives and sometimes yield different results even when the same soils, solutes, and concentrations are studied

The simplicity of the batch-adsorption technique accounts in part for its popularity. With this technique an aqueous solution containing solutes of known compositions and concentrations is mixed with a given mass of adsorbent for a given period of time. The solution is then separated from the

adsorbent and chemically analyzed to determine changes in solute concentration. The amount of solute adsorbed by the adsorbent is assumed to be the difference between the initial concentration (before contact with the adsorbent) and the solute concentration after the mixing period. Although the approach is relatively simple, several experimental parameters can affect the adsorption of a given constituent. These parameters include contact time, temperature, solution pH, and adsorbent-solution ratio.

2.2.3.1 Effects of Temperature

Adsorption at the solid-liquid interface tends to occur when the attractive forces between the surface and ionic solutes are greater than between the solute and the solvent [Zettlemoyer and Micalo, 1971]. The adsorption of an ionic or polar solute is often the result of a thermodynamically favorable change in the enthalpy (ΔH) [Hassett et al., 1981]. Sometimes it can be of a favorable change in the entropy (ΔS) of the system in which the $-T\Delta S$ term from the Gibbs-Helmholtz equation compensates for the positive value of ΔH [Thomas, 1961] where T is the temperature of the system. The adsorption of non-polar organic solutes is thought to result primarily from a thermodynamically favorable change in the entropy (ΔS) involving little energy transformation as heat. Thus the adsorption behavior of ions or polar solutes will probably show some temperature dependency, whereas the adsorption of non-polar solutes may not be greatly influenced by the temperature of the system.

2.2.3.2 Effects of Solution pH

The adsorption capacity can be a function of the pH of the liquid. Normally when performing laboratory evaluations, the pH of the process stream is used [Cheremisinoff et al., 1978]. If the desired degree of adsorption does not take place at the process pH, then various pH levels should be investigated.

2.3 Charcoal

Man's use of charcoal extends back as far as human history itself. It was first used more than 30,000 years ago to make some of the earliest cave paintings [Harris, 1999]. Much later, charcoal played an important role in what might be considered mankind's first technology, the smelting and working of metals. In more recent times, charcoal has remained a technologically important material, primarily as a result of its adsorptive properties. The use of activated charcoal in gas masks during World War I saved many thousands of lives, and today charcoal is used on an enormous scale for the purification of air and water. From a scientific perspective, charcoal is also of great interest since we are beginning to achieve a detailed picture of its atomic structure for the first time [Harris, 1999].

The dictionary defines charcoal as "The black porous residue obtained by the destructive distillation of animal or vegetable matter in a limited supply of air". In fact charcoal, or more correctly *char*, can be produced from a range of synthetic materials, such as polymers, as well as from natural sources. The basic atomic structure of the char is independent of the precursor, although the larger scale morphology may differ. It is important not to confuse charcoal with other forms of impure non-crystalline carbon such as coke and soot. Although coke, like charcoal, is produced by solid-phase pyrolysis (usually of bituminous coal), it is distinguished from charcoal in that a fluid phase is formed during carbonization. The structure and properties of cokes and chars are quite different, as discussed further below. In the case of soot, this is formed in the gas phase by incomplete combustion rather than by solid-phase pyrolysis, and it has a microstructure quite distinct from either coke or charcoal.

The origins of charcoal production are intimately bound up with the beginnings of metallurgy approximately 5000 years ago. Attempts to smelt metals using wood fires could never have been entirely successful, since it would have been impossible to achieve sufficiently high temperatures. When plain wood is burned there is a large quantity of water driven off, plus

assorted volatiles, and this limits the temperature of the fire. Burning charcoal, on the other hand, produces a much higher fire temperature (well over 1000°C), with little smoke: ideal conditions for metal smelting and working. Oxide ores of copper were first reduced with charcoal in about 3000 BC, initiating the era we know as the Bronze Age. Iron is more difficult to smelt than copper, requiring higher temperatures and a greater blast of air, and was first achieved in about 1200 BC, marking the beginning of the Iron Age [Harris, 1999].

The earliest method for producing charcoal probably involved the "pit kiln" process, in which wood was slowly burned in a shallow pit covered with soil. However, this eventually gave way to the more efficient and manageable aboveground "forest kiln" method. Charcoal was still being produced in this way until the 1950s in Forest of Dean and elsewhere [Harris, 1999]. The first stage in constructing the pile is the raising of a center log, around which a shaft is left to act as a chimney. Wood is then stacked around this to form a hemispherical heap, which is then covered with earth or turf. Around the base of the pile some small air inlets are opened. To light the kiln, some kindling is thrown down into the central shaft, followed by a burning torch. When the wood is alight, the hatch is closed. Opening and closing the air inlets at the base regulates the intensity of the fire. Controlling the input of air ensures that the wood smolders rather than bursting into flames, and in this way it is slowly converted into charcoal, a process which typically takes around ten days. Ideally, charcoal should be produced in kilns capable of reaching high temperatures, since higher temperatures drive off greater proportions of acids, tars and volatile gases thus making the resulting charcoal purer with a higher carbon content. Good quality charcoal requires temperatures of up to 500°C to achieve a fixed carbon content of 75%. However high purity charcoal is more friable than charcoals produced in lower temperature kilns and so a maximum kiln temperature of 450-500°C is often considered as the optimum. The variation of carbon contents with kiln temperatures is given in Table 2.3.2.

Table 2 3 2 Carbon contents of charcoal at different kiln temperatures (Kristoferson, 1987)

Carbonization Temperature (°C)	Proportion of Carbon as % of dry weight of charcoal
200	52.3
250	70.6
300	73.2
500	89.2
700	92.8
800	95.7
900	96.1
1000	96.6

Charcoal is produced locally mainly for domestic use as a source of energy. It is prepared using traditional methods; that is, wood is chopped into small logs and arranged on the ground. The logs are then buried with soil and lighted. The soil ensures that the logs burn without oxygen. Unlike activated carbon, charcoal is prepared under uncontrolled temperatures and is not activated. This means that the temperature is not controlled and therefore not constant. The charcoal is also not activated meaning that it has not gone through a process of making it more porous by driving away impurities. Local charcoal is prepared using wood from different types of trees but the most common tree is the acacia mearnsii tree commonly known as the black wattle tree.

2.3.1 Charcoal as an adsorbent

The use of charcoal as an adsorbent, like most of its other applications has a very long history [Patrick, 1994] Egyptian papyri from around 1500 BC describe the use of charcoal to adsorb malodorous vapors from putrefying wounds, and there is an Old Testament reference (Numbers 19:9) to the ritual purification of water using the charred remains of a heifer. The Swedish scientist Carl Wilhelm Scheele made the first scientific study of the adsorptive properties of charcoal in the late 18th century. He described how the vapors adsorbed by charcoal could be expelled by heating, and taken up again during cooling [Scheele; 1780]. He filled a retort half-full with very dry powdered charcoal and tied it to a bladder, emptied of air. As soon as the retort became red-hot at the bottom, the bladder would no longer expand. He left the retort to cool and the air returned from the bladder into the coals. He again heated the retort, and the air was again expelled, and when it was cool the coals again adsorbed the air. This air filled 8 times the space occupied by the coals.

During the 19th century, work on the adsorptive properties of charcoal continued at a fairly low level. There were still relatively few applications for charcoal as an adsorbent, apart from specialized areas like sugar refining, and little incentive for research. It was the use of poisonous gas in World War I which created an urgent need for effective adsorbent materials [Hall and King, 1988]. Gas was first used in the second battle of Ypres in April 1915, when the Germans released chlorine over the allied trenches. The British and French troops were completely unprepared for this new weapon, the only protection being a piece of damp cloth tied over the face. Subsequently, slightly improved defense against chlorine was achieved by using cloth saturated with chemicals such as photographers' Hypo solution. However, it was clear that a far better form of protection was going to be needed. The first true gas masks were made using wood charcoal, which was activated chemically. Subsequently, research in the USA showed that charcoal made from coconut shells had the best characteristics for use in gas

masks, since its more open macroporous structure allowed for a more rapid flow-through of air

Today, activated charcoal is used on an enormous scale in both vapor-phase and liquid-phase purification processes. It is still used widely in respirators, as well as in air-conditioning systems and in the clean-up of waste gases from industry. In the liquid-phase, its largest single application is the removal of organic contaminants from drinking water. Many water companies in Europe and the USA now filter all domestic supplies through granular activated carbon filters, and household water filters containing activated carbon are also in widespread use. Other applications include decontamination of groundwater and control of automobile emissions. As a result of its commercial importance, charcoal has been the subject of a huge amount of research in both industrial and academic laboratories [Harris, 1999]

2.3.2 The structure of charcoal

Franklin [Franklin 1950], described X-ray diffraction (XRD) studies of a char prepared from the polymer polyvinylidene chloride. By rigorous quantitative analysis of the diffraction data, Franklin was able to propose the first reliable model for the structure of a char. In this model, 65% of the carbon in char is contained in individual graphite layers, highly perfect in structure but only about 1.6 nm in diameter, with the remainder of the carbon being disordered. This was followed by a detailed study of the effect of high temperature heat treatments on the structures of cokes and chars. Franklin's results came as a surprise: while the cokes could be graphitized by heat treatments above about 2200°C, the chars could not be transformed into crystalline graphite, even at 3000°C [Franklin 1951]. Instead, they formed a porous, isotropic material, which only contained tiny domains of graphite-like structure. These results demonstrated, for the first time, the key distinction between cokes and chars. Franklin coined the terms *graphitizing carbons* and *non-graphitizing carbons* to describe the two classes of material identified, and proposed models for their microstructures. In these models, the basic units are small

graphitic crystallites containing a few layer planes, which are joined together by cross-links. The structural units in a graphitizing carbon are approximately parallel to each other and the links between adjacent units are assumed to be weak. The transformation of such a structure into crystalline graphite would be expected to be relatively facile. By contrast, the structural units in non-graphitizing carbons are oriented randomly and the cross-links are sufficiently strong to impede movement of the layers into a more parallel arrangement.

2.4 Acacia mearnsii (The black wattle tree)

The black wattle is a small tree native to Australia where it grows from southern New South Wales to Tasmania. It has now been introduced worldwide and is grown in huge plantations in South Africa, Kenya, Tanzania and Zimbabwe (Lewington, 1990). A rounded or rather shapeless tree and up to 15m in height, the black wattle is commonly planted in the highlands up to 2500m and is widely naturalized. It is grown in commercial plantations and farm woodlots in western Kenya. The trunk is often bent when trees are grown outside plantations. The bark is smooth and black in mature trees and is split to give resinous gum. The leaves are feathery dull green with extremely small leaflets and the upper surface of leaf stalk is scattered with glands. The black wattle has many pale yellow fragment flowers, in small round heads and numerous pods, which are dull brown when dry with small and black seeds.

The black wattle is propagated as seedlings or direct sowing. As a pre-sowing treatment the seeds are immersed in hot water and soaked for 12 hours. The tree is fast growing but thin if established by direct sowing. The black wattle produces hard, timber and is generally useful for fencing and implement handles and excellent for firewood and charcoal (Noad and Birnie, 1989). Other uses of the black wattle are tannin, short fibre pulp, windbreaks, ornamental, soil conservation and gum.

Chapter Three

3.0 EXPERIMENTAL SET-UP

3.1 Introduction

The potential for ground charcoal was evaluated on the basis of the removal of a synthetic dye. *Congo red* The dye removal was investigated through laboratory batch tests The time required to attain equilibrium concentration of the dye in the solution was determined The concentration of the dye and the pH were investigated to determine the optimum operating conditions

3.2 Data Collection Methodology

3.2.1 Preparation of the sample stock solution

The tests were carried out using clean water spilled with a synthetic dye, *Congo red*. The water was prepared by dissolving 0.1 grams of a synthetic dye, *Congo red*, in one litre of tap water to form a concentration of 0.1 g/l Ground charcoal from black wattle tree obtained from a local charcoal dealer was used as the adsorbent.

3.2.2 Materials

3.2.2.1 *Congo red dye*

Congo red dye used in this study was obtained from Industrial Chemicals Distributors, located at Nairobi's industrial area

3.2.2.2 **Ground Charcoal**

Ordinary black wattle tree charcoal is common and easy to produce Charcoal, which is sold as a domestic source of energy, is produced in conditions whose carbonization temperatures are not controlled It was for this reason that a small amount of charcoal was prepared using a furnace at 450 °C in the laboratory for the purpose of comparing it with commercial charcoal, which was used in this study Both commercial and laboratory prepared charcoal were made from the black wattle tree

The charcoal was washed thoroughly with distilled water to avoid the presence of foreign impurities. Then the washed and dried charcoal was pulverized and sieved to get the required size range (0.42 to 0.6mm). The sieved ground charcoal was washed thoroughly with distilled water to remove the fine particles. The washed ground charcoal was dried at 110°C for 10 hrs and then cooled in a desiccator to the room temperature. The ground charcoal was once again sieved to the required size.

Characteristics of Ground Charcoal

i. Size

The size of the ground charcoal used was in the range of 0.42 to 0.6mm. The choice of the range was based on preliminary studies. Preliminary studies showed that particle size greater than this range took over 48 hours to come to equilibrium with the dye while those less than the range proved difficult to separate from the mixture with the dye solution.

ii. Relative Density

The relative density was determined by using a density bottle with careful weighing. The densities were determined after all air had been expelled from the sample by shaking the bottle. Since charcoal is a porous material it was soaked in water for 24 hours with slow stirring as recommended by Ives (1990). Several samples had their densities determined and their averages taken. The densities of the ground charcoal are given in Table 3.2.1.

iii. Acid solubility

A test with hydrochloric acid is commonly required in filter media specifications. The test ensures the integrity of the grains; that they are solid and not aggregated particles which may be cemented. Acid solubility is a surrogate test for the chemical inertness that is desirable for filter materials.

The media were subjected to the acid test according to the University College London procedure (Ives, 1990). where they were immersed in 20 percent HCl for 24 hours at 20 °C They were then washed in distilled water, and dried at 110 °C and re-weighed In the University College London procedure, a weight loss of more than 2 percent is unsatisfactory The results of the acid test are given in Table 4 1

iv **Carbon content**

The amount of carbon in ground charcoal was determined using the Exeter Analytical Model 440 Elemental Analyzer, which provides a direct automated elemental analysis. In the 440 Analyzer, the carbon, hydrogen, and nitrogen content in organic and inorganic compounds can be determined Combustion of the weighed sample (typically 1-3 mg; in certain cases up to 500 mg) occurs in pure oxygen under static conditions.

The combustion train and analytical system are shown in Figure 4.3 Helium is used to carry the combustion products through the analytical system to the atmosphere, as well as for purging the instrument Helium was selected for this purpose because it is chemically inert relative to tube packing chemicals, and it has a very high coefficient of thermal conductivity Argon can be used with some model 440 modifications, but is not recommended since instrument performance deteriorates Solenoid valves **A** through **G** control the gas flow through the system; valves **H** and **I** are used for automatic leak testing and other maintenance purposes

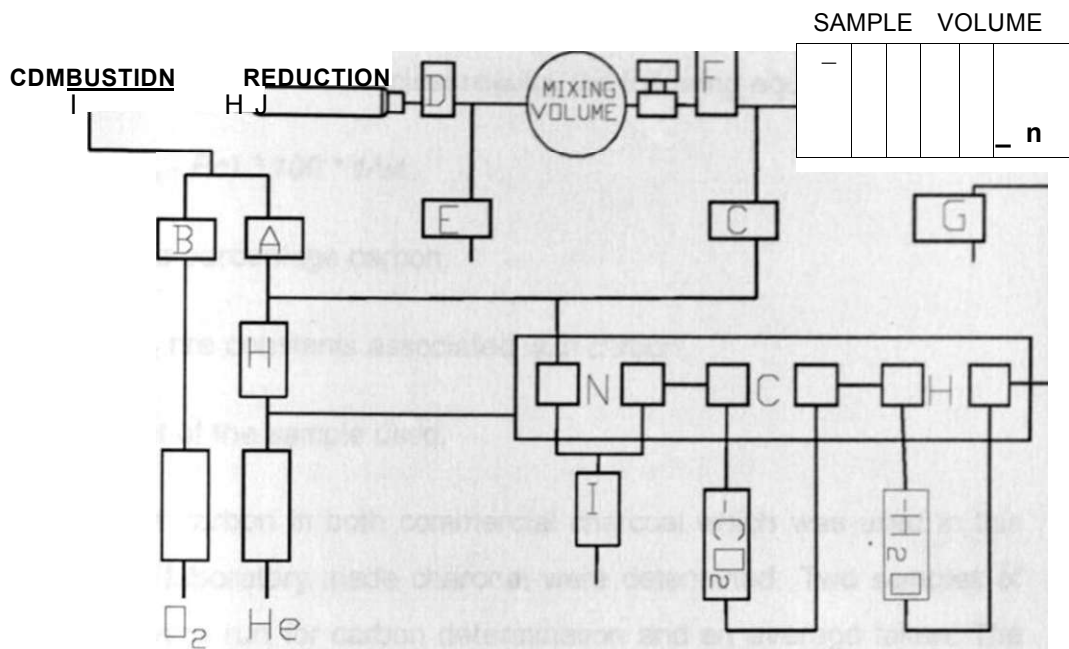


Figure 3.1: Model 440 Elemental Analyzer flow diagram

The products of combustion are passed over suitable reagents in the combustion tube to assure complete oxidation and removal of undesirable by-products such as sulphur, phosphorous, and halogen gases. In the reduction tube, oxides of nitrogen are converted to molecular nitrogen and residual oxygen is removed. In the mixing volume the sample gases are thoroughly homogenized at precise volume, temperature, and pressure. This mixture is released through the sample volume into the thermal conductive detector

Between the first three pairs of the thermal conductivity cells an absorption trap removes water from the sample gas. The differential signal before and after the trap reflects the water concentration and, therefore, the amount of hydrogen in the original sample. A similar measurement is made of the output of a second pair of thermal conductivity cells, between which a trap removes carbon dioxide, thus determining the carbon content. The remaining gas now consists only of helium and nitrogen. This gas passes through a thermal conductivity cell and the output signal is compared to a reference cell through

which pure helium flows. This gives the nitrogen concentration. Raw results were, obtained. To obtain the actual results, the following equation was used:

$$\%C = 1/K_c * (R_z - B_e) * 100 * 1/wt$$

where %C is the percentage carbon,

K_c , B_e , and R_z are constants associated with carbon,

w_t is the weight of the sample used.

The amount of carbon in both commercial charcoal which was used in this study and the laboratory made charcoal were determined. Two samples of the charcoal were run for carbon determination and an average taken. The results are given in Table 3.2.1 below. They were derived from data given in the Appendix A1

Table 3.2.1: Characteristics of ground charcoal

Sample	Relative Density	Percent Weight Loss	% Carbon content
Commercial charcoal	1.138	1.47	76.53
Laboratory made charcoal	1.129	1.23	80.3

The content of carbon in the laboratory made charcoal is in agreement with the results given in literature. Cheremisinoff and Ellerbusch (1978) reported that nearly 80 percent elemental carbon can be effected by prolonged exposure of the product of carbonisation to 400-600 °C. Kristoferson and Bokalders (1987), have also reported that good quality charcoal requires temperatures up to 500 °C, with kiln temperature of 450-500 °C producing

charcoal with a fixed carbon content of about 75 percent. The carbon content of 76.5% in commercial charcoal also shows that the ordinary charcoal sold as a domestic source of energy is made at temperatures that are within the same range given by these authors and may therefore be applied as filter media.

3.2.3 Experimental procedure

Experiments were carried out using clean water spilled with dye prepared by dissolving a synthetic dye, *Congo red*, in tap water. Charcoal used was from black wattle tree and was obtained from a local charcoal dealer. The study involved laboratory batch tests.

3.2.3.1 Rate Studies

Synthetic water samples (100 ml) of 10 mg/l concentration of *Congo Red* dye were taken in separate set of containers and the 3 grams of ground charcoal was added to these. The dosage of 3 grams was selected after preliminary studies (Table 3.2.2). Dosages less than 3 grams proved to be inadequate and saturation occurred before equilibrium was reached and dosages greater than 3 grams conglomerate and therefore were not effective. The sample containers were shaken on a mechanical shaker at 150 rpm. The experiments were carried out for a duration of 32 hours at 20°C and the samples were collected every 2 hours. Filtering through filter papers using a suction pump separated ground charcoal from the containers and the filtrate was measured for residual dye. 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.

Table 3.2.1: Preliminary Results For Dye removal

Ground Charcoal Mass (g)	Initial Concentration (mg/l)	Final Concentration (mg/l)
1	30	21.22
2	30	14.63
3	30	7.93
4	30	3.17
5	30	2.44
6	30	1.83
7	30	1.24
8	30	1.47
9	30	1.66
10	30	1.77

For the investigation of the effect of pH, a pH range of 4 to 12 was selected. A sample solution of 10 mg/l was prepared. 100 grams samples were adjusted to the required pH using either 0.01 M NaOH to raise the pH or 0.01 M HCl to lower the pH. 100 grams samples were used because of ease of operation. 3 grams of ground charcoal were then added to the solutions. The mixture was then mixed thoroughly by shaking. The time of mixing, and the pH of the sample were recorded and the samples set aside. They were shaken continuously to ensure thorough mixing. The samples were filtered after a contact time of 18 hours and the concentration of each determined.

3.2.3.2 Equilibrium Studies

Batch experiments were conducted for the development of adsorption isotherms. Containers of 150 ml capacities were used in all the experiments. Dye-spiked synthetic water samples (100 ml) of 2, 3, 5, 10, 20, 50, and 100 mg/l concentration, were taken in different containers and different masses of

ground charcoal were added to them. The sample containers were shaken on a mechanical shaker at 150 rpm. After the required equilibrium time of 18 hours, obtained from the rate studies, 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 10 grams of ground charcoal were used. A room temperature of 20°C was maintained in all the experiments.

3.2.3.3 Determination of dye removal

The concentration of the dye was determined using Beer's and Lambert's laws combined which gives for a monochromatic light -

$$D = \log_{10} (I_0/I) = 0.434kcl \dots\dots\dots \text{Equation 3.1}$$

Where D is the absorbance

c is the concentration of absorbing species

l is the cell length

k is the extinction coefficient

The absorbance of the dye solution was determined by the use of Unicam SP 600 Series 2 Spectrophotometer and a 1-cm light path cell. A predetermined wavelength was used in order to obtain maximum absorbance. This **was** done by varying the wavelength setting of the spectrophotometer and reading the absorbance of samples of a pre-selected dye concentration. The absorbance was plotted against the wavelength and the wavelength corresponding to the maximum absorbance selected. The constant, k, was determined using samples of 10 mg/l. The absorbance of the samples was measured, their average taken and Equation 3.1 applied. The removal was calculated as the difference between the initial concentration and the final concentration.

Chapter Four

4.0 Results and Discussion

4.1.0 Data Analysis

The data collected from the batch tests were used to formulate the following relationships-

- (i). Variation of wavelength with absorbance,
- (ii). Rate studies,
- (iii). Adsorption isotherms.
- (iv). Variation of final dye concentration with pH,

4.1.1 Variation of Absorbance with Wavelength

The absorbance of a sample of 10 mg/l initial dye concentration measured at different wavelengths are recorded in Table 4 1 below

Table 4.1: Variation of Absorbance with Wavelength

Wavelength	460	470	480	490	500	510	520	530	540
Absorbance	0.308	0.335	0.360	0.395	0.410	0.405	0.388	0.345	0.300

From Table 4 1. the graph in Figure 4.1 below was plotted to show the variation of absorbance with wavelength The absorption spectrum obtained by the spectrophotometer is characteristic of the individual dye; it might in fact be regarded as its fingerprint.

From the graph, the wavelength at which the absorbance is a maximum was found to be 500nm. This is the wavelength at which the slightest change in concentration is easily recorded thus, this was the wavelength that was used for the measurement of absorbance of the test samples

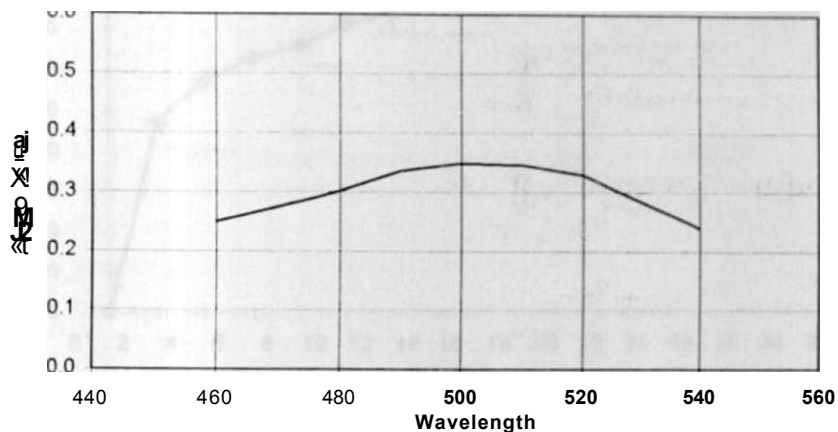


Figure 4.1: Variation of Absorbance with wavelength.

4.1.2 Rate Studies

Sorption isotherms are usually determined under equilibrium conditions, that is, when the rate of sorption is equal to the rate of desorption, unless special conditions are applied and short-term isotherms are measured [Giles, et al, 1970], Rate studies were carried out for Congo red dye on charcoal. The results are as tabulated in Table 4.2 and Figure 4.2 below. They were derived from the data presented in appendix A2

Table 4.2: Variation of Percentage Dye Removal with Time

Time (Hours)	0	2	4	6	8	10	12	14	16	18	20	22	24
% Removal	0	47	57	63	66	71	74	77	79	81	81	81	81

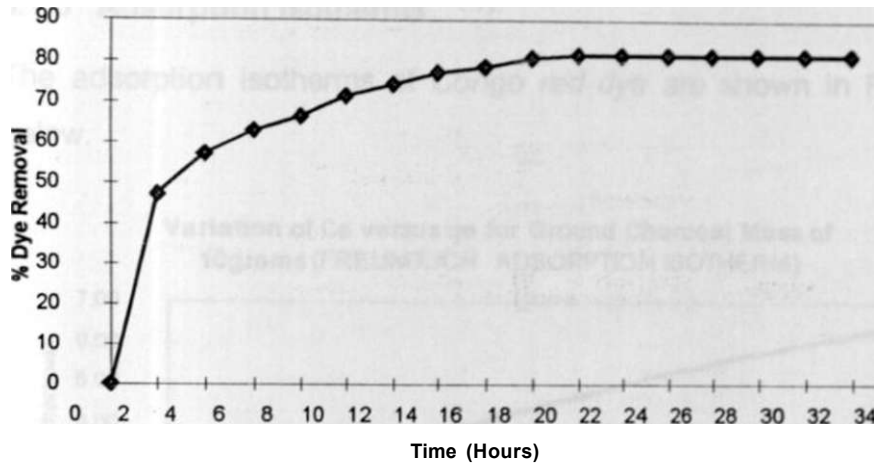


Figure 4.2: Variation of Percentage Dye Removal with Time.

Adsorption of *Congo red* dye on the charcoal was rapid with 58% of the dye adsorbed by the charcoal after 24 hours being already sorbed after the first 1 hour and 70% after 2 hours. The rapid uptake of the dye initially followed by the slow uptake of the dye can be explained to occur as a result of the driving forces being very high initially, due to availability of adsorbing sites. The force diminishes with the occupation of the sites by the dye molecules and hence the slow uptake. This is because the rate at which adsorption proceeds is proportional to the driving force, which is the difference between the amount adsorbed at a particular concentration and the amount that can be adsorbed at that concentration [Metcalf and Eddy, Inc., 1979]. At equilibrium this difference is zero. Figure 4.2 shows the equilibration time necessary for *Congo red* to attain equilibrium to be 18 hours, which is only relevant when the equilibrium conditions are kept constant. These conditions include temperature, which was maintained at 20°C and media size, which was in the range of 0.42mm to 0.6mm. This was the contact time taken for subsequent tests. A constant initial dye concentration of 10mg/l was used since as determined by other researchers initial concentration has little influence on the time of contact necessary to reach equilibrium [Poots, et al 1978]

4.1.3 Adsorption isotherms

The adsorption isotherms of Congo red dye are shown in Figures 4.3-4.7 below.

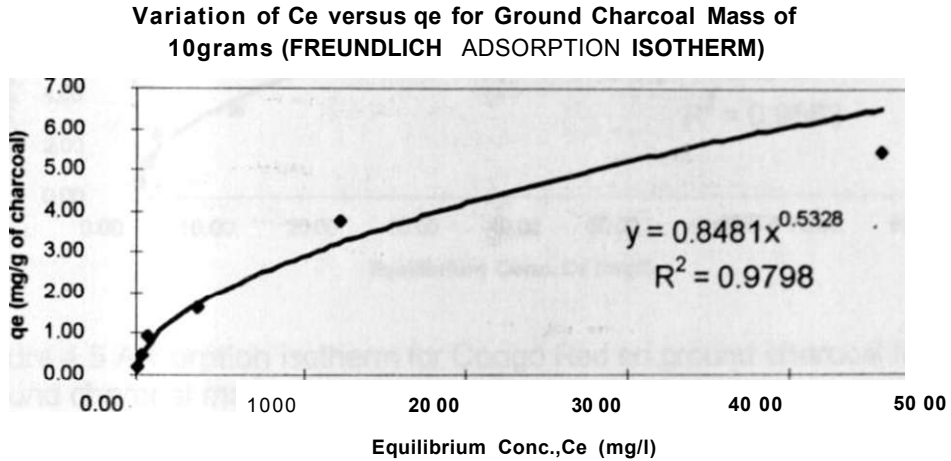


Figure 4.3 Adsorption isotherm for Congo Red on ground charcoal for a ground charcoal mass of 10 grams

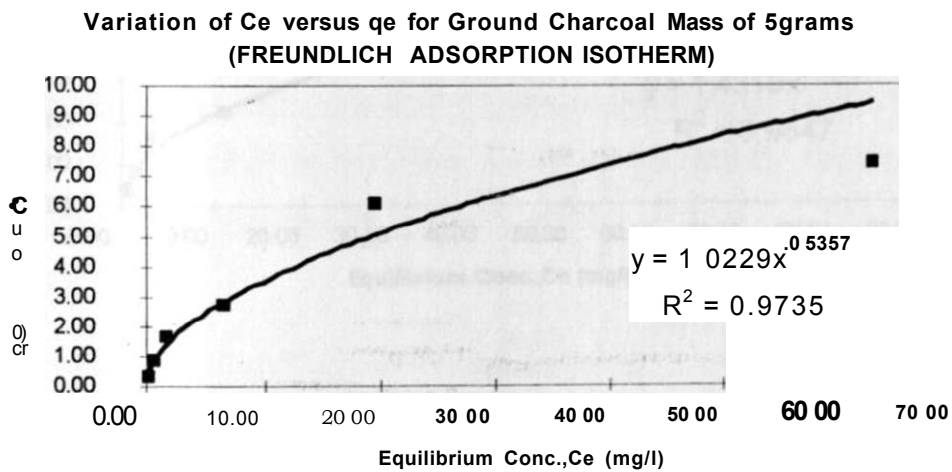


Figure 4.4 Adsorption isotherm of Congo Red on ground charcoal for a ground charcoal mass of 5 grams

Variation of C_e versus q_e for Ground Charcoal Mass of 3grams
(FREUNDLICH ADSORPTION ISOTHERM)

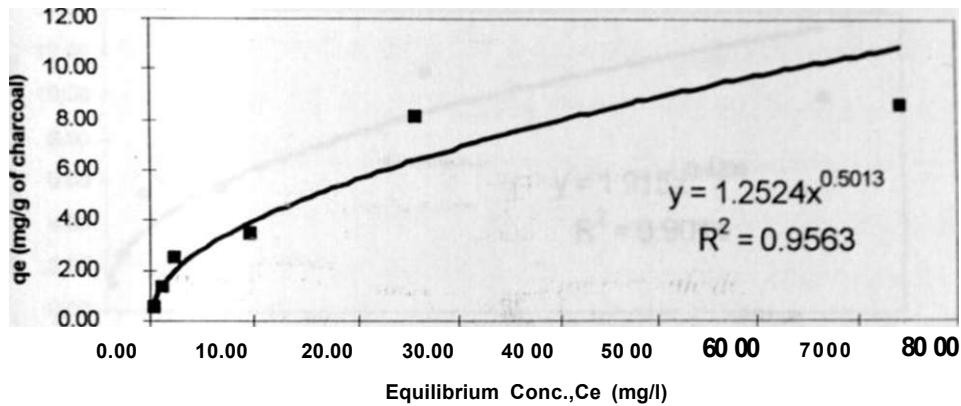


Figure 4.5 Adsorption isotherm for Congo Red on ground charcoal for a ground charcoal mass of 3 grams

Variation of C_e versus q_e for Ground Charcoal Mass of 2grams
(FREUNDLICH ADSORPTION ISOTHERM)

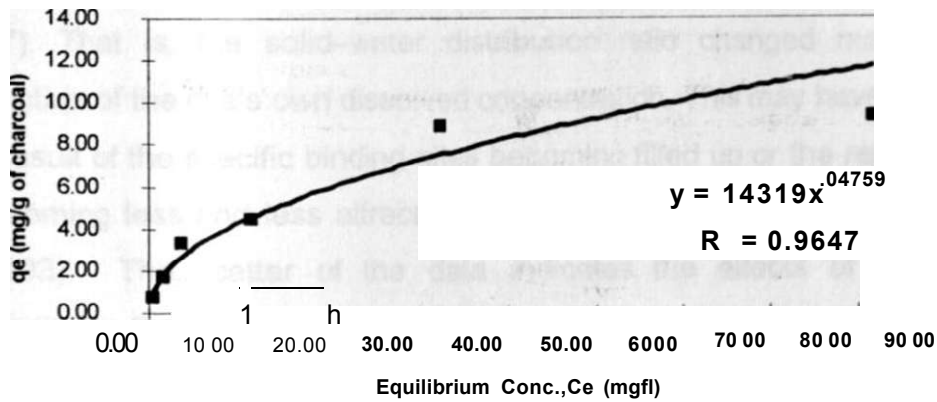


Figure 4.6 Adsorption isotherm for Congo Red on ground charcoal for a ground charcoal mass of 2 grams

Variation of C_e versus q_e for Ground Charcoal Mass of 1 grams
(FREUNDLICH ADSORPTION ISOTHERM)

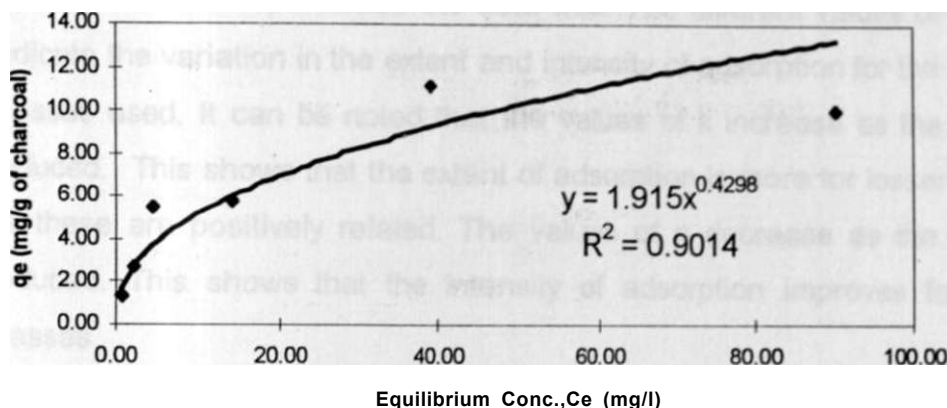


Figure 4.7 Adsorption isotherm of Congo Red on ground charcoal for a ground charcoal mass of 1 grams

As observed by Schwarzenbach (1993), the isotherms of congo red dye, an organic compound that is charged in solution, were all nonlinear (Figures 4.3-4.7). That is, the solid-water distribution ratio changed markedly as a function of the dye's own dissolved concentration. This may have occurred as a result of the specific binding sites becoming filled up or the remaining sites becoming less and less attractive to the sorbate molecules Schwarzenbach (1993). The scatter of the data indicates the effects of experimental conditions that cannot be met in a real situation but can be met in an ideal condition.

The values of the Freundlich constant k and n and the correlation coefficients R for different masses of ground charcoal are give in Table 4.3.

Table 4.3 Values of Freundlich Adsorption isotherm constants and the correlation coefficients

Ground Charcoal Mass (grams)	k	n	Correlation coefficients R
10	0.8481	0.5328	0.9798
5	1.0229	0.5357	0.9735
3	1.2524	0.5013	0.9563
2	1.4319	0.4759	0.9647
1	1.915	0.4298	0.9014

The high correlation coefficients obtained indicate that the Freundlich isotherm models represented the data well. The different values of n and k indicate the variation in the extent and intensity of adsorption for the different masses used. It can be noted that the values of k increase as the mass is reduced. This shows that the extent of adsorption is more for lesser masses as these are positively related. The values of n decrease as the mass is reduced. This shows that the intensity of adsorption improves for lesser masses.

4.1.4 Effect of pH on the removal of the dye

Table 4.4 below gives the results of the variation of dye concentration with pH at the end of the contact time. The results were derived from the data presented in appendix A3

From the table the graph in fig 4.8 on page 45 was plotted to show the variation of dye concentration at equilibrium with pH.

Table 4.4: Variation of Final Dye Concentration with pH.

PH	5	6	7	8	9	10	11	12
Final Dye Concentration	1.7	1.7	1.7	1.7	1.7	2.7	3.0	3.6

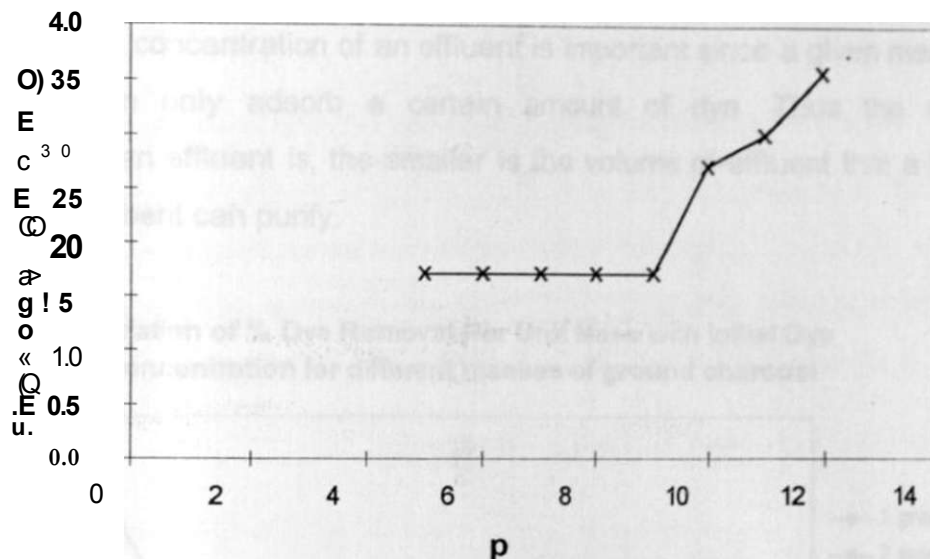


Fig 4.8: Variation of Final Dye Concentration with pH

From the graph, it can be observed that pH in the range of 4-9 had no effect on the removal of the dye. Increase in pH beyond pH 9 resulted in decrease in the dye removal. Some charged organic compounds include a sufficiently large hydrophobic portion in their structure that transfer onto the solid surface is favoured. Such adsorption requires the co-transfer of a counterion to maintain local electro-neutrality [Schwarzenbach ET al., 1993], Thus the hydrophobic force driving the dye ions onto the surface of the charcoal could be high enough between pH 4 and 9 to resist the electrostatic force due to the sodium ions introduced into the solution. However at higher pH the electrostatic force become higher and the hydrophobic force is overcome by the electrostatic force forcing the dye ions to stay in the solution and thus less and less adsorption

Another explanation could be that since the ionic species of the dye are negatively charged, there could be competition for adsorption sites with the hydroxyl anions as observed for alkylbenzenesulphonate on Columbia carbon [Morris and Weber, 1964], The hydroxyl anions are more favourable than the dye anions since they are smaller molecules and therefore moves faster.

4.1.5 Effect of initial dye concentration on the removal

The initial dye concentration of an effluent is important since a given mass of adsorbent can only adsorb a certain amount of dye. Thus the more concentrated an effluent is, the smaller is the volume of effluent that a fixed mass of adsorbent can purify.

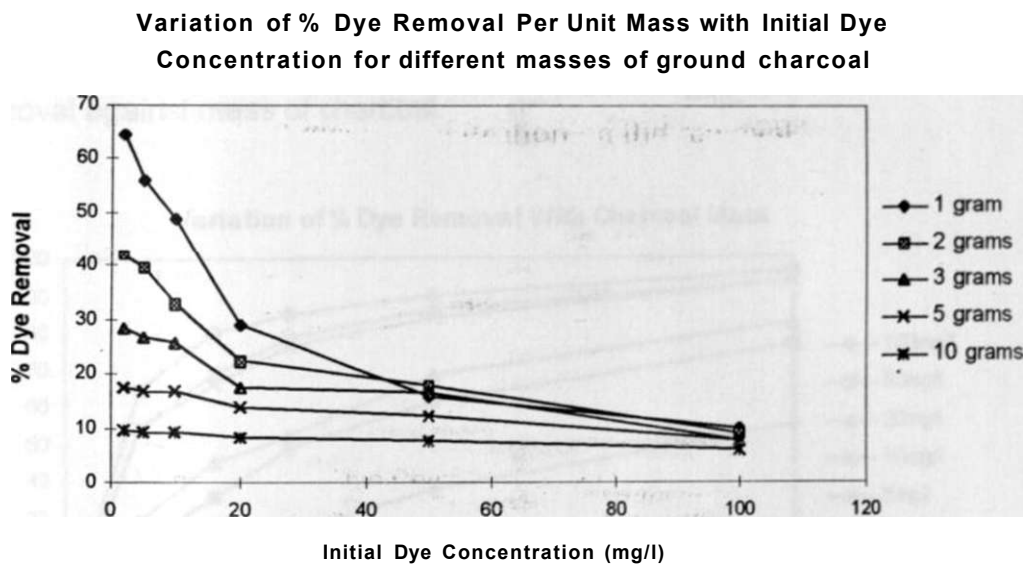


Figure 4.9: Effect of Initial Dye Concentration on Removal

The influence of dye concentration was studied and experimental results are shown in Figure 4.9. At high concentrations the lines lie close together indicating that fractional adsorption is low. However, for low concentrations the lines lie far apart indicating that fractional adsorption is high. Consequently, the concentration of dye will greatly affect the extent and rate of dye uptake on ground charcoal. A similar trend observed indicated that the mechanism of removal predominant is most effective for low dye concentrations, below 20mg/l. This shows the saturation of charcoal by dye i.e. the active sites are fixed and get saturated. At reduced uptake at high concentration, there is possibility of dye-dye molecule interaction. This is consistent with solution thermodynamics considerations if the solution concentration exceeds the infinite dilution value and the Henrys Law becomes invalidated. There was near constant percentage dye removal by 10 grams at 10% and 5 grams at below 20% for all the concentrations

investigated because of conglomeration of particles and hence lower adsorption per unit mass

4.1.6 Effect of mass of ground charcoal on the removal of the dye

The effect of mass of ground charcoal (1, 2, 3, 5 and 10grams) was studied on the dye when experimental conditions were maintained constant. In all cases the rate of dye uptake increased with increasing ground charcoal mass; the results are shown in Figure 4.10 as a plot of percentage dye removal against mass of charcoal.

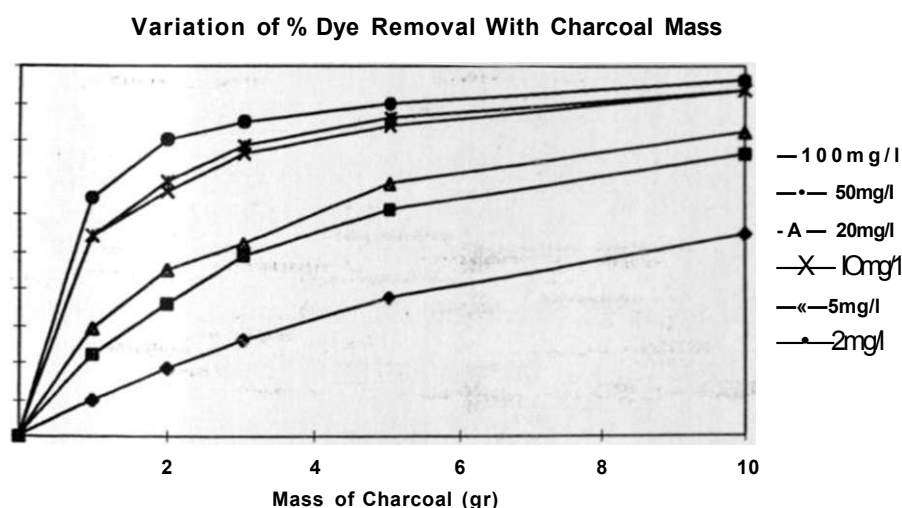


Fig 4.10: Variation of Percentage Dye Removal with Mass of Ground Charcoal

The rate of adsorption depends on the driving force per unit area, and in this case, since C_0 is constant, increasing the mass of charcoal increases the surface area for the adsorption and hence the rate of dye removal is increased. Since the particle size range is constant, the surface area will be directly proportional to the mass of ground charcoal in the system.

4.2 Method and possibilities of Media Regeneration

The most effective approach that has been used to regenerate the spent carbon is thermal methods. In this process the spent carbon is subjected to temperatures in the range of 1200 to 1600°F for several seconds in an

Potential for ground charcoal for synthetic dye removal

oxygen-deficient atmosphere. As a result water associated with the spent carbon is volatilised and oxidised. This method is cost intensive and therefore the cost of regeneration would be prohibitive in the case of charcoal, and a throwaway basis may be more economical

Chapter Five

5.0 Conclusions and Recommendations

5.1 Conclusions

The following conclusions were drawn from the study:

1. Ground charcoal has a potential for use in wastewater treatment to remove dyes.
2. A long contact time required for the dye to reach equilibrium (18 hours for a size range of 0.42 to 6mm) indicates slow mechanism. This may be as a result of dye molecule's time to penetrate through the charcoal micro pores, formation of new bonds between the dye molecules and the charcoal and slow reaction at the surface could also be responsible to the slow process of attainment of equilibrium.
3. The removal of the dye is independent of the pH of the solution in the range of 5-9. Therefore pH adjustment is not required in this range for the removal of the dye using ground charcoal sorption.
4. Removal rate of the dye decreases with the increase in dye concentration and therefore dilute solutions are favorable for the removal.

5.2 Recommendations

1. Charcoal with variable carbon content and from other sources such as plastic materials should be investigated.
2. A pilot scale operation of dye removal using ground charcoal is necessary.

Chapter Six

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APPENDICES

APPENDIX A1 DETERMINATION OF CARBON CONTENT

Sample		Counter	Run	Weight (ng)
Laboratory Sample 1		474	8	1552
Laboratory Sample 2		475	9	1639
commercial Sample 1		472	6	1303

Sample	Counter	v	Kc	Average Kc	Be	Average (Be)	Fill time
Commercial	472	25128	24.787	24.782	414	416.5	19
Laboratory	474	31543	24.777		419		18
	475	32788					18

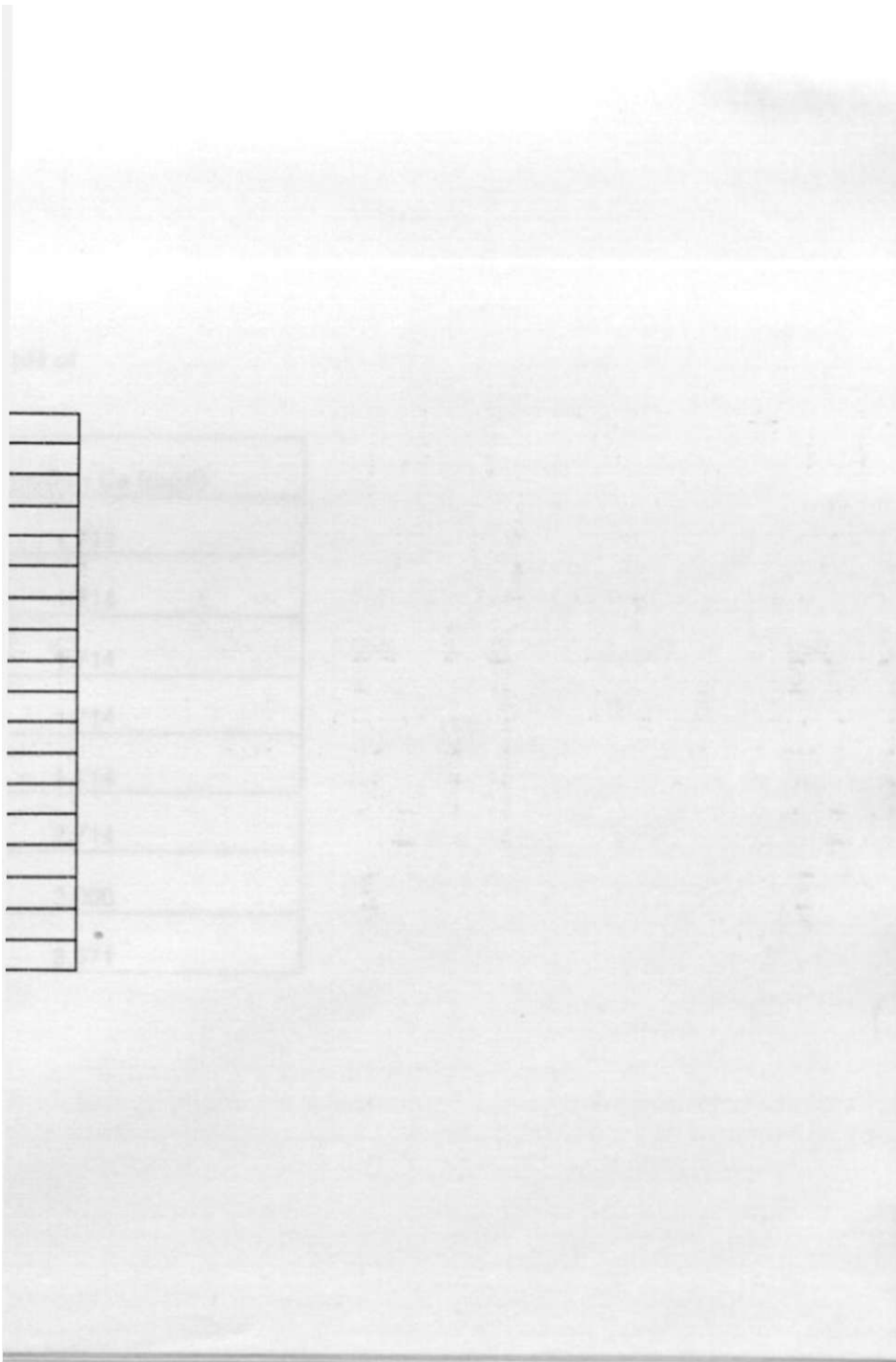
Sample	Raw results	% Actual Carbon Content (%C) %C=1/Kc*(Rj-Bc)* 100* 1/wt	
		%c	Average %C
Commercial	% C=83.526, %H=3.272, %N=-0.860, %Residue= 13.288	76.53	76.53
Laboratory	% C=88.258, %H=3.466, %N=-0.210, %Residue= 8.486	80.9	80.3
	% C=86.905, %H=3.348, %N=-0.191, %Residue= 9.938	79.7	

Appendix A2: Variation of the absorbance with time for a ground charcoal of mass 2g and initial dye concentration of 10mg/l

Time (Hours)	Mass (g)	Average Absorbance	Initial conc., Co(mg/l)	Final conc., Ce(mg/l)	removal	% Removal
0	3	0.3500	10	10	0	0
2	3	0.1850	10	5.286	4.714	47.143
4	3	0.1500	10	4.286	5.714	57.143
6	3	0.1300	10	3.714	6.286	62.857
8	3	0.1175	10	3.357	6.643	66.429
10	3	0.1000	10	2.857	7.143	71.429
12	3	0.0900	10	2.571	7.429	74.286
14	3	0.0800	10	2.286	7.714	77.143
16	3	0.0750	10	2.143	7.857	78.571
18	3	0.0675	10	1.929	8.071	80.714
20	3	0.0650	10	1.857	8.143	81.429
22	3	0.0650	10	1.857	8.143	81.429
24	3	0.0650	10	1.857	8.143	81.429
26	3	0.0650	10	1.857	8.143	81.429
28	3	0.0650	10	1.857	8.143	81.429
30	3	0.0650	10	1.857	8.143	81.429
32	3	0.0650	10	1.857	8.143	81.429

Temperature = 20o

Time (Hours)	Mass (g)	Absorbance	
		Sample 1	Sample 2
2	3	0.185	0.185
4	3	0.150	0.150
6	3	0.125	0.135
8	3	0.115	0.120
10	3	0.095	0.105
12	3	0.090	0.090
14	3	0.080	0.080
16	3	0.075	0.075
18	3	0.070	0.065
20	3	0.065	0.065
22	3	0.065	0.065
24	3	0.065	0.065
26	3	0.065	0.065
28	3	0.065	0.065
30	3	0.065	0.065
32	3	0.065	0.065



Appendix A4: Variation of the absorbance with pH of

PH	Absorbance	Final concentrtrion Ce (mg/l)
5	0.06	1.714
6	0.06	1.714
7	0.06	1.714
8	0.06	1.714
9	0.06	1.714
10	0.095	2.714
11	0.105	3.000
12	0.125	3.571

Mass of Ground Charcoal(g)	Absorbance	Initial concentration Co (mg/l)	Final concentration Ce (mg/l)	Removal	qe
1	0.315	100	90.000	10.000	10.000
1	1.360	50	38.857	11.143	11.143
1	0.498	20	14.214	5.786	5.786
1	0.160	10	4.571	5.429	5.429
1	0.080	5	2.286	2.714	2.714
1	0.025	2	0.714	1.286	1.286
2	0.285	100	81.429	18.571	9.286
2	1.130	50	32.286	17.714	8.857
2	0.388	20	11.071	8.929	4.464
2	0.120	10	3.429	6.571	3.286
2	0.055	5	1.571	3.429	1.714
2	0.014	2	0.400	1.600	0.800
3	0.260	100	74.286	25.714	8.571
3	0.895	50	25.571	24.429	8.143
3	0.335	20	9.571	10.429	3.476
3	0.083	10	2.357	7.643	2.548
3	0.038	5	1.071	3.929	1.310
3	0.011	2	0.300	1.700	0.567
5	0.220	100	62.857	37.143	7.429
5	0.680	50	19.429	30.571	6.114
5	0.223	20	6.357	13.643	2.729
5	0.058	10	1.643	8.357	1.671
5	0.025	5	0.714	4.286	0.857
5	0.007	2	0.200	1.800	0.360
10	0.160	100	45.714	54.286	5.429
10	0.430	50	12.286	37.714	3.771
10	0.130	20	3.714	16.286	1.629
10	0.025	10	0.714	9.286	0.929
10	0.012	5	0.343	4.657	0.466
10	0.003	2	0.084	1.916	0.192

qe = mass of sorbate adsorbed per gram of charcoal