Removal of Dissolved Reactive Red Dye from Aqueous Solution by Coconut Coir Carbon

By

NASHRUL IZZUAN BIN ABDUL KARIM

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Universiti Teknologi Petronas
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Civil Engineering Programme
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Approved:

Prof. Malay Chaudhuri
Project Supervisor

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

Nashrul Izzuan Bin Abdul Karim

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ABSTRACT

Previous studies have proved that industrial effluents, especially reactive dyes have been one of the major pollutants to the environment. This paper consists of the progress and development of using coconut coir carbon as the remover material for the reactive dyes in aqueous solution. The main objective of the study is to produce a low cost adsorbent from readily available material to remove dissolved reactive red dye from aqueous solution by adsorption, using the coconut coir carbon as well as to evaluate the effectiveness of the method such as finding the optimum condition for removal of reactive red dye by studying the effect of contact time, pH, initial concentration of the reactive red, and temperature on the reactive red adsorption process. The adsorbent was the coconut coir carbon. The activated carbon was prepared by crushing the coconut coir to finer particles, treated with sulphuric acid H_2SO_4 and kept into an air oven with 105°C temperature for 24 hours. Several test for the studies were done to prove and determine the effectiveness of the method such as dye adsorption studies and regeneration studies. The study is divided into two stages. The first stage involving literature reviews and background studies and the stage 2 by laboratory test, final report and results presentation. The exact completion of the study is within a year; completion of stage 1 in first half of the year and stage 2 in second half of the year.

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CHAPTER 1

INTRODUCTION

1.1. Background of the Study

The effluents discharged from textile industries generates a large amount of wastewater, high cost maintenance and are toxic to aquatic life in ecological cycle. Reactive dyes are known as the greatest problem in term of colour, widely used in textile dyeing and as additives in petroleum products. Over 7×10^5 tons and approximately 10,000 different types of dyes and pigments are produced world wide annually. "It is estimated that 10 to 15% of the dye is lost in the effluent during the dyeing process. Contamination of water resources with dyes is not desirable, as they are aesthetically displeasing." (Garg et al., 2003; Young and Yu, 1997).

The reactive dyes prevent reoxygenation in receiving waters by cutting off sunlight penetration. In addition, most of the dyes used as coloring material are toxic to aquatic organism. Existing technologies for dye effluent treatment such as advanced oxidation process, electrochemical reduction, etc. may be efficient in the removal of dyes but their initial and operational costs are high. Adsorption has proved to be more versatile and efficient compared to conventional physico-chemical methods of dye removal (Khairasheh et al., 2002)

The recovery of dyes/organics and easy operational procedures have made adsorption technique being widely used for textile waste treatment. Reactive dye is known to have low adsorbability on a wide range of adsorbents. Reactive dye wastewater has limited biodegradability in an aerobic environment. Many reactive dyes, constituting the largest dye groups decompose to potential carcinogenic aromatic amines under anaerobic conditions (Lazearidis et al., 2003; Netpradit et al., 2003).

The coconut coir, a waste material from coir industries, can cause a disposal problem because it is resistant to biodegradation. Since the material is rich in lignocelluloses content, an effective solution to the problem may lie in the use of the material for the preparation of activated carbon (Krishnamoorthy, 1998). Activated carbon prepared from coconut coir pith was successfully used for removal of the dye, 2-chlorophenol and heavy metals. In a previous study by Santhy and Selvapathy (2004) activated carbon from coconut coir pith showed remarkable efficiency for the removal of heavy metals from metal polishing industrial effluent. Hence feasibility of applying activated carbon from coir for the removal of reactive dyes from aqueous and industrial effluents is approached.

1.2. Problem Statement

There are various ways of treating the reactive red dye in the fabric and textile industries. Most of the methods to remove industrial effluents used are costly and complicated. Moreover, the methods also need professional operation and the materials used are quite rare and hard to obtain. So it is encouraged to use abundant components or materials from surrounding which are cheaper and effective. One method of removing reactive red dye is adsorption by using the coconut coir pith, a method used by Santhy and Selvapathy (2004) to remove aqueous reactive dye.

The problems occur when textile industry is less concerned about their responsibility to the environment. The effluents that contain excess dye are often released directly into the drainage system without being treated, so the waste water from the drainage enters and pollutes the rivers. This issue should not be held back only by these small scale operators because they surely cannot afford or consider to have expensive treatment plants or in other words, they cannot risk themselves and their business to handle hazardous chemical agent.

The excess dye content can cause health hazard to organic life. It can cause severe dermatitis, eye irritation, asthma, convulsions, and even coma to humans. This is because the dye mixtures in the effluent textile waste may contain aluminum hydroxide and hydrogen peroxide that brings harmful effects to human. More than that, the number of small scale textile manufacturers is large and unregistered; law enforcers have problems to make sure all of them obey the procedure of waste water management.

The usage of waste material in the treatment will give benefit in term of cost reduction compared to the conventional treatment process. In Malaysia, coconut coir is considered a waste or by-products and is abundant. Utilization of the waste material will also contribute to reduction to the landfill use for solid waste management.

1.3. Significance of the Project

The importance of this study would be to ascertain the efficiency of coconut coir activated carbon as the adsorbent in textile waste treatment. By using the locally available material, the water treatment cost is expected to be lower, thus be a cost affective alternative to the existing chemical adsorbents. The comparison between coconut coir activated carbon and industrial activated carbon as primary adsorbent is essential in determining the effectiveness of the coconut coir carbon in treating textile waste effluents from drainage system or other aquatic systems with different condition and concentration.

Other than that, application of coconut coir carbon as primary adsorbent will definitely give an idea in reducing the cost as it can be used for many times. In addition, coconut coir carbon does not give any significant impact to pH of water. They are also not toxic to humans or animals. Therefore, exploring an alternative by using natural coagulant might help in developing an economical, environmental friendly and low health risk method in textile waste treatment.

1.4. Objectives of the Project

The objectives of this study are:

1. To investigate the effectiveness of using coconut coir activated carbon in removing the reactive red dye from aqueous solution.
2. To investigate the adsorption isotherm using coir activated carbon as adsorbent for reactive red dye removal.
3. To determine the optimum condition of reactive dyes removal using for coconut coir carbon in pre-fixed solution.

1.4. Scope of the Study

The scope of the study covers mainly on laboratory works, which are dye adsorption studies. By running the test on different concentration, pH, contact time and temperature of solution, the optimum condition of the coconut coir activated carbon will be obtained. Besides that, the optimum condition of the chemical adsorbent, the condition for aqueous solution of reactive dye needs to be found out precisely. The results will be used for comparison with the industry activated carbon. The pH will be measured before and after the test to determine the effect of pH on adsorption. The parameters in the study are pH, colour, temperature, contact time and optimum dosage. A conclusion to the study will be made based on the results.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1. Reactive Dye

Introduction

Reactive dyes first appeared commercially in 1956, after their invention in 1954 by Rattee and Stephens at the Imperial Chemical Industries Dyestuffs Division site in Blackley, Manchester, United Kingdom. Reactive dyes are used to dye cellulosic fibers. The dyes contain a reactive group, either a haloheterocycle or an activated double bond which is when applied to a fiber in an alkaline dye bath, forms a chemical bond with a hydroxyl group on the cellulosic fiber. Reactive dyeing is now the most important method for the coloration of cellulosic fibers. Reactive dyes can also be applied on wool and nylon; in the latter case they are applied under weakly acidic conditions. Reactive dyes have a low utilization degree compared to other types of dyestuff, since the functional group also bonds to water, creating hydrolysis (Venkataraman, 1972). Table 1 shows the advantages and disadvantages of the reactive dyes generally.

Advantages	**Disadvantages**
Simplifies dyeing process	Hydrolysis accompanies fixation
Improve fastness	Large amount of electrolytes used

[**Table 1**: Advantages and disadvantages of reactive dyes]

2.1.1 Structures and Properties

The structure of reactive dye is attributed to chemical bonding between suitable groups in the dye molecule and hydroxyl groups in the cellulose fiber. Before the introduction of reactive dyes, cotton was often dyed with direct, vat, sulphur and azoic dyes. For about four decades before the use of reactive dyes, these dyes remained the only feasible method of achieving dyeing of high fastness to wash cellulose textiles (Venkataraman, 1972).

The characteristic structural features of a typical reactive dyes molecule are:

1) The reactive system, enabling the dyes to form covalent bonds between the dye and the substrate,
2) The chromophoric grouping, contributing to the color and much to the substantivity for cellulose,
3) A bridging group that links the reactive system to the chromophore, and solubilising groups.

The reactive grouping is attached directly to the chromophore, and most reactive systems contain a heterocyclic ring which contributes to substantivity for cellulose. The nature of the bridging group and other substituents on the heterocyclic ring greatly influences the reactivity and other dyeing characteristics of reactive dyes. Many reagents can be used as a reactive system, but only a few have met the requirements to become commercially established in a significant segment of the market (Frank et. al., 1994)

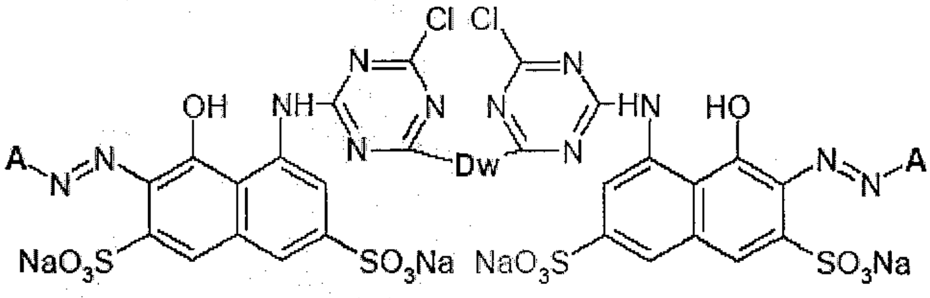
The chlorotrazinyl and vinylsulphone groups have been firmly established as the main reactive system for cellulose. Dye manufacturers have for a long time recognized the need to improve the fixation levels of reactive dyes. As a result, some of the reactive dyes with more than one reactive group in the dye molecule have been investigated. Reactive systems are often classified according to the number of reactive groups contained in the dye molecule, as mono-, bi- and poly-functional reactive systems (Hall et al., 1966).

Reactive dye is a class of highly colored organic substances, primarily utilized for tinting textiles that attach themselves to their substrates by a chemical reaction that forms a covalent bond between the molecule of dye and that of the fiber. The dyestuff thus becomes a part of the fiber and is much less likely to be removed by washing than are dyestuffs that adhere by adsorption.

The very first fiber-reactive dyes were designed for cellulose fibers, and are still used mostly in this way. There are also commercially available fiber-reactive dyes for protein and polyamide fibers. In theory, fiber-reactive dyes have been developed for other fibers, but these are not yet practical commercially. The dyes contain a reactive group that, when applied to a fiber in a weakly alkaline dye bath, form a chemical bond with the fiber. Reactive dyes can also be used to dye wool and nylon, in the latter case they are applied under weakly acidic conditions.

The most important characteristic of reactive dyes is the formation of covalent bonds with the substrate to be colored, i.e. the dye forms a chemical bond with cellulose, which is the main component of cotton fibers (Attia et al., 2004).

Fiber reactive dye is the most permanent of all dye types. Unlike other dyes, it actually forms a covalent bond with the cellulose or protein molecule. Once the bond is formed, what you have is one molecule, as the dye molecule has become an actual part of the cellulose fiber molecule. No wonder you can safely wash a garment that has been dyed in bright fiber reactive colors with white clothing, a hundred times, without endangering the whites in the least - even if it is all different bright colors, or even solid black. In contrast to all other dyes the reactive dyes bind chemically to the textile fibers, significantly improving the product's color stability and washability. Thus reactive dying of cotton is currently the most widespread textile dying process in the world. Referring to Figure 1, the general structure of reactive dyes is formed by covalent and ionic bonds.



[**Figure 1**: General formula of reactive dyes]

Where: A – the active component;

A-1 orthanilic acid

A-2 anthranilic acid

A-3 4-(β-ethylsulphate)sulphonylaniline

Dw – diamines;

Dw-1 phenylene-1, 2-diamine

Dw-2 phenylene-1, 3-diamine

Dw-3 phenylene-1, 4-diamine

Dw-4 diaminestilbene-2, 2'-disulphonic acid

Dw-5 4, 4'-diaminebenzoanilide

Dw-6 ethylene-1, 2-diamine

2.1.2 Type of Reactive Dyes

Dycrofix 'M' Dyes: These are called Cold Brand Dyes. These dyes are having very good reactivity fastness properties. These dyes require milder alkaline conditions for applications & fixation at the optimum temperature of 25-35^{0}C.

Dycrofix 'H' Dyes: These are named as Hot Brand Dyes. These dyes are applied under strong alkaline conditions at high temperature of application compared to 'M' Dyes. These dyes contain very good fastness properties to wash, perspiration, light etc. These dyes are suitable particularly for printing cotton, viscose, cuprammonium raysons & natural silk.

Dycrofix Vynil Sulphone Dyes: These are vinyl sulphone based reactive dyes widely used for dyeing & printing of cellulosic fibres for its very good fastness properties. These dyes are having very good features like, good solubility even in presence of alkali, very good fastness properties, can be applied both by exhaust & padding methods, possesses less affinity hence very good leveling property & suitable for resist & discharge printing very much effectively.

Dycrofix 'HE': These are bifunctional reactive dyes. The chromogen of the color is supported through a stillbene in the molecule. This structure provides good light fastness and as well good washing fastness because of having high molecular weight.

Dycrofix 'ME': The optimum fixation temperature of HE type dyes is 80-85 C. Today, dye manufacturers introduced a new range of Bifunctional Reactive DYCROFIX 'ME' Dyes for customers who are too conscious of energy consumption. In DYCROFIX 'ME' Dyes one molecule is fused with two Reactive Group Vinyl Sulphone as well as Monochloro Triazine. These dyes have advantage of high exhaustion, high fixation, high alkali stability, very good leveling property, excellent all around fastness properties like light, washing, perspiration, rubbing chlorine peroxide bleach. These dyes give exceptionally good results on various textile printing including on discharge printing (Pierce, 1994).

2.2. Adsorption

2.2.1 Definition and Concept

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or, more rarely, a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term *sorption* encompasses both processes, while desorption is the reverse process. Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification. Adsorption, ion exchange and chromatography are sorption processes in which adsorbate are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column (Perineau et al., 1982).

Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent or metallic) of the constituent atoms of the material are filled. But atoms on the (clean) surface experience a bond deficiency, because they are not wholly surrounded by other atoms. Thus it is energetically favorable for them to bond with whatever happens to be available. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorptions or chemisorptions (Demirbas et al., 2004).

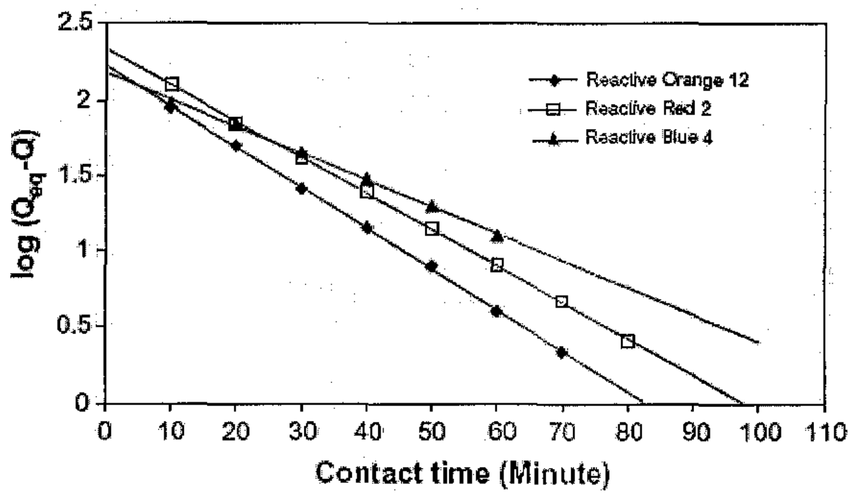
2.2.2 Kinetics of Adsorption

At least 25 models are reported in the literature, all attempting to describe quantitatively the kinetic behavior during the adsorption process. Each adsorption kinetic model has its own limitation and is derived according to certain initial conditions based on certain experimental and theoretical assumptions. A number of these models assume linear equilibrium isotherms,while fewer models assume the equilibrium isotherms to be nonlinear. Among many mathematical models, the first order reaction rate model known as the Lagergren kinetic equation is widely employed (Trivedi et al., 1973).

The Lagergren kinetic equation:

$$\log(Q_{eq} - Q) = \log Q_{eq} - (K_{ad}/2.303)t$$

Where Q and Q_{eq} are the amounts of dye adsorbed (mg/g) of carbon at time, t (min) and at equilibrium time, respectively, and K_{ad} is the rate constant of adsorption ($time^{-1}$). Figure 2 shows the plot of log (Q_{eq} - Q) against contact time. The straight line nature of the plot confirmed adherence to the Lagergren equation and showed that the removal of reactive dyes by adsorption followed the first order kinetics. The rate constants K_{ad} calculated from the slope of the linear plot for the reactive dyes studied are presented in a table (Lagergren, 1898).



[**Figure 2**: Graph for log (Q_{eq} - Q) against reaction time]

2.3. Reactive Red Dye Removal by Adsorption

The previous experimental results by Santhy and Selvapathy (2005) showed that activated carbon prepared from coir pith was a suitable adsorbent for the removal of reactive dyes from both synthetic and textile effluent. In batch studies, the adsorption increased with an increase of contact time and carbon dose and decreased with an increase in solute concentration. Removal of dyes was higher at the acidic pH range. The results showed that the carbon affinity is high on reactive red. The increase in bed height and decrease in flow rate increased the adsorption capacity of the column. The Bed Depth Service Time (BDST) analysis of sorption of dyes by Hutchins (1974) showed linear relationship between bed depth and service time, which could be used successfully for scale-up purposes. Regeneration of the carbon was found to be effective with 1.0 M NaOH and the regenerated carbon was found to be effective up to 3 cycles of operation. Application of the carbon to textile effluent decolourization studies showed significant removal of color and COD (McKay and Bino, 1990).

2.4. Regeneration Studies

The exhausted carbon must be regenerated and reused. To render the use of activated carbon economically feasible in wastewater treatment, the carbon bed was washed with 0.5 M NaOH percolating through the bed at a flow rate of 5 mL/min. The carbon was washed several times with water and again used in the next cycle. The regeneration cycle was repeated several times until the adsorption capacity of carbon was exhausted. Uptake of dye by the adsorbent (as percent) was calculated as ([C0 _ Ct]/C0) · 100 where C0 and Ct are the initial and dye concentrations at time t, respectively. (Allen et al., 1973) The absorbance of the samples was measured at wavelengths characteristic of dyes using spectrophotometer. The color intensity of the sample was expressed as absorption coefficient calculated from the equation:

$$\text{Colour (absorbance, m}^{-1}\text{)} = \frac{\text{absorbance} \times \text{dilution factor}}{\text{pathlength (m)}}$$

[**Figure 3**: Colour Intensity Formula]

2.5. Coconut Structure

Coconuts are the seed of the coconut trees, these palms flower on a monthly basis and the fruit takes 1 year to ripen. A typical palm tree has fruit in every stage of maturity. A mature tree can produce 50-100 coconuts per year. Coconuts can be harvested from the ground once they have ripened and fallen or they can be harvested while still on the tree. A human climber can harvest approximately 25 trees in a day, while a knife attached to a pole can up the number to 250 trees harvested in a day. Monkeys can also be trained to harvest the coconuts, but this practice is less efficient than other methods. Green coconuts, harvested after about six to twelve months on the plant, contain pliable white fibers. Brown fiber is obtained by harvesting fully mature coconuts when the nutritious layer surrounding the seed is ready to be processed into copra and desiccated coconut. The fibrous layer of the fruit is then separated from the hard shell (manually) by driving the fruit down onto a spike to split it (De-husking). A well seasoned husker can manually separate 2,000 coconuts per day. Machines are now available which crush the whole fruit to give the loose fibers. These machines can do up to 2,000 coconuts per hour (Namasivayam and Karitha, 2003).

2.5.1 Coconut Coir Structure

Coir fibers are found between the husk and the outer shell of a coconut. The individual fiber cells are narrow and hollow, with thick walls made of cellulose. They are pale when immature but later become hardened and yellowed as a layer of lignin is deposited on their walls. There are two varieties of coir. Brown coir is harvested from fully ripened coconuts. It is thick, strong and has high abrasion resistance. It is typically used in mats, brushes and sacking. Mature brown coir fibers contain more lignin and less cellulose than fibers such as flax and cotton and so are stronger but less flexible. They are made up of small threads, each about 1 mm long and 10 to 20 micrometers in diameter. White coir fibers are harvested from the coconuts before they are ripe. These fibers are white or light brown in color and are smoother and finer, but also weaker. The coir fiber is relatively water-proof and is one of the few natural fibers resistant to damage by salt water. Fresh water is used to process brown coir, while sea water and fresh water are both used in the production of white coir (Namasivayam and Karitha, 2002).

2.5.2 Coconut Brown Fibre

The fibrous husks are soaked in pits or in nets in a slow moving body of water to swell and soften the fibers. The long bristle fibers are separated from the shorter mattress fibers underneath the skin of the nut, a process known as wet-milling. The mattress fibers are sifted to remove dirt and other rubbish, dried in the sun and packed into bales. Some mattress fiber is allowed to retain more moisture so that it retains its elasticity for 'twisted' fiber production. The coir fiber is elastic enough to twist without breaking and it holds a curl as though permanently waved. Twisting is done by simply making a rope of the hank of fiber and twisting it using a machine or by hand. The longer bristle fiber is washed in clean water and then dried before being tied into bundles or hunks. It may then be cleaned and 'hackled' by steel combs to straighten the fibers and remove any shorter fiber pieces. Coir bristle fiber can also be bleached and dyed to obtain hanks of different colors (Rengaraj et al., 1999).

2.5.3 Coconut White Fibre

The immature husks are suspended in a river or water-filled pit for up to ten months. During this time micro-organisms break down the plant tissues surrounding the fibers to loosen them - a process known as retting. Segments of the husk are then beaten by hand to separate out the long fibers which are subsequently dried and cleaned. Cleaned fiber is ready for spinning into yarn using a simple one-handed system or a spinning wheel (Zhang et al., 2004).

2.5.4 Coconut Coir Uses

Brown coir is used in floor mats and doormats, brushes, mattresses, floor tiles and sacking. A small amount is also made into twine. Pads of curled brown coir fiber, made by *needle-felting* (a machine technique that mats the fibers together) are shaped and cut to fill mattresses and for use in erosion control on river banks and hillsides. A major part of brown coir pads are sprayed with rubber latex that bonds the fibers together (rubberized coir) to be used as upholstery padding for the automobile industry in Europe. The material is also used for insulation and packaging. The major use of white coir is in rope manufacture. Mats of woven coir fiber are made from the finer grades of bristle and white fiber using hand or mechanical looms. White coir also used to make fishing nets due to its strong resilience to salt water. In horticulture, coir is recommended as substitute for peat because it is free of bacteria and fungal spores, and is sustainably produced without the environmental damage caused by peat mining (Namasivayam and Kadirvelu, 2001).

2.6. Activated Carbon

Activated carbon, also called activated charcoal or activated coal, is a general term which covers carbon material mostly derived from charcoal. For all three variations of the name, "activated" is sometimes substituted by "active". By any name, it is a material with an exceptionally high surface area. Just one gram of activated carbon has a surface area of approximately 500 m^2, typically determined by nitrogen gas adsorption, and includes a large amount of microporosity. Sufficient activation for useful applications may come solely from the high surface area, though often further chemical treatment is used to enhance the absorbing properties of the material.

2.6.1 Production

Activated carbon can be produced in two different processes from a variety of carbonaceous source materials, e.g., nutshells, wood, coal. It can be produced using one of the two following processes:

1. Physical reactivation: The precursor is developed into activated carbons using gases. This is generally done by using one of or combining the following processes:
   - Carbonization: Material with carbon content is pyrolysed at temperatures in the range 600-900 °C, in absence of air (usually in inert atmosphere with gases like argon).
   - Activation/Oxidation: Raw material or carbonized material is exposed to oxidizing atmospheres (carbon dioxide, oxygen, or steam) at temperatures above 250 °C, usually in the temperature range 600-1200 °C.
2. Chemical activation: Impregnation with chemicals such as acids like phosphoric acid or bases like potassium hydroxide, sodium hydroxide or salts like zinc chloride, followed by carbonization at temperatures in the range 450-900 °C. It is believed that the carbonization / activation step proceeds simultaneously with the

chemical activation. This technique can be problematic in some cases because, for example, zinc trace residues may remain in the end product. However, chemical activation is preferred over physical activation owing to the lower temperatures and shorter time needed for activating material. Saturated activated carbon can be regenerated by heating (Kim et al., 2003).

2.6.2 Properties of Activated Carbon

A gram of activated carbon can have a surface area in excess of 500 m^2, with 1500 m^2 being readily achievable. For comparison, a tennis court is about 260 m^2. Carbon aerogels, while more expensive, have even higher surface areas, and are used in special applications.

Under an electron microscope, the structure of activated carbon looks a little like ribbons of paper which have been crumpled together, intermingled with wood chips. There are a great number of nooks and crannies, and many areas where flat surfaces of graphite-like material run parallel to each other, separated by only a few nanometers or so. These micropores provide superb conditions for adsorption to occur, since adsorbing material can interact with many surfaces simultaneously. Tests of adsorption behavior are usually done with nitrogen gas at 77 K under high vacuum, but in everyday terms activated carbon is perfectly capable of producing the equivalent, by adsorption from its environment, liquid water from steam at 100 °C and a pressure of 1/10,000 of an atmosphere.

Physically, activated carbon binds materials by Van der Waals force or London dispersion force. Activated carbon does not bind well to certain chemicals, including alcohols, glycols, ammonia, strong acids and bases, metals and most inorganics, such as lithium, sodium, iron, lead, arsenic, fluorine, and boric acid. Activated carbon does absorb iodine very well and in fact the iodine number, mg/g, (ASTM D28 Standard Method test) is used as an indication of total surface area.

Activated carbon can be used as a substrate for the application of various chemicals to improve the adsorptive capacity for some inorganic (and problematic organic) compounds such as hydrogen sulphide H_2S), ammonia (NH_3), formaldehyde (HCOH), radioisotopes iodine-131 (^{131}I) and mercury (Hg). This property is known as chemisorption.

2.6.3 Classifications of Activated Carbon

Powdered activated carbon (PAC)

Traditionally, active carbons are made in particular form as powders or fine granules less than 1.0 mm in size with an average diameter between .15 and .25 mm. Thus they present a large internal surface with a small diffusion distance. PAC is made up of crushed or ground carbon particles, 95–100% of which will pass through a designated mesh sieve or sieve. Granular activated carbon is defined as the activated carbon being retained on a 50-mesh sieve (0.297 mm) and PAC material as finer material, while ASTM classifies particle sizes corresponding to an 80-mesh sieve (0.177 mm) and smaller as PAC. PAC is not commonly used in a dedicated vessel, owing to the high headloss that would occur. PAC is generally added directly to other process units, such as raw water intakes, rapid mix basins, clarifiers, and gravity filters.

Granulated activated carbon (GAC)

Granulated activated carbon has a relatively larger particle size compared to powdered activated carbon and consequently, presents a smaller external surface. Diffusion of the adsorbate is thus an important factor. These carbons are therefore preferred for all adsorption of gases and vapors as their rate of diffusion are faster. Granulated carbons are used for water treatment, deodorization and separation of components of flow system. GAC can be either in the granular form or extruded. GAC is designated by sizes such as 8x20, 20x40, or 8x30 for liquid phase applications and 4x6, 4x8 or 4x10 for vapor phase applications. A 20x40 carbon is made of particles that will pass through a U.S. Standard Mesh Size No. 20 sieve (0.84 mm) (generally specified as 85% passing) but be retained on a U.S. Standard Mesh Size No. 40 sieve (0.42 mm) (generally specified as 95% retained). Normally people use the 50-mesh sieve (0.297 mm) as the minimum GAC size. The most popular aqueous phase carbons are the 12x40 and 8x30 sizes because they have a good balance of size, surface area, and headloss characteristics.

Pelleted Activated Carbon (EAC)

The EAC consists of extruded and cylindrical shaped activated carbon with diameters from 0.8 to 5 mm. These are mainly used for gas phase applications because of their low pressure drop, high mechanical strength and low dust content.

Impregnated Carbon

Porous carbons containing several types of inorganic impregnant such as iodine, silver, cation such as Al, Mn, Zn, Fe, Li, Ca have also been prepared for specific application in air pollution control especially in museums and galleries. Silver loaded activated carbon is used as an adsorbent for purifications of domestic water. Drinking water can be obtained from natural water by treating the natural water with a mixture of activated carbon and flocculating agent $Al(OH)_3$. Impregnated carbons are also used for the adsorption of H_2S and mercaptans. Adsorption rates for H_2S as high as 50% by weight have been reported.

Polymers Coated Carbon

This is a process by which a porous carbon can be coated with a biocompatible polymer to give a smooth and permeable coat without blocking the pores. The resulting carbon is useful for hemoperfusion. Hemoperfusion is a treatment technique in which large volumes of the patient's blood are passed over an absorbent substance in order to remove toxic substances from the blood.

2.6.4 Adsorption Concept in Activated Carbon

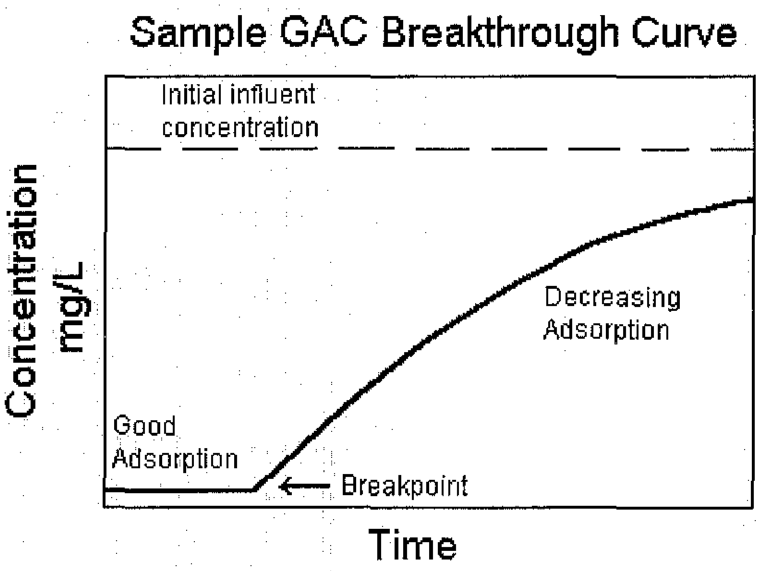
Adsorption efficiency decreases over time and eventually activated carbon will need to be replaced or reactivated. Isotherms are empirical relations which are used to predict how much solute can be adsorbed by activated carbon. The three most well known isotherms are the Freundlich, Langmuir and Linear. In environmental engineering and specifically drinking water treatment application the most commonly used isotherm is the Freundlich. Shown below is the Freundlich isotherm equation in general form (Kharaisheh et. al., 2002).

$$\frac{X}{M} = K * C_e^{\frac{1}{n}}$$

X = mass of solute adsorbed
M = mass of adsorbent
C_e = equilibrium concentration of solute
K, n = experimental constants

[**Figure** 4: Freundlich isotherm equation]

The graph below illustrates a general Freundlich isotherm equation and a sample breakthrough curve. Each individual type of GAC has its own isotherm curve and breakpoint characteristics. These help to predict the adsorptive capacity of particular activated carbons and give a design estimate for adsorptive life. Reactivation becomes necessary once the breakpoint has been reached.

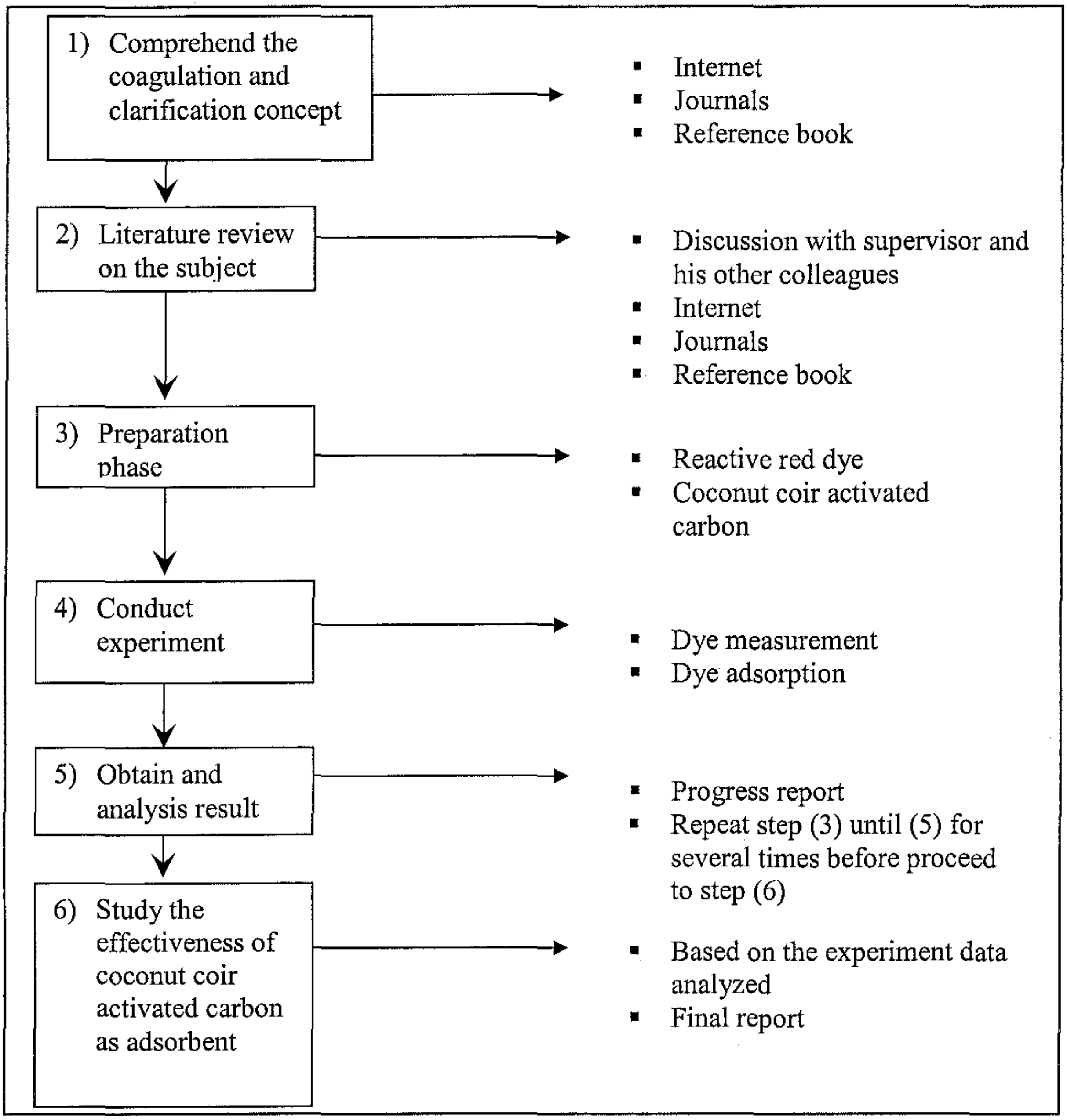


[**Figure 5**: Breakthrough curve]

CHAPTER 3

METHODOLOGY

3.1 General Flow Diagram



[**Figure 6**: General Flow Diagram]

3.2. Preparation of the Materials

3.2.1 Coir Activated Carbon

According to the method used by Santhy and Selvapathy (2005), activated carbon was prepared by treating 50 g of dried coir with 50 mL of concentrated sulphuric acid (H_2SO_4) and keeping this in an air oven maintained at 105 ± 5 °C for 24 h. The resulting char was washed with water followed by a 2% solution of sodium bicarbonate until effervescence ceased and then kept in a 2% solution of sodium bicarbonate overnight. The char was then be separated and washed with water until free from bicarbonate and dried, and then activated at a temperature of 900 °C in an atmosphere of carbon dioxide for 30 min.

The activated material was repeatedly washed with water and soaked in 10% HCl to remove calcium oxide. The acid washed material was repeatedly washed with water to remove the free acid and then dried at 110 °C. Activated carbon with particle sizes in the range of 0.2–0.5 mm (400–500 μm) (retained to a maximum of 85%) was used for the studies.

3.2.2 Dye

The dye was obtained from a proposed textile company, Noor Hakim Batik (106, Kampung Pusu Tinggi, 22000 Jerteh, Terengganu). The dyes came in powder form and weighted about 100 grams. The reactive dyes obtained was Remazol Red 3BS (Colour Index R195).

3.3. Dye Measurement

Aqueous solutions for the obtained dye was prepared by diluting 100mg/L of dye into distilled water as well as the dye measurement was done. The aqueous solution was prepared according to different concentrations which are 1.5 mg/L, 3 mg/L, 5 mg/L, 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L, 50 mg/L 75 mg/L and 100 mg/L.

After the completion of the aqueous solution, a sample was taken from one of the concentrations. A 10 ml pipette was used to take the sample and placed in the cell and inserted to the specific place. The absorbance then was taken using the spectrometer by following the detail procedures.

For the taken sample of concentration previously, the absorbance value was jotted down against different wavelength varying from 400 nm to 700 nm. After obtaining all the absorbance value for the concentration, the maximum absorption was found out. After the determination of the maximum wavelength for the concentration, the absorbance value for all the rest was determined using same methods.

The standard curve was generated by plotting absorbance of the optimum wavelength against corresponding concentration of the dye. The standard curve was used in the analysis of the dye.

3.4. Adsorption Studies

Adsorption studies was carried out by shaking 100 mL of dye solution with 0.2 g of the adsorbent in glass stoppered conical flasks at a temperature of 20 °C at the rate of 150 rpm. The effect of various parameters such as initial concentration, contact time, pH and adsorbent dose on the adsorption process was investigated. The progress of adsorption during the experiments was determined by removing flasks after desired contact time, centrifuging and analyzing the supernatant using spectrophotometer for dye concentration.

Uptake of dye by the adsorbent (as percent) was calculated as $([C_0 - C_t]/C_0) \times 100$ where C_0 and C_t are the initial and dye concentrations at time t, respectively. The absorbance of the samples was measured at wavelengths characteristic of dyes using spectrophotometer. (Santhy and Selvapathy, 2005).

3.5. Hazard Analysis

The project conducted must comply with the UTP Laboratory General Rules and Regulations with conjunction to Health, Safety, and Environment (HSE) policies. The objectives are to prevent accident, to avoid any harm to students and people surrounding, to prevent properties damage and loss event, and to take care of university image and performance.

As far as the project is concerned, it is an experimental research type that dealing with various chemical solutions and equipments, and mostly conducted in the Environmental Engineering Laboratory. Hazard analysis was prepared to ensure the necessary action has been taken care before, during, and after the related experiment is done.

Hazard analysis is the process of study and analyzes anything that can cause harm (e.g. physical, chemical, etc). The conclusion of hazard identification should result in a list of hazard sources, the particular form in which that hazard occurs, the areas of workplace or work process where it occurs and the persons exposed to that hazard. Thus, from the analysis, the precaution action will be taken to reduce the probability of harm that may be dangerous to the respective people involved in the project. The hazard analysis related to the project is tabulated in **Table 2** below:

Types of Hazard	Applications/Job Sequence	Potential Hazards/Accidents	Recommended Safe Job Procedure
Chemical	Sulphuric Acid/ Hidrocloric Acid/ Sodium Bicarbonate	• Splashing • Spill material on to body • Inhalation (in dust form)	• Wear Personal Protective Equipment (PPE), including dust mask, goggles and protective rubber gloves • prevent eye and skin contact • conduct experiment in fume cupboard • irrigate and water flush immediately if contact; ➢ Eyes → Flush with water for at least 15 minutes ➢ Skin → Flush vigorously with water ➢ Ingestion → If victim is conscious, dilute by drinking large quantity of water; get prompt medical attention
Chemical	Remazol Red 3BS	• Inhalation (in dust form) • Eye irratation	• Wear goggle • Wear protective gloves • Wear mask
Physical	Preparing activated carbon	• Strong odour • Effected by sulphuric acid • Splashing	• Wear PPE including protective mask, gloves and goggles • Avoid eye and skin contact

[**Table 2**: Hazard Analysis]

CHAPTER 4

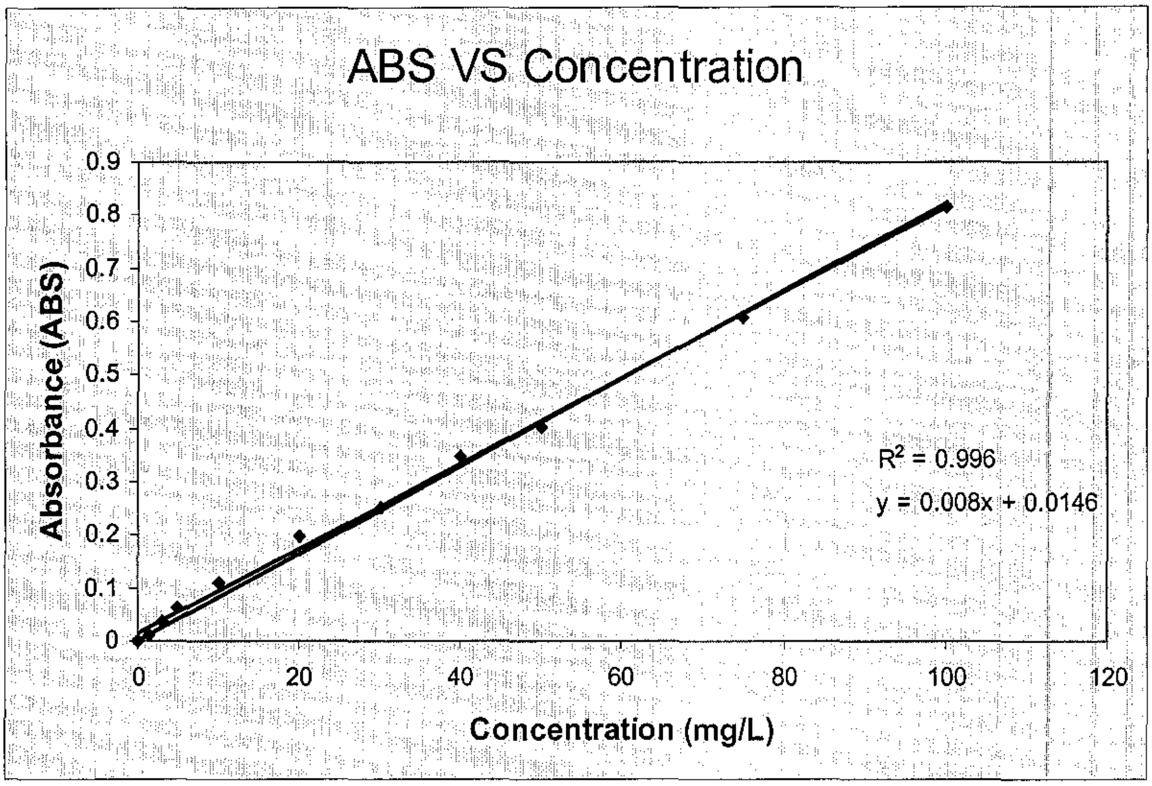
RESULT AND DISCUSSION

4.1. Dye Measurement Studies

An aqueous solution for reactive red dye was prepared by initial solution of 100 g/mL. Then, the solution was diluted into different concentration. For this experiment, the concentration are 1.5 mg/L, 3 mg/L, 5 mg/L, 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L, 50 mg/L 75 mg/L and 100 mg/L. The result for absorbance for every concentration is shown below (**Table 3**).

Jar #	Concentration (mg/L)	Absorbance	pH
1	0	0	7
2	1.5	0.01	6.96
3	3	0.035	6.88
4	5	0.061	6.85
5	10	0.108	6.84
6	20	0.198	6.83
7	30	0.251	6.81
8	40	0.347	6.78
9	50	0.403	6.72
10	75	0.609	6.68
11	100	0.815	6.65

[**Table 3**: Concentration (mg/L) vs. Absorbance (ABS)]



[**Figure 7**: Concentration (mg/L) vs. Absorbance (ABS)]

From **Table 3** we can plot linear graph to find R^2 value and y value. From **Figure 7** the values for dye absorbance were not spread widely so the linear line was accurate. It is because the reading was taken by diluting all the 10 samples first. A sample of 100 mg/L was used as the base solution for diluting the samples. Then the value for R^2 was obtained which is 0.996. The value is valid because the standard curve for the reactive red is 0.998.

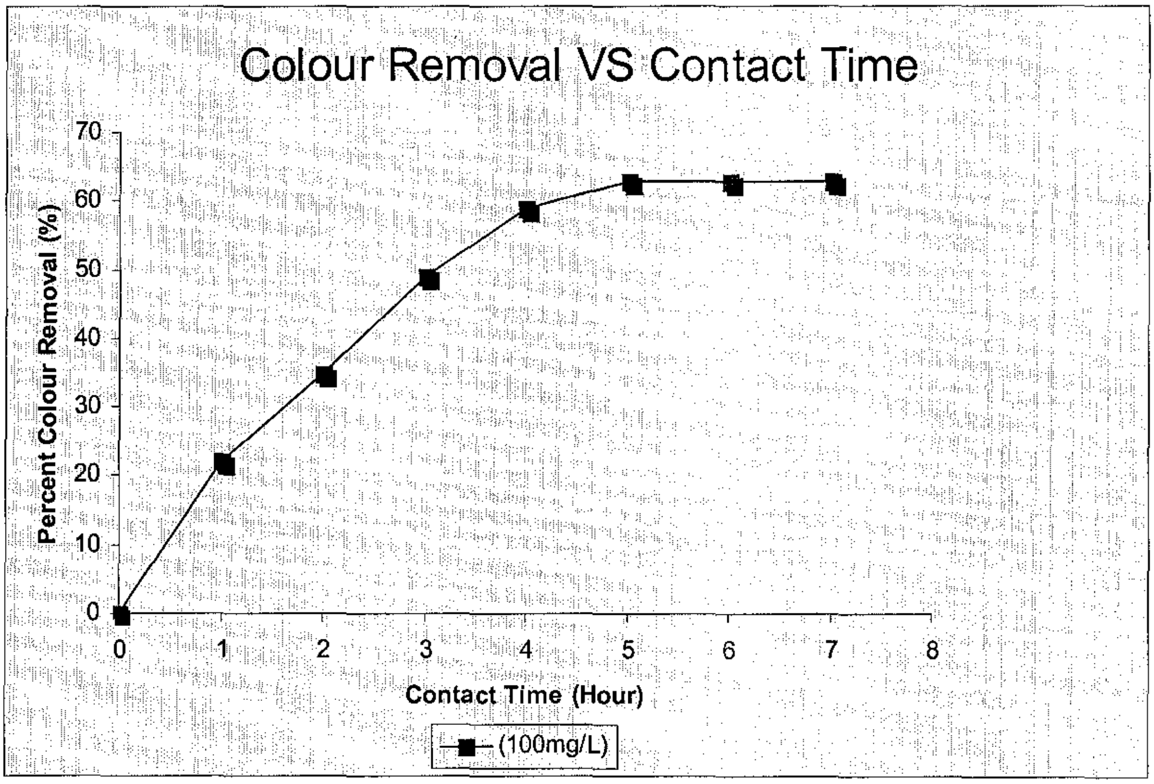
4.2. Dye Adsorption Studies

4.2.1 Effect of initial concentration and contact time

The effect of initial dye concentration and contact time on the removal of Remazol Red 3BS is shown in **Table 3.** From the table, we can plot the percent colour removal against contact time. From the **Figure 8**, it was proven that the removal of dye increased with decreasing dye concentration. Adsorption increased with an increase in contact time. It was found that equilibrium was attained at 5 to 7 h. Removals of Reactive Remazol Red 3BS were found to be 63%, at 4 h equilibration time and at 100 mg/L initial concentration.

Time (hour)	**Percent colour removal %**	**pH**
0	0	6.68
2	22	6.69
2	35	6.72
3	49	6.76
4	59	6.81
5	63	6.83
6	63	6.85
7	63	6.88
8	63	6.91

[**Table** 4: Time, Percent colour removal and pH]



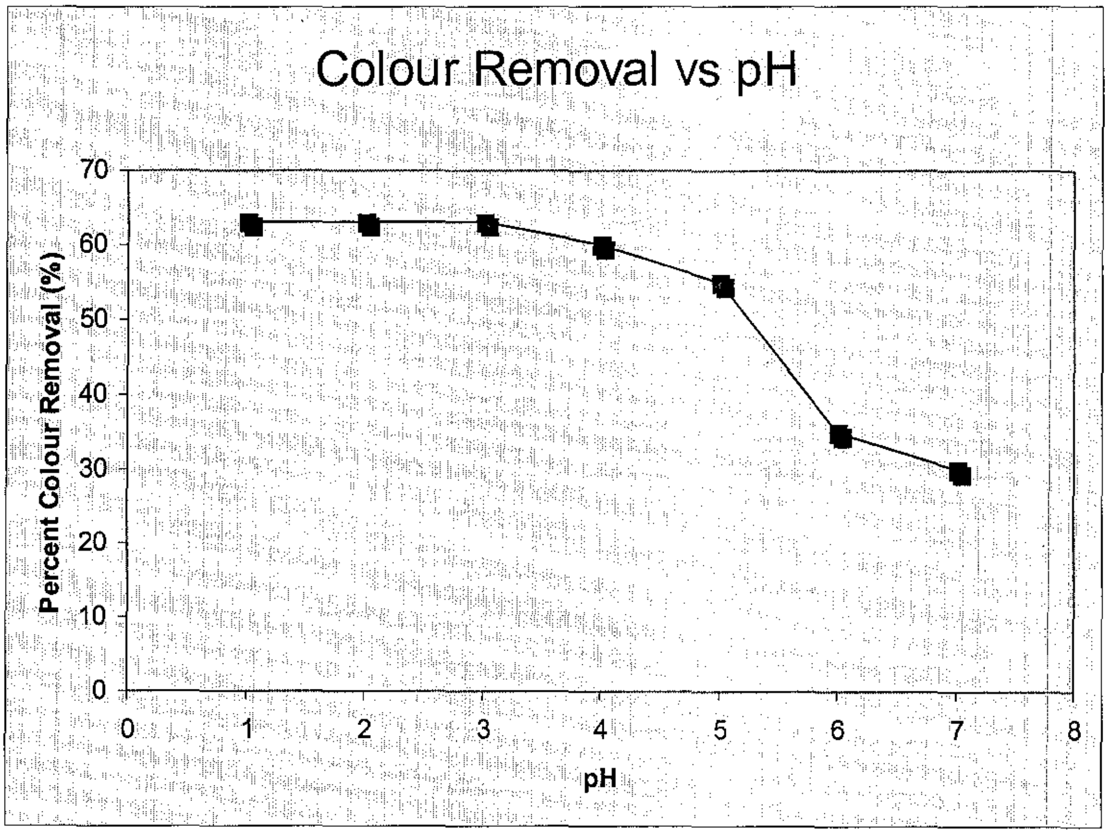
[**Figure 8**: Color removal versus contact time]

4.2.2 Effect of pH

The removal of dyes as a function of pH is shown in **Table 5**.The color concentration was 100mg/L. The removal of reactive dyes by coir activated carbon was found to be a maximum in the acidic pH range of 2–4. The pH value of the dye solution plays an important role in the whole adsorption process and particularly on the adsorption capacity. Using the data from **Table 5**, we can create a graph of colour removal versus pH. As shown in **Figure 9,** as the pH of the adsorption solution was lowered, the positive charges on the surface increased. This would attract the negatively charged functional groups located on the reactive dyes. In subsequent studies, it was decided to maintain a pH of 3.0, at which the removal was maximum.

pH	Percent colour removal %
1	63
2	63
3	63
4	60
5	55
6	35
7	30

[**Table 5**: pH level and percent colour removal]

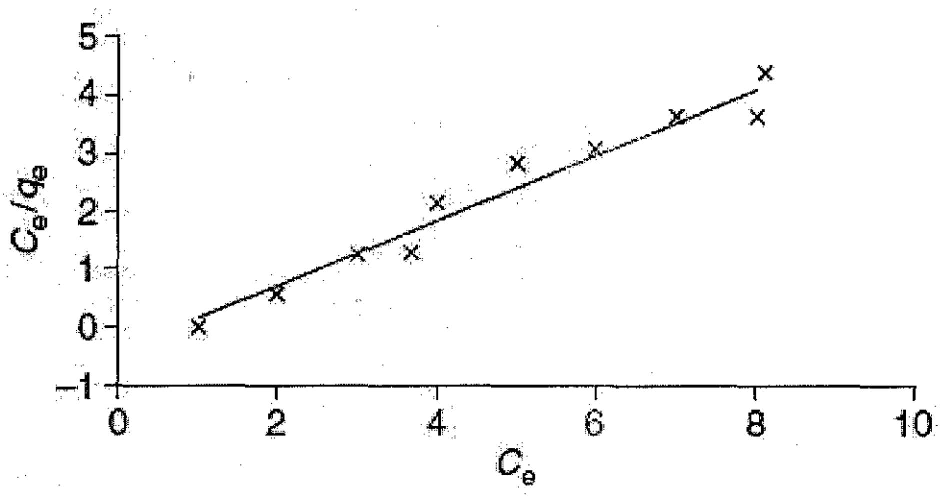


[**Figure 9**: Color removal versus pH]

4.3. Adsorption Isotherm

4.3.1 Langmuir adsorption isotherm

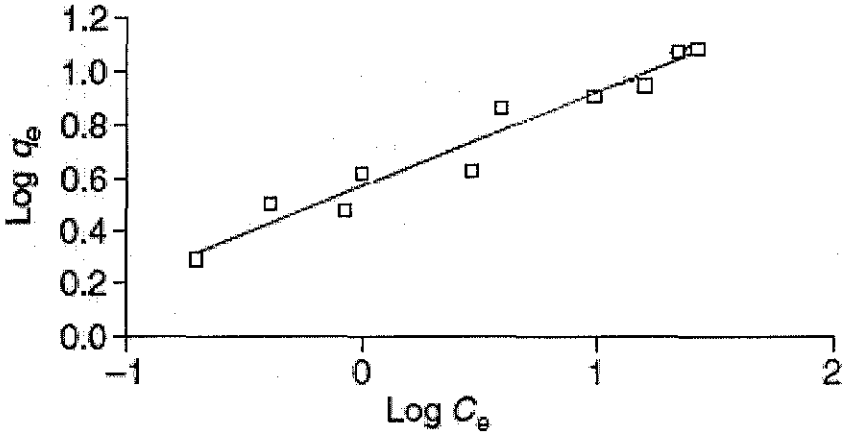
The R^2 value for the Langmuir adsorption isotherm was 0.9191. The coefficient for Langmuir were a = 4.30mg/g and b = 01.89 L/mg.



[**Figure 10**: Langmuir isotherm of different concentrations]

4.3.2 Freundlich adsorption isotherm

The R^2 value for the Freudlich adsorption isotherm was 0.8726. The coefficient for Freudlich were k_f = 4.30mg/g and 1/n = 0.2147.



[**Figure 11**: Freudlich isotherm of different concentrations]

CHAPTER 5

CONCLUSION AND RECOMMENDATION

The study is to produce low cost adsorbent from readily available material and abundant in surrounding to remove dissolved reactive red dye from aqueous solution by coconut coir and coconut coir carbon as well as to find the optimum condition for removal of reactive red by studying the effect of contact time, pH, initial concentration of the reactive red, and temperature on the reactive red adsorption process.

The estimated value for R^2 value is 0.9962 from the linear graph line for Remazol Red 3BS Reactive Dye. The value obtained is nearly the value from the standard value obtained from the previous experimentation.

The maximum adsorption of Remazol Red 3BS is at pH 3 and contact time of 3 to 4 hour. Removal of dyes was higher at the acidic pH range and the maximum adsorption at 5 to 7 hour.

The R^2 value for the Langmuir adsorption isotherm was 0.9191. The coefficient for Langmuir were a = 4.30mg/g and b = 01.89 L/mg. The R^2 value for the Freudlich adsorption isotherm was 0.8726. The coefficient for Freudlich were k_f = 4.30mg/g and 1/n = 0.2147

It is proven that activated carbon prepared from coconut coir was a suitable adsorbent for removal of reactive dyes from both synthetic and textile effluent. In batch studies, the adsorption increased with an increase of contact time and carbon dose and decreased with an increase in solute concentration.

CHAPTER 6

REFERENCES

Allen, S.J., Khadher, K.Y.H. and Bino, M. 1995. Oxidation of dyestuffs in wastewaters. *Journal of Chemical Technology and Biotechnology* 62, 111–117.

Attia, A.A., El-Hendawy, A.A., Khedr, S.A. and El-Nabarawy, Th. 2004.Textural properties and adsorption of dyes onto carbons derived from cotton stalks. *Adsorption Science and Technology* 22, 411–426.

Bousher, A., Shen, X. and Edyvean, R.G.J. 1997. Removal of coloured organic matter by adsorption onto low cost waste materials. *Water Research* 31, 2084–2092.

Demirbas, E., Kobya, M., Senturk, E. and Ozkan, T. 2004. Adsorption kinetics for the removal of chromium (VI) from aqueous solutions on the activated carbons prepared from agricultural wastes. *Water SA* 30, 533–539.

Frank, G., Frank, H. and Wilhelm, O. 1994. Ozonation—an important technique to comply with new German laws for textile wastewater treatment. *Water Science and Technology* 30, 255–263.

Garg, V.K., Gupta, R., Yadav, A.B. and Kumar, R. 2003. Dye removal from aqueous solution by adsorption on treated sawdust. *Bioresource Technology* 89, 121–124.

Hall, K.R., Eagleton, L.C., Acrivos, A. and Vermeulen, T. 1966. *Industrial and Engineering Chemistry Fundamentals* 5, 212–223.

Hutchins, R.A. 1974. New method simplifies design of activated carbon systems. *Chemical Engineering* 80, 133–138.

Kannan, N. and Meenakshisundaram, M. 2002. Adsorption of Congo Red on various activated carbons. A comparative study. *Water, Air, and Soil Pollution* 138, 289–305.

Kharaisheh, M.A.M., Al Degs, Y.S., Allen, S.T. and Ahmad, M.N. 2002. Elucidation on controlling steps of reactive dye adsorption on activated carbon. *Industrial and Engineering Chemistry Research* 41, 1651–1657.

Kim, T.Y., Baek, I.H., Jeoung, Y.D., and Park, S.C. 2003. Manufacturing activated carbon using various agricultural wastes. *Journal of Industrial and Engineering Chemistry* (Seoul, Republic of Korea) 9, 254–260.

Krishnamoorthy, V. and Rao, K.B. 1998. Nutritive status of coir pith of varying age and from different sources. *Coir News* 27, 17–19.

Lagergren, S. 1898. Zur theorie der sogenannten adsorption gelo¨ ster stoffe. Kungliga Svenska Vetenskapsakademiens. *Handlingar*, Band 24 (4), 1–39.

LazeaNidis, N.K., Darapantsios, T.D. and Geiogantas, D. 2003. Kinetic analysis for the removal of a reactive dye from aqueous solution onto hydrotalcite by adsorption. *Water Research* 37, 3023–3033.

McKay, G. and Bino, M.J. 1990. Fixed bed adsorption for the removal of pollutants from water. *Water Environment pollution* 66, 33–53.

Namasivayam, C. and Kadirvelu, K. 2001. Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste. *Bioresource Technology* 76, 63–69.

Namasivayam, C. and Kavitha, D. 2002. Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste. *Dyes and Pigments* 54, 47–48.

Namasivayam, C. and Kavitha, D. 2003. Adsorptive removal of 2-chlorophenol by low-cost coir pith carbon. *Journal of Hazardous Materials* 98, 257–274.

Netpradit, S., Thiravetyan, P. and Towprayoon, S. 2003. Evaluation of metal hydroxide sludge for reactive adsorption in a fixed-bed column system. *Water Research* 38, 71–78.

Perineau, F., Molinier, J. and Gaset, A. 1982. Adsorption of ionic dyes on charred plant material. *Journal of Chemical Technology and Biotechnology* 32, 749–758.

Pierce, J. 1994. Colour in textile effluents—the origins of the problem. *Journal of the Society of Dyers and Colourists* 110, 131–133.

Rengaraj, S., Arabindoo, B. and Murugesan, V. 1999. Preparation and characterisation of activated carbon from agricultural wastes. *Indian Journal of Chemical Technology* 6, 1–4.

Santhy, K. and Selvapathy, P. 2004. Removal of heavy metals from wastewater by adsorption on coir pith activated carbon. *Separation Science and Technology* 39, 3331–3351.

Santhy, K. and Selvapathy, P. 2005. Removal of reactive dyes from wastewater by adsorption on coir pith activated carbon. *Bioresource Technology*, in press, doi:10.1016/j.biortech.2005.05.016.

Trivedi, H.C., Patel, V.M. and Patel, R.D. 1973. Adsorption of Cellulose triacetate on calcium silicate. *European Polymer Journal* 9, 523–531.

Venkataraman, K. 1972. The Chemistry of Synthetic Dyes, Vol. 7.*Academic Press New York*

Walker, G.M. and Weatherly, L.R. 1997. Adsorption of acid dyes on to granular activated carbon in fixed beds. *Water Research* 8, 2093–2101.

Young, L. and Yu, J. 1997. Lignase-catalysed decolourisation. *Water Research* 31, 1187–1193.

Zhang, T., Walawender, W.P., Fan, L., Fan, M., Daugaard, D. and Brown, R.C. 2004. Preparation of activated carbon from forest and agricultural residues through CO2 activation. *Chemical Engineering Journal (Amsterdam, Netherlands)* 105, 53–59.

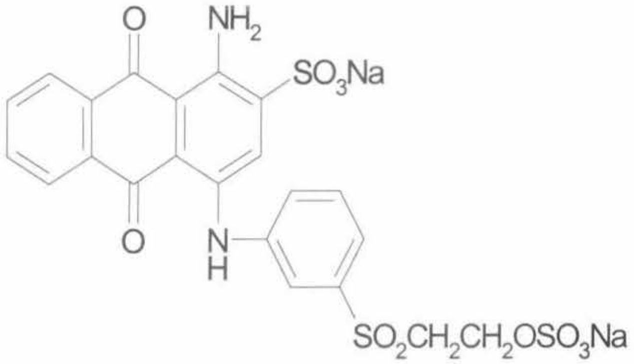
CHAPTER 7

APPENDICES

Reactive Blue Dyes-(KN-R 19#)

[Products name]: Reactive Blue KN-R
[Molecular Formula]: C22H16N2Na2O11S3
[Colour Index]: C.I. Reactive Blue 19
[Cas No]. 2580-78-1
[Molecular Weight]: 626.54
[Colour Index Number]: 61200
[Appearance]: Dark blue even Powder
[Strength]: 100%
[Shade]: To the similar standard of the factory
[Moisture%]: 1.0 Max
[Particle size(-60 mesh)%]: 89
[Solubility]: 300g/l
[Properties]: It is soluble in water and alcohol
[Use]: Dyeing and printing for Cotton Fabric

[Packages]:25KG Iron Drums, Cartons and Woven bags
[Storage & Transportation]: The product must be stored in shade, dry & well-ventilated warehouse. Avoid to be contacted with oxidizing chemicals and combustible organic substances. Keep it away from direct sunlight, heat, sparks and open flames. Carefully handle the product and avoid damaging the package.



[**Figure 12**: Reactive Blue Dyes KNR Formula]

Product Name Cibacron Brilliant Red 3B-A, Dye content 50 %

Product Number 228451

Product Brand Sigma-Aldrich

CAS Number 17681-50-4

Molecular Formula $C_{32}H_{24}ClN_8Na_4O_{14}S_4$

Molecular Weight 1000.25

TEST SPECIFICATION

APPEARANCE PURPLE TO MAROON POWDER

INFRARED SPECTRUM CONFORMS TO STRUCTURE AND STANDARD AS ILLUSTRATED ON PAGE 1005C OF EDITION I, VOLUME 2 OF "THE ALDRICH LIBRARY OF FT-IR SPECTRA".

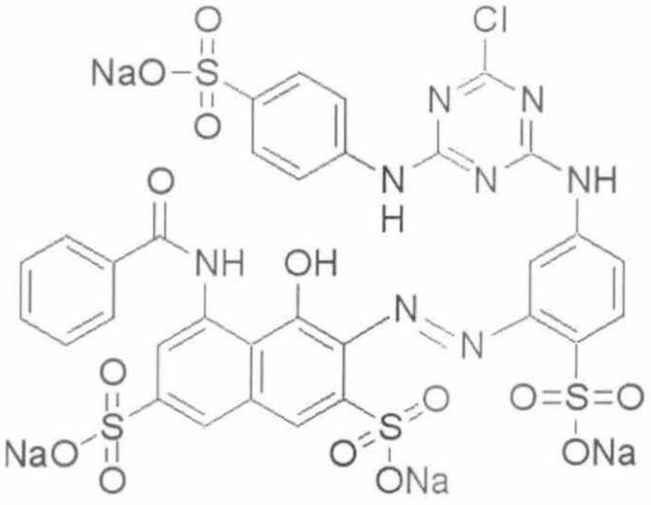
UV-VISIBLE SPECTRUM 0.01G/L, H2O E(517 +/- 3 NM) = >14,000 E(281 +/- 3 NM) = >37,000 E(227 +/- 3 NM) = >50,000

ELEMENTAL ANALYSIS CARBON 19.3% (MINIMUM) NITROGEN 5.6% (MINIMUM)

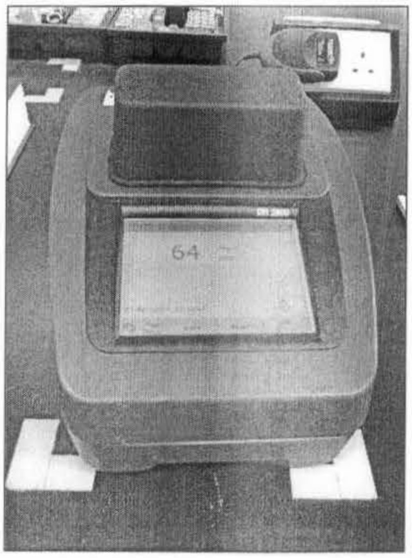
THIN-LAYER CONSISTENT WITH CONTROL

SOLUBILITY 1MG/ML H2O; CLEAR, PINK TO DARK RED SOLUTION

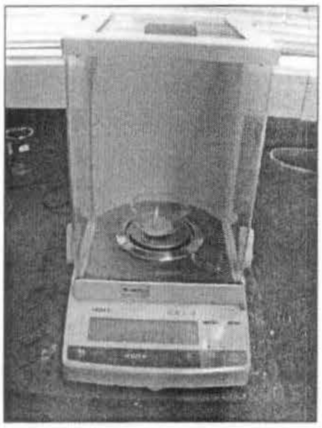
APPROVED OCTOBER 7, 1996 JSB



[**Figure 13**: Reactive Red Brilliant Red 3B-A, Dye content 50 %]

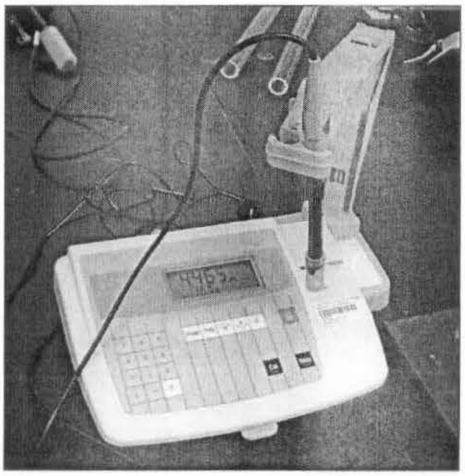


[**Figure 14**: HACH Spectrophotometer model DR 2800]



[**Figure 15**: Mettler Toledo model AB204-5 weighing machine]

[**Figure 16**: HACH 2100P Turbidimeter]



[**Figure 17**: Mettler Toledo model MP230 pH meter]