THE REMOVAL OF REACTIVE DYES FROM DYE LIQUOR USING ACTIVATED CARBON FOR THE REUSE OF SALT, WATER AND ENERGY

Report to the
WATER RESEARCH COMMISSION

by

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EXECUTIVE SUMMARY

Introduction

The aims of the project were to:

- establish the process parameters governing the recovery of water and chemicals for reuse from reactive dye baths using activated carbon.
- develop an economically viable process using activated carbon for recovering water and chemicals from reactive dyeing.

The deliverables were:

Deliverable 1 - A report outlining the mechanism of dye removal by activated carbon, the chemistry of reactive dyes and the effect of temperature and ionic strength on adsorption equilibria.

Deliverable 2 - A report detailing the design of the equipment, the experimental protocols, the calculation and reporting procedure and preliminary results.

Deliverable 3 - A report detailing the dyeing procedure to produce fabric samples within an acceptable shade tolerance.

Deliverable 4 - A report on the dye isotherms for a series of dyes (work in progress).

Deliverable 5 - A report on the dye isotherms for a series of dyes. The equipment and protocols for thermal reactivation will be described.

Deliverable 6 - A report on the effect of temperature for the short-listed dyes. Preliminary results on the reactivation of carbon will be reported.

Deliverable 7 - A report describing the results of the project (objectives, literature survey, experimental method, results, discussion, conclusions and recommendations).

Deliverable 8 - A final report incorporating the input from the Focus Group and technical advisors.

At the inaugural project meeting it was agreed that economic aspects would not be considered and that the project would focus only on the on technical aspects of dyeing and dye recovery. It was also agreed that the thermal regeneration of carbon by the textile industry would not be technically feasible so this aspect would not be considered.

Background

The textile industry is characterised by high water consumption and as one of the largest industrial producers of wastewaters. Textile effluents from cotton dyeing represent severe environmental problems as they contain highly coloured and high conductivity wastewater resulting from dye baths and dye rinse waters, which contain unfixed dyes. Reactive dyes are the major cause for complaint. Exhaust reactive dyeing requires high salt concentrations (up to 80 g/L of Na_2SO_4/NaCl). Reactive dye bath and first rinse represent 6 to 30 L effluent per kg of fabric and most of the colour and salt. The main challenges that textile industries face from dyeing of cellulose with reactive dyes is to reduce water consumption and high salinity coloured effluents.

The removal of colour from effluent after dyeing of cellulosic fibres is a major problem due to the difficulty in treating such effluents by conventional treatment methods. Cellulosic fibres of a specific shade (colour) are produced by reacting the fibres with a mixture of reactive dyestuffs, salt and auxiliary chemicals. Reactive dye exhaustion to the fibre is about 80%, i.e. 20% remains in the effluent; this is hydrolysed dye which cannot be reused for dyeing. The exhausted reactive dye bath together with first rinse represents 6 to 30 L effluent/kg of fabric and most of the colour and salt. The total water consumption for reactive dyeing ranges from 25 to 100 L effluent/kg fabric while the water consumption from total textile finishing ranges from 30 to 150 L effluent/kg fabric. Thus the concentration of the dye and salts are 5 times more concentrated when obtained at source.

There have been a large number of studies describing the use of activated carbon for the removal of colour from textile effluents but these studies have been unsuccessful for a number of reasons:

- the studies focused on the combined dye house or factory effluent. The dye concentrations are low, and the volumes are large. This resulted in low driving forces and large carbon inventories.
- the salt concentrations were low. Dyeing with reactive dyes requires a high electrolyte concentration (up to 80 g/L) in order to force the dye equilibrium towards the fabric. This will improve the driving force of the dye onto the carbon. Treatment of the dilute dye house effluent reduces the *salting out effect.*
- modern reactive dyes have bifunctional or more bonding groups and thus have a much higher affinity for the fabric, thus there is less residual dye in the dye effluent, hence the mass of carbon required per mass of textiles is reduced.

The proposed activated carbon process will be *close-coupled* to the dye machine and will treat the hot dye liquor. The dye will be removed and the hot water containing the electrolyte will be recycled directly to the dye bath for the subsequent dyeing.

The most important parameter is the amount of carbon to treat the exhausted dye bath for each type of dye chemistry for a fixed shade. The feed concentration to the activated carbon column is the exhausted dye bath from each shade.

Dye Chemistry

A literature review (**Chapter 2**) on the reactive dyes (unique pure molecules) and dyestuffs (commercial preparations containing a complex mixture of synthesis chemicals, dyes, by-products, additives and diluents, etc.) describes the progress in commercially available dyestuffs and the technical and environmental advantages in using newer classes of dyestuffs. The chapter also contains background information on the properties, use and theory of activated carbon for the treatment of reactive dye bath effluents.

Dye Selection

The selection of dyestuffs (**Chapter 3**) was based on the results from a previous WRC project (*WRC project K5/1363: The promotion of biodegradable chemicals in the textile industry using the score system: Phase 1 – pilot study*). Representatives of those dyestuffs that produced low environmental impact were selected. The range of shades selected corresponded to shades that were of interest to the fashion industry in South Africa in that they were selected from the colour pallet of a local commission dyehouse which specialised in the dyeing of reactive dyes. Four shades (requiring a combination of up to three different dyestuffs with different chemistries) were selected for the investigation.

Table 1: Selected Dyestuffs

Shade	Class	Chemistry	Supplier	Dyestuffs		
Navy*	Drimarene HF	trifluoropymidine	Clariant	navy	red	yellow
Black**	Cibacron S	not available	Ciba	black-R	black-G	
Beige*	Procion HE	monochlorotriazine	Dystar	yellow H-E4R	red H-E7B	blue H-ERD
Turquoise	Remazol L	vinylsulphone	Dystar	brilliant yellow 3GL	turquoise blue G	Levafix blue CA

Laboratory Dyeings

Laboratory dyeings (**Chapter 3**) were conducted at a local dye house using the industrial equipment and procedures which are used to determine the recipes and conditions necessary for the full-scale production. The effluent from the different washing, soaping and rinsing stages were analysed to determine the colour loads from these stages (Figures 1 to 4).

Dye exhaustion to the fabric for Navy (trifloropyrimidine chemistry), Black (chemistry not divulged), Beige (monochlorotriazine chemistry) and Turquoise (vinylsulphone) shades was about 79%, 78%, 81% and 79% respectively. Therefore, 19% up to 22% of the dye used is discharged in the effluent resulting in high colour effluent from reactive dyeing operations.

High dye concentration liquor with all the salt used was obtained in the dye bath effluent. Treatment of dye bath with reverse osmosis would not be possible because of the high salt concentrations.

Moderate dye and low salt concentrations were found in the first rinse effluent. Thus treatment of the first rinse effluent with membrane filtration may be possible.

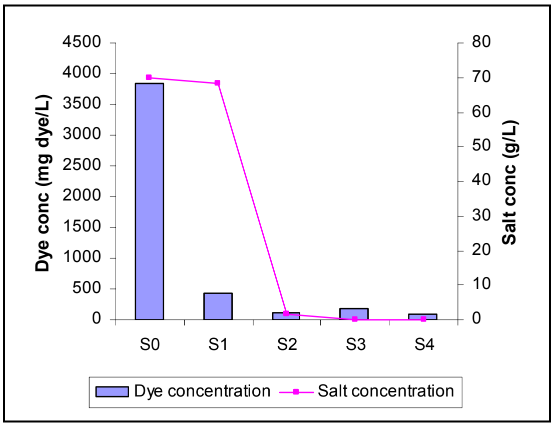

Figure 1: Dye and salt concentrations before and after dyeing of Navy shade. S0-unexhausted dye bath, S1-exhausted dye bath, S2-warm water rinse, S3-cold neutralisation, S4-hot soaping

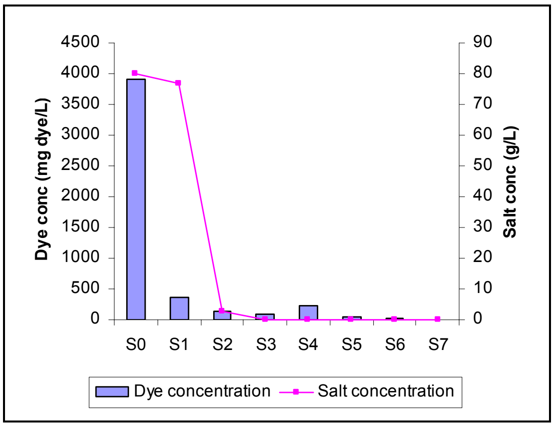

Figure 2: Dye and salt concentrations before and after dyeing of Black shade. S0-unexhausted dye bath, S1-exhausted dye bath, S2-warm water rinse, S3-cold neutralisation, S4-hot soaping and S5-hot water rinse, S6-warm water rinse and S7-cold water rinse

Effluent with high dye concentrations and no salt were measured in the soaping process and traces of dye concentration with no salt were obtained in the neutralisation, second and final rinse effluents.

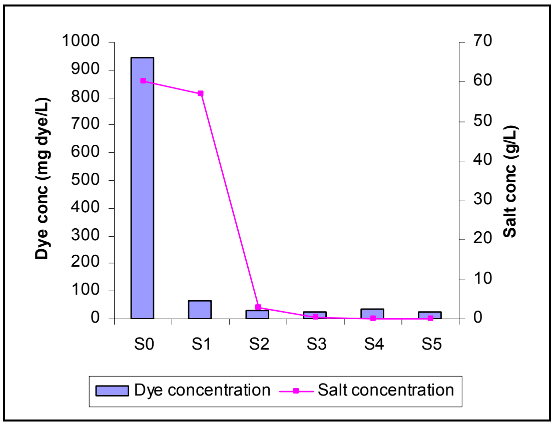

Figure 3: Dye and salt concentrations before and after dyeing of Beige shade. S0-unexhausted dye bath, S1-exhausted dye bath, S2-hot water rinse, S3-cold water rinse, S4-hot soaping and S5-cold water rinse

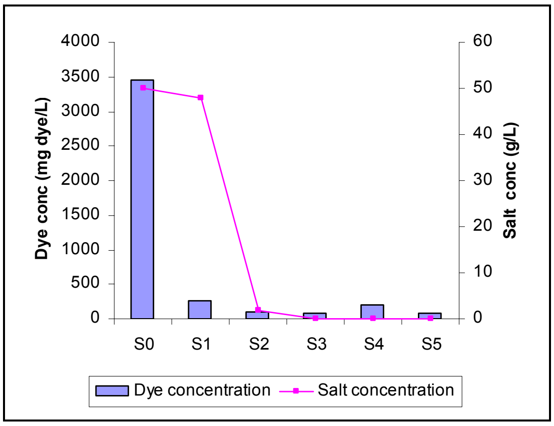

Figure 4: Dye and salt concentrations before and after dyeing of Turquoise shade. S0-unexhausted dye bath, S1-exhausted dye bath, S2-cold water rinse, S3-cold neutralisation, S4-hot soaping and S5-cold water rinse

Mass balance estimates (Figure-1) show that the removal of colour for the studied reactive dye shades from the exhausted dye bath is necessary. Water recovery ranging from 14 to 25%, salt recovery of about 94 to 97% and energy savings of 17 to 32% could be achieved.

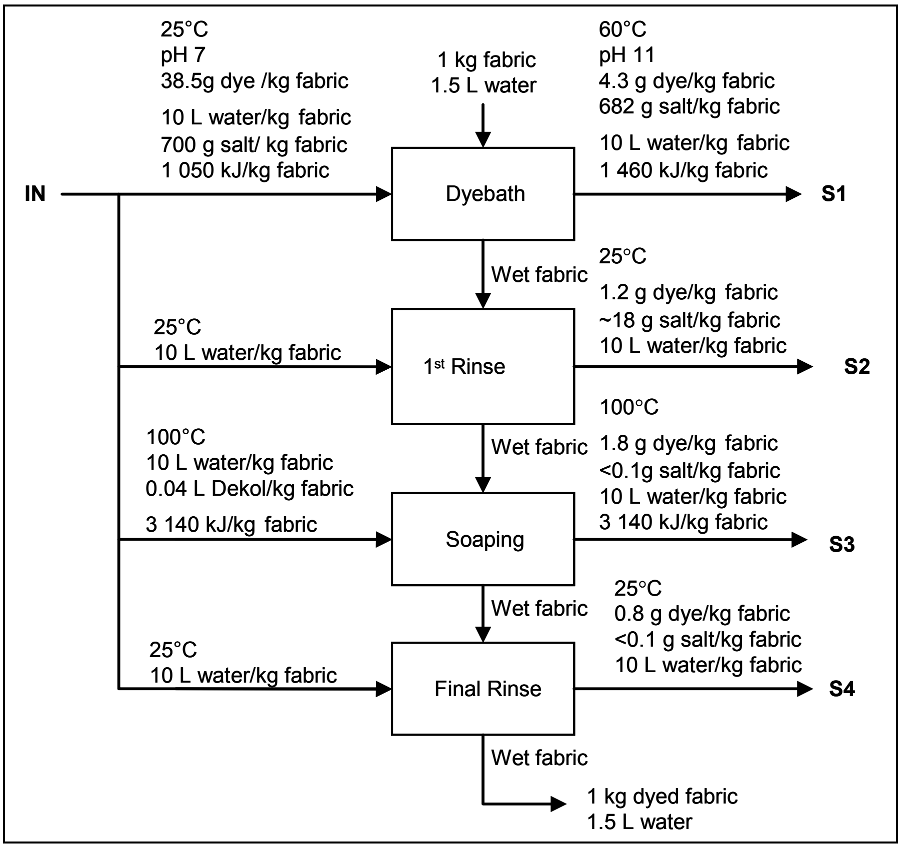

Figure 5: Flow diagram and mass balance for dyeing of Navy shade

These results can be used to predict of the amount of dye and salt remaining in the dye bath effluent before adsorption studies are undertaken.

Carbon Equilibrium Tests

Batch equilibrium tests (**Chapter 4**) were undertaken using high temperature equipment developed at the South African Sugar Milling Research Institute (Durban) in order to determine the degree of adsorption of different reactive dye chemistries onto powdered activated carbon. The tests were undertaken for different temperatures, pH values and salt concentrations. The influence of temperature at constant recipe pH and salt concentration for the four different shades on activated carbon adsorption was examined. It was observed that:

- the mass of dye adsorbed increased as the temperature increases. The adsorption capacity [(mg dye/g carbon) / (mg dye/L)] from 20 to 100˚C ranged from 61.54 to 78.16 for Navy shade; 55.99 to 72.02 for Black shade; 2.096 to 3.873 for Beige shade and 33.13 to 53.18 for Turquoise shade.
- the mass of dye adsorbed increased slightly as the pH decreases from pH 11 to 4. The adsorption capacity (pH 4 to pH 11) [(mg dye/g carbon) / (mg dye/L)] decreased from 84.83 to 78.16 for Navy shade; 84.53 to 72.02 for Black shade; 3.950 to 3.873 for Beige shade and 64.79 to 53.18 for Turquoise shade.
- the mass of dye adsorbed increased as the electrolyte concentration increases. The increase in adsorption capacity [(mg dye/g carbon) / (mg dye/L)] ranged from 61.85 to 98.20 for Navy shade; 57.94 to 89.04 for Black shade; 3.129 to 5.061 for Beige shade and 39.93 to 60.74 for Turquoise shade.

A high amount of dye uptake by powdered activated carbon was observed at high temperature, high electrolyte concentration and low pH values. These conditions favour the use of removing unreacted dyes from the exhausted dye bath after neutralisation (which is a necessary step prior to reuse).

Column Tests

Laboratory-scale column break-through tests (**Chapter 5**) were undertaken in order to evaluate the kinetics of dye uptake. The criterion for breakthrough was the amount of residual colour that would be just acceptable for reuse using a similar shade to the test shade.

Adsorptive capacities ranging from 20 to 39 mg dye per gram carbon were observed for 60˚C (highest temperature for this column study) for all the shades evaluated. For low temperature (20˚C), the adsorptive capacity ranged from 2 to 16 mg dye per gram carbon.

The dye volumes for 95% exhaustion ranged from 81 to 89 bed volumes for high temperature (60˚C) while for low temperature (20˚C) was 85 to 102 bed volumes.

A decrease in flow rate increases the adsorption capacity of the column. The carbon capacity at low flow rate ranged from 20 to 37 mg dye per gram carbon while at high flow rate ranged from 15 to 20 mg dye per gram carbon.

Regeneration

The carbon was regenerated using 1 M NaOH as the eluent (**Chapter 6**). The influent was allowed to percolate through the saturated carbon bed of 70.6 mL at a flow rate of 0.625 mL/min. From these results it was assumed that 3 bed volumes of 1 M NaOH would be sufficient. At least three cycles of regeneration were carried out within the standard limit for reuse. Significant deterioration of the carbon was observed at the fourth cycle. A small decline in GAC adsorption capacity was observed from the first to the third regeneration cycles. The role of dye auxiliaries on the activated carbon were not evaluated in the study and it is possible that they could have major effects that are detrimental on the performance of activated carbon.

The effectiveness of chemical regeneration of saturated carbon using NaOH was not satisfactory in terms of industrial application because of the number of cycles achieved. The results obtained showed that the use NaOH compared to other chemical regenerants need to be investigated for the implementation of activated carbon for removal of reactive dyes.

Conclusions

In this study four different dye classes were investigated (Drimarene HF, Cibacron S, Procion HE and Remazol Levafix using four standard shades (Navy, Black, Beige and Turquoise). The reactive dyestuffs contained different functional groups (chemistries). Reactive dye exhaustion to the fibre for the four reactive dye classes was about 80%, i.e. 20% remains in the effluent. Reactive dyeing of the four studied shades resulted in salt concentrations over 90% and hot coloured water remaining in the dye bath effluent. The efficiency of the dyeing process for a specific shade is associated with various parameters such as substantivity and diffusion rate of dyes, hardness of water, pH and temperature of the dye liquor, type and concentration of reactive dye used. The use of granular activated carbon for the adsorption of reactive dyes has been examined and results obtained indicated that activated carbon could effectively remove colour from exhausted reactive dye bath effluent and allow re-use of hot decolourised water with high concentration of salt.

From the adsorption results obtained using activated carbon, it was concluded that the most important factor influencing the adsorption rate and capacity for the reactive dye shades studied is the adsorption temperature. Textile processes require hot water for reactive dyeing of cotton. There is great potential in the textile industry for hot water recovery. The use of heat exchangers to transfer heat to the incoming dyeing feed water can be eliminated when using granular activated carbon columns. The pH values and electrolyte concentration also played a vital role in the whole adsorption process and particularly in adsorption capacity. Colour removal of 100%, salt recovery of 94 to 97% and energy savings 17 to 32% in the dye bath effluent were achieved. Reactive dyeing of cotton is performed at high temperatures and in this study the results were discussed based on 60˚C, which was the common temperature used for dyeing for all four shades selected.

The colour breakthrough from column breakthrough curves for 60˚C occurred at 14, 21, 45 and 24 bed volumes for Navy, Black, Beige and Turquoise shades respectively. The exhaustion or saturation volumes for the granular activated carbon were at 24, 41, 45 and 35 bed volumes for Navy, Black, Beige and Turquoise shades respectively. The variation in the slope of the breakthrough curve may be explained on the basis of mass transfer fundamentals of adsorption capacity of granular activated carbon. Increase in flowrate caused an increase in zone speed, resulting in decrease in the volume required to achieve breakthrough, while a decrease in flowrate resulted in an increased breakthrough volume. This was due to decreased contact time between the dye and carbon at higher flow rates.

From the column test results shown, the values of carbon capacity per kilogram of fabric obtained from the column test were much lower than those of the adsorption equilibrium test. The reason is that more of the adsorption sites are exposed in powdered activated carbon than in the granular activated carbon. The Freundlich isotherms measured in the adsorption equilibrium experiments do not apply to the column tests, perhaps due to that the equilibrium is not reached in column tests. One of the advantages of using granular activated carbon in the column test is the possibility of regeneration. From studies presented in the literature; it was shown that the required water quality for textile process is not stated. The textile industries are using drinking water quality for dyeing, therefore the 75 ADMI could be used as the standard limit when treating water for reactive dyeing reuse. Dyeing of the same shades or dyeing of a darker shade with treated light shade effluent would not need drinking water quality.

The regenerated carbon for this study was found to be effective up to 3 cycles of operation within the acceptable limit for reuse. Significant deterioration of the carbon was observed at the fourth cycle. The poor performance could be associated with role of dye auxiliaries in the overall adsorption process because of their unknown composition and chemistry (this was not divulged by the manufacturer for confidentiality). This led to the activated carbon not economically feasible for industrial application. Fewer bed volumes were treated when using regenerated carbon compared to virgin carbon. The possibility of savings exists when using regenerated GAC for treatment. Regeneration should also ensure that the eluted solution is not posing any disposal problems in terms of high acidity and high colour concentration. A further investigation of thermal regeneration of the spent granular activated carbon for the removal of reactive dyes is needed to determine its advantages and disadvantages over chemical regeneration. The design, operation and maintenance of carbon adsorption and regeneration processes depend on costs and characteristics of textile water to be treated and the capacity of the plant. Therefore the designer is responsible for selecting a system that will meet the discharge permit requirements at the lowest cost possible. Once the optimum flowrate, bed depth and operating capacity of granular activated is determined, the carbon contactors configurations can be estimated. The use of rapid small-scale column test method for designing in this study has the major potential advantage over other methods in predicting the performance of pilot-scale.

Recommendations

Further research in this area should concentrate on evaluating different activated carbons and role of auxiliaries in activated carbon adsorption studies. When implementing the laboratory-scale plant in textile industry, the effect change in temperature, pH and electrolyte concentration should be noted and the chemical parameters should also be researched. The first rinse stream has a moderate colour with low salt concentration effluent. If further colour removal is required, this stream could be treated by reverse osmosis. The permeate can be used for the first rinse and the concentrate can join dye bath effluent. The further investigation should also be expanded to the evaluation of other chemical regenerants and thermal regeneration of saturated activated carbon. The use of granular activated carbon adsorption and the regeneration of granular activated carbon should also be taken into account for water, salt and energy savings for the textile industry. This study proved that the activated carbon adsorption technique is the solution in reactive dyeing textile industries because of the possibility for re-use of water, salt and energy; thus enabling environmental improvements with savings in salt, energy and water.

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The chairman and members of the Reference Group:

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Mr C Fennemore : eThekwini Municipality
Mrs Claudia Botha : eThekwini Municipality
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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES (appearing on enclosed CD)

LIST OF SYMBOLS

α	Langmuir constant related to the area occupied by a monolayer of adsorbate
A_L	Pilot-scale column surface area
A_S	Small-scale column surface area
b	Langmuir direct measure for the intensity of adsorption
C	Dye residual concentration for the equilibrium tests [mg dye/L]
C_0	Initial dye feed concentration – column test
C_t	Residual dye concentration in the effluent – column test
d_L	Pilot-scale column carbon particle diameter
d_S	Small-scale column carbon particle diameter
ε	Carbon bed void fraction
EBCT_L	Pilot-scale empty bed contact time
EBCT_S	Small-scale empty bed contact time
ID_L	Pilot-scale column internal diameter
ID_S	Small-scale column internal diameter
L_S	Small-scale column length
M	Mass of carbon
M_{CL}	Pilot-scale mass of carbon
M_{CS}	Small-scale mass of carbon
pb	Carbon particle density
Q_L	Pilot-scale flow rate
Q_S	Small-scale flow rate
Re_L	Pilot-scale Reynold’s number
Re_S	Small-scale Reynold’s number

tb_L	Pilot-scale time for break through
tb_S	Small-scale time for break through
v	Water viscosity
V	Volume of dye solution - column test
V_{bL}	Pilot-scale volume of carbon bed
V_{bS}	Small-scale volume of carbon bed
V_L	Pilot-scale hydraulic loading rate
V_0	Volume of carbon bed – column test
V_{0L}	Pilot-scale feed volume
V_S	Small-scale hydraulic loading rate
V_L	Pilot-scale hydraulic loading rate
X	Amount of dye adsorbed [mg]

GLOSSARY

Activated carbon	A carbon material produced by roasting of cellulose base substances, such as wood, coal or coconut shell to promote active sites that yield a porous structure, creating a very large internal surface area, which can adsorb pollutants.
Adsorbate	A substance that becomes adsorbed at the interface or into the interfacial layer of another material, or adsorbent.
Adsorbent	The substrate material onto which a substance is adsorbed
Adsorption	The adhesion of the molecules of dissolved substances, or liquids known as adsorbate in more or less concentrated form, to the surface of solids or liquids known as adsorbent with which they are in contact.
Anchor	Reactive group that form a covalent bond with the textile material
Anthraquinone dye	Dye based on the structure of 9, 10-anthraquinone, with powerful electron donor groups in one or more of the four alpha positions.
Azo dye	Dye which contain a least one azo group (-N=N-), and can contain up to four azo bonds.
Cellulose	A complex carbohydrate that is composed of glucose units, forms the main constituent of the cell wall in most plants, and is important in the manufacture of numerous products, such as paper, textiles, pharmaceuticals, and explosives.
Chromogen	A compound not itself a dye but containing a chromophore and so capable of becoming a dye.
Chromophore	The chemical group that gives colour to a molecule
Dye	A colouring substance used to colour cloth, paper etc.
Electrophile	A chemical species (an ion or a molecule) which is strongly attracted to a region of negative charge and tends to attract or accept electrons.
Exhaust	To use up all the colour potential of a dyebath
Fibre	A fine thread used to make textiles, which is flexible and fine. A general name for the raw material, such as cotton, flax, hemp, etc., used in textile manufactures.
Hue	Quality of a colour as determined by its dominant wavelength.
Nucleophile	A chemical species (an ion or a molecule) which is strongly attracted to a region of positive charge and tends to donate or share electrons.
Nucleophilic addition	Addition of a nucleophile to a chemical compound
Nucleophilic substitution	Substitution of a halogen by a nucleophile in a chemical compound
Reactivation	Restoration of the activated carbon to a state where it is virtually identical to the properties of the virgin pre-cursor
Reactive dye	A dye which is capable of reacting chemically with a substrate to form a covalent dye-substrate bond.
Substantivity	The attraction between a substrate and a dye or other substance under the precise conditions of test whereby the latter is selectively extracted from the application medium by the substrate.

1 INTRODUCTION

Water resources management has become an important operational and environmental issue especially in the context of South Africa as water is becoming incrementally scarce. Even though it appears to be in plentiful supply on the earth's surface, water is a rare and precious commodity, and only an infinitesimal part of the earth's water reserves (approx. 0.03%) constitutes the water resource, which is available for human activities (Allegre et al., 2004). South Africa is a semi-arid country. It is predicted that in future, increasing demands will be made on our dwindling water resources. It is therefore imperative that all water use sectors use water optimally and efficiently to ensure that the needs of both the environment and people are satisfied for now and future generations (DWAF, 1998). Due to the limited water resources in South Africa, it is important to encourage industries to implement water and effluent management strategies and reduce waste at source (Barclay and Buckley, 2002).

Increasingly stringent environmental legislation and generally enhanced intensity, efficiency and diversity of treatment technologies have made the reuse of water more viable in many industrial processes. Wastewater reclamation and reuse are effective tools for sustainable industrial development programmes. The use and re-use of industrial wastewater is a common activity throughout the industrial sector in South Africa today. The reality is that discharge of wastewater through the municipal sewer system is costly to industries, which must pay the relevant municipal authority to receive and treat this wastewater. Alternatively, for industries who wish to discharge directly into water resource they are required to treat the wastewater to acceptable standards in terms of the water use authorisation issued. The treatment costs of crude water supplies, and wastewater disposal have increased the economic incentive for implementing water reuse and recycle processes in industry (Dvarioneine et al., 2003). Thus the way industries think about and use water is an important factor in determining the country's future.

1.1 Textile Industry

The textile industry is characterised by high water consumption and as one of the largest industrial producers of wastewaters. Textile effluents from cotton dyeing represent severe environmental problems as they contain highly coloured and high conductivity wastewater resulting from dye baths and dye rinse waters, which contain unfixed dyes (Faria et al., 2004). Reactive dyes are the major cause for complaint. Exhaust reactive dyeing requires high salt concentrations (up to 80 g/L of Na_2SO_4/NaCl). Reactive dye bath and first rinse represent 6 to 30 L effluent per kg of fabric and most of the colour and salt. The main challenges that textile industries face from dyeing of cellulose with reactive dyes is to reduce water consumption and high salinity coloured effluents. **Error! Reference source not found.** is a schematic representation of the main stages involved in the reactive dyeing of cotton. This section will describe the three different stages used in the colouration of fabric by reactive dyeing namely: preparation, dyeing and finishing.

The cotton contains a significant amount of contamination resulting from fertilizers, insecticides and fungicides. Preparation removes all the natural impurities from the cotton and chemical residues from previous processing. Natural impurities include waxes, oils, proteins, mineral matter, and residual seeds. All the impurities on the cotton must be removed before dyeing because they can interfere with dyeing process resulting in uneven dyeing, spotting and permanently damaging the cotton fibre. The processes involved in preparation are desizing, scouring and bleaching. The second stage in colouration of cotton is dyeing. Different reactive dye classes require specific dyeing procedures; however a common factor is that high volumes of water, auxiliaries, salt and alkali are required to produce a dyed cotton fabric. The total volume of water from the dyeing process is determined by a liquor ratio, which is the volume of dye solution required to dye a mass of fabric. The liquor ratio ranges from 30:1 L effluent/kg fabric in old equipment or short runs to 3:1 in ultramodern airflow equipment. A typical value for the liquor ratio is 10:1. Subsequent rinsing of the reactive dyed cotton fabric gives rise to large volumes of coloured effluent with high salts. The third stage is finishing, which improves the quality of the cotton fabric after dyeing (Hendrickx and Boardman, 1995). The water consumption resulting from the dyeing process from reactive dyeing ranges from 75 to 150 L effluent per kg of fabric.

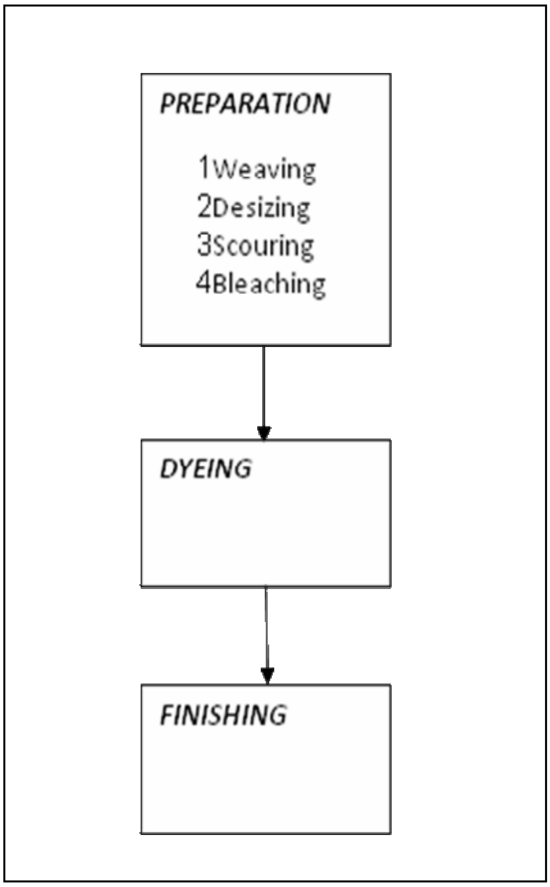


Figure 1-1 : Sequence for reactive dyeing of cotton

1.2 Textile Wastewater Treatment

The rapid development of textile industries has given rise to multiple environmental problems which led to the development of cleaner technologies and waste minimisation techniques. Sustainability assessment is the approach to evaluate the cleaner technologies and waste minimisation for waste discharges. The sustainability of any technology or technique is assessed from three points of view: economic, environmental and social impacts. Waste minimisation techniques can be grouped into four major categories: inventory management and improved operations, modification of equipment, production process changes, and recycling and reuse (Eckenfelder, 2000; Barclay and Buckley, 2002).

The main challenge that textile industries face from dyeing of cellulose with reactive dyes is to reduce water consumption and the highly saline coloured effluents. Coloured effluent disposed by textile industries into Sterkspruit River was observed in the Hammarsdale area of KwaZulu-Natal in the last decade. The inadequate treatment of Hammarsdale Wastewater Treatment Works resulted in poor quality final effluents, which have an adverse environmental impact on Sterkspruit River. The eThekwini municipality is encouraging the textile industries to be involved in waste minimisation and cleaner production technologies. The removal of colour from dyeing of cellulose effluent is a major problem due to the difficulty in treating such effluents by conventional treatment methods. Biological treatment, chemical precipitation, membrane technology, activated carbon adsorption and evaporation are the common wastewater treatment techniques of textile industry effluents (Wenzel et al., 1996). Removing colour from reactive dye bath for reuse by conventional processes such as chemical precipitation, evaporation and biological treatment have been ineffective because of the high salt content resulting from reactive dyeing. This is because only water can be reclaimed and not the salt and energy (Wenzel et al., 1996; Allegre et al., 2004). Membrane filtration techniques such as reverse osmosis can reclaim water, salt and energy (Dvarioniene et al., 2003) but high concentrations of salt used in reactive dyeing will increase osmotic pressure which reduces the net pressure driving force and permeate flow (Allegre et al., 2004).The salt and the residual dye still need to be separated.

Activated carbon adsorption is the one promising technique for recovery of water, salt and energy from exhausted dye bath. The advantage of using this stream is that the high salt concentration could shift the dye equilibrium towards the carbon resulting in very high removal efficiencies. It is hypothesised that dye removal using activated carbon will be more complete in the presence of high concentration of salt and the decolourised dye solution can be reused preventing the discharge of large masses of salts and water. Much work has been done on activated carbon for the treatment of combined dye effluent; however there has been very little work on the treatment of the reactive dye bath effluent using activated carbon. Furthermore the hot saline decolourised dye bath is suitable for direct reuse thus reducing the total dissolved solids load from the textile mill and allowing for direct energy reuse. Cleaner Textile Production Project funded by Danida supported Dyefin Textiles and Vivendi Water Treatment (equipment suppliers) in the pilot assessment of the system. The cost of the system is directly related to the capacity of the carbon for dyestuffs and the amount of unexhausted dye in the effluent. Continuous pilot-scale activated carbon trials on exhausted reactive dye bath effluent which were undertaken by Vivendi Plant on Dyefin Textile industry effluent concluded that Chemviron F-400 carbon could treat 68 L effluent per kg carbon, i.e. 147 g carbon/kg fabric and the performance of thermally regenerated carbon was similar to that of virgin carbon (Hoffman, 2004). Further tests were needed to quantify the effect of temperature, salt and pH on the adsorption characteristics. Investigation of new high performance dyes with greater exhaustion is allowing a trade-off between more expensive high performance dyes and the cost of activated carbon.

1.3 Project Outline

There are a large number of studies describing the use of activated carbon for the removal of colour from textile effluents but these studies have been unsuccessful for a number of reasons:

- The studies focused on the combined dye house or factory effluent. The dye concentrations are low, and the volumes are large. This resulted in low driving forces and large carbon inventories (Wenzel et al., 1996; Santhy and Selvapathy, 2006).
- The salt concentrations were low. Dyeing with reactive dyes requires a high electrolyte concentration (up to 80 g/L) in order to force the dye equilibrium towards the fabric. This will improve the driving force of the dye onto the carbon Treatment of the dilute dye house effluent reduces the *salting out effect* (Wenzel et al., 1996).
- Modern reactive dyes have bifunctional or more bonding groups and thus have a much higher affinity for the fabric, thus there is less residual dye in the dye effluent hence the mass of carbon required per mass of textiles is reduced (Allegre et al., 2006).

- The proposed activated carbon process will be *close-coupled* to the dye machine and will treat the hot dye liquor. **Error! Reference source not found.**Figure 1-2 shows an overall sketch of activated carbon process close-coupled to the dye machine. The dye will be removed and the hot water containing the electrolyte will be recycled directly to the dye bath for the subsequent dyeing.

The most important parameter is the amount of carbon to treat the exhausted dye bath for each type of dye chemistry for a fixed shade. The feed concentration to the activated carbon column should be the exhausted dye bath from each shade.

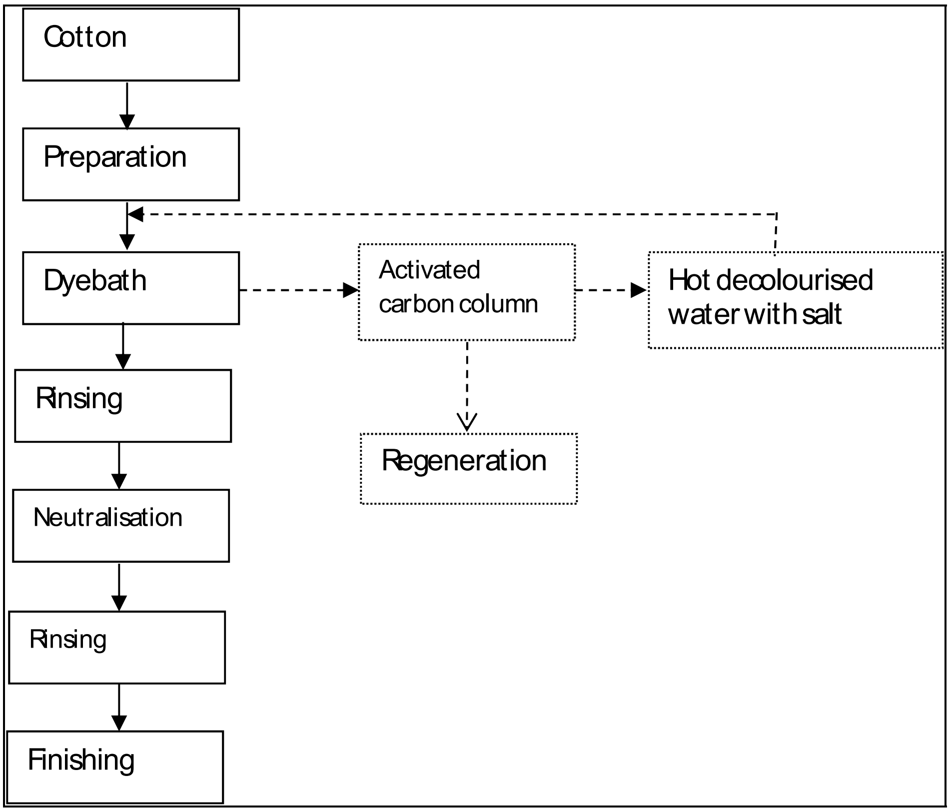


Figure 1-2 : Overall sketch of dye machine close coupled with proposed activated carbon process

The objective of this study is to establish the process parameters governing the recovery of water and chemicals for reuse from reactive dye baths using activated carbon and to investigate a process for recovering water and chemicals from reactive dyeing. The following approach was adopted to achieve these aims:

- The first phase of this project involved researching of the relevant literature on reactive dyes and activated carbon adsorption. The reactive dye chemistry and the factors that affect adsorption equilibrium were investigated.
- The experimental work on dyeing a range of shades using different dye chemistries being undertaken in terms of WRC Project K5/1363 - *The promotion of biodegradable chemicals in the textile industry using the score system: phase 1 - pilot study*, was of particular relevance to this project in selecting dye chemistries and dyestuffs to be evaluated. The four selected dye chemistries represent almost all reactive dye chemistries used in Dyefin textile factory. Four reactive dye classes of Drimarene HF, Cibacron S, Procion HE and Remazol L with different dye

chemistries were selected from the WRC Project K5/1363 to produce four different laboratory shades. Laboratory dyeing for four different shades (Navy, Black, Beige and Turquoise) with associated auxiliaries and salts were undertaken following a specific dye recipe for each of the shades. Each shade consisted of up to 3 dyestuffs. The Navy shade was made of three Drimarene HF reactive dyes, Black shade consisted of two Cibacron S reactive dyes, Beige shade made of three Procion HE reactive dyes and Turquoise shade consisted of two Remazol and one Levafix reactive dyes.

- The dye bath liquor from each of these laboratory dyeings was then tested against activated carbon. One grade of F-400 activated carbon from Chemviron was selected. Adsorption isotherm experiments were undertaken on the dye liquor bath. The effect of three different salt concentrations, three pH values and four different temperatures on the adsorption isotherm was determined for all four shades. Column tests were undertaken using the exhausted dye bath at three different temperatures to determine the kinetics of dye adsorption. The results would be used to determine the parameters for standard adsorption theory.
- Finally, the carbon was chemically regenerated at a laboratory scale under a range of conditions. Column experiments for the regenerated carbon were performed to determine the performance of the regenerated carbon. This procedure was repeated for a number of cycles to evaluate the regenerated carbon adsorption capacity. The results were used to assess the overall performance of the reuse system. The possible system for removal of colour for the reuse of salt, water and energy was designed. Table 1-1 shows the overall summary of the project.

Table 1-1 : Summary of the project outline

Class	**Drimarene HF**		**Cibacron S**		**Procion HE**		**Remazol L**			
***Shades**	**Navy**	**Black**	**Navy**	**Black**	**Navy**	**Beige**	**Navy**	**Black**	**Beige**	**Turquoise**
Selected shades	X			X		X				X
Dyeing	X			X		X				X
Isotherms	X			X		X				X
Column evaluation	X			X		X				X
Column Regeneration	X			X		X				X
System design	X			X		X				X

*Possible shades from Score study (WRC Project K5/1363)

1.4 Report Outline

The report begins with a literature survey on reactive dyes and activated carbon adsorption presented in **Chapter 2**. **Chapter 3** presents results on the reactive dyeing for all four shades. **Chapter 4** presents results on activated adsorption isotherms. In **Chapter 5**, the column results of the dye adsorption are explained and in **Chapter 6** the regeneration of activated carbon results are presented.

Chapter 7 explains the system design of the adsorption of dye by activated carbon. An overall conclusion of the results obtained and recommendations are presented in **Chapter 8**.

2 LITERATURE REVIEW

From **Chapter 1**, the main objective of this investigation is to establish the process parameters governing the recovery of water and chemicals for reuse from reactive dye baths using activated carbon. The textile industry plays an important role in our economy in increasing consumer interests by producing cotton fabric with value, comfort and styling using reactive dyes. At the same time large volumes of water are used for reactive dyeing and large quantities of coloured wastewater with high salt contents are generated. Treatment of textile effluent resulting from reactive dyeing is major problem facing textile industries today. The failure of most conventional treatment process resulted in the need to develop alternative treatment methods such as activated carbon adsorption. Activated carbon adsorption has been studied in more detail than the other treatment methods in this chapter. In this chapter the relevant literature on reactive dyes and activated carbon has been reviewed. Section 2.1 discusses an overview of reactive dyes while Section 2.2 discusses the activated carbon and its adsorption characteristics. Water quality for reuse and system design for activated carbon treatment is discussed in Section 2.3 and 2.4 respectively.

2.1 Reactive Dyes - an Overview

Reactive dyes gained popularity in the 20th century as dyes that give a permanent colouration to cellulosic textile substrates, and an important criterion was that the colour did not fade or discolour on laundering. Reactive dyes are dyes which have groups capable of forming bonds between a carbon or phosphorus atom of the dye ion or molecule and oxygen, nitrogen or sulphur atom of a hydroxyl, an amino or mercapto group respectively of the textile substrate. This section discusses the development of reactive dyes of cotton, their chemistry, chemical constitution, classes, reactivity, application and storage.

2.1.1 Development of reactive dyes

The most important distinguishing characteristics of reactive dyes are that they form covalent bonds with the substrate that is to be coloured during the application process. Thus, the dye molecule contains specific functional groups that can undergo addition or substitution reactions with the OH, SH and NH_2 groups present in textile fibres (Hunger, 2003).

The concept of immobilising a dye molecule by covalent bond formation with reactive groups in a fibre originated in the early 1900s (Broadbent, 2001). Cross and Bevan first succeeded in fixing dyes covalently onto cellulose fibres, but their multi-step process was too complicated for practical application. Early work by Schroter with sulfonyl chloride-based dyes was unsuccessful, but Gunther later did succeed in fixing derivatives of isatoic anhydride onto cellulose fibres. Haller and Heckendorn, and Heyna and Schumacher in the 1940s also contributed in the approach of modifying the fibres and introduced coloration (Hunger, 2003). In 1955, Rattee and Stephen, working for ICI in England, developed a procedure for dyeing cotton with fibre-reactive dyes containing dichlorotriazine groups. They established that dyeing cotton with these dyes under mild alkaline conditions resulted in a reactive chlorine atom on the triazine ring being substituted by an oxygen atom from the cellulose hydroxyl group (Broadbent, 2001).

The discovery of reactive dyes was an event of great technical and commercial importance. Not only did this class of dye function by the complete *new fixation* method of covalent bonding with the substrate, but it also offered the cotton dyer a desirable blend of properties such as high wet fastness, brilliance and variety of hue and versatility of application (Hunter and Renfrew, 1999).

2.1.2 Reactive dye chemistry

A dye is dissolved in the application medium, usually water, at some point during colouration. It will also usually exhibit some substantivity for the material being dyed and be absorbed from the aqueous solution (Hunger, 2003). The molecular structures of reactive dyes resemble those of acid and simple direct cotton dyes, but with an added reactive group. Reactive groups are of two main types:

- Those reacting with cellulose by nucleophilic substitution of a labile chlorine, fluorine, methyl sulphone or nicotinyl leaving group activated by an adjacent nitrogen atom in a hetero-cyclic ring (Broadbent, 2001). The reaction is called hetero-aromatic nucleophilic substitution (Hunter and Renfrew, 1999).
- Those reacting with cellulose by nucleophilic addition to a carbon-carbon double bond, usually activated by an adjacent electron-attracting sulphone group (Broadbent, 2001). Overwhelmingly, sulphonyl has emerged as the preferred activating group with α-halo-amido group playing a minor role. While vinyl sulphones are applied to all cellulosic and protein fibres, the α-haloacrylamido types are largely confined to the latter, especially wool (Hunter and Renfrew, 1999).

The dyes can also react with water and these reactions compete with one another. The reactive group must exhibit adequate reactivity towards cotton, but have lower reactivity towards water molecules which can deactivate the dye by hydrolysis. The hydrolysis of the reactive group of the dye is similar to its reaction with cellulose but involves a hydroxyl ion in water rather than a cellulosate ion in the fibre (Broadbent, 2001). All dyes are hydrolysed, the extent of which determines the efficiency of dyeing, and as a result 100% efficiency (or fixation) is never achieved. Commercial reactive dyes vary in molecular mass and complexity in that they contain one, two and/or three chromophoric units and up to three different reactive groups, which will be discussed in subsequent sections.

Chemical constitution of reactive dyes

In a dye molecule, a chromophore is combined with one or more functional groups, the so called anchors that can react with cotton. Under suitable conditions, covalent bonds are formed between dye and cotton fibre (Hunger, 2003). Reactive groups increase the molecular mass of a dye but do not enhance chromogenic strength (Hunter and Renfrew, 1999).

Monofunctional

Most mono-anchor dyes are derivatives of cyanuric chloride (2,4,6-trichloro-1,3,5-triazine), a molecule of wide synthetic potential because the three chlorine atoms on the triazine ring differ in their reactivity. The first chlorine atom exchanges with nucleophiles in water at 0 to 5°C, the second at 35 to 40°C and the third at 80 to 85°C (Hunger, 2003).

Bifunctional dyes

The concept of reactive dyes with two reactive groups was well established in the early years of reactive dyeing but at that time fixation efficiency was not a major issue and bifunctional dyes were the exception rather than the rule until textile industries observed that more that 50% of the monofunctional dyes could be lost to hydrolysis and discarded in the dye effluent (Hunter and Renfrew, 1999). Since the 1980s considerable interest has been shown in strongly fixing reactive dyes, and the required high fixation values have increasingly been achieved with the aid of double anchors (Hunger, 2003).

Double-anchor dyes can be divided into two categories: those containing two equivalent reactive groups called homo-bifunctional dyes (e.g. bis-β-sulphatoethylsulphone (CI Reactive Black 5)) and those with mixed-anchor systems called hetero-bifunctional dyes (e.g. CI Reactive Red 194). A homo-bifunctional reactive dye encompasses products containing two vinylsulfonyls or sulfoxyethylsulfonyl group, which increase the probability of reaction with the fibre. Introduction of homo-bifunctionality into cellulose reactive dyes is achieved by different molecular structures: mono azo bis-monochlorotriazinyl, dis azo bis-monochlorotriazinyl, non-azo-bis-monochlorotriazinyl, Procion H-EXL and bis-vinylsulphonyl reactive dyes (Hunger, 2003; Hunter and Renfrew, 1999).

In a mixed-anchor system the two reactive groups have different reactivities: a more reactive 2-sulfohydroxyethysulfonyl group and a less reactive monochlorotriazinyl residue (Hunger, 2003). Hetero-bifunctional reactive dyes , which have different optimal fixation towards cotton gives a more uniform degree of fixation over a wide range of dyeing temperature and fixation pH values than homo-bifunctional reactive dyes (Broadbent, 2001).

Multifunctional dyes

The introduction of more than two anchor groups has only a minor influence on dye fixation characteristics, so multiple-anchor dyes play only a subordinate role in world markets (Hunger, 2003), increasingly this has been an area of patent interest (Hunter and Renfrew, 1999). A number of tri-functional dyes containing bis-vinyl sulphone/monochlorotriazine and bis-vinyl sulphone/monofluorotriazine reactive groups have been disclosed by dye suppliers (e.g. Ciba, etc.). Four (tetra-functional dyes) and five (penta-functional dyes) independent reactive groups have been developed (Hunter and Renfrew, 1999).

2.1.3 Reactive dye classes

Virtually every conceivable chromophore has been used in the synthesis of reactive dyes.

Azo dyes

Most reactive dyes fall in the category of azo dyes. Virtually every hue in the dye spectrum can be achieved by appropriate structural modifications (mono- and di-azo dyes, combinations involving either single or multiple aromatic and heterocyclic ring systems) (Hunger, 2003).

Metal-Complex (formazan) dyes

Exceptionally lightfast colours are obtained with metal-complexed azo dyes. Copper complexes of disubstituted azo compounds produce a wide range of colours (yellow, ruby, violet, blue, brown, olive, black) (Hunger, 2003).

Anthraquinone dyes

Anthraquinone-based dyes are significant because of their brilliance, good light fastness and chromophore stability under both acidic and basic conditions. Recently, in the 21st century, they dominated the market for brilliant blue reactive dyes in spite of their relatively low colour strength and comparatively high cost. The shades of commercial reactive anthraquinone dyes range from violet to blue, e.g. *C.I. Reactive Blue* 19 (Hunger, 2003).

Triphenodiaxazine dyes

Dyes derived from triphenodioxazine ring system have been commercially available since 1928 when Kranzlein and co-workers discovered dyes with this basic structure augmented by sulfonic acid groups. The triphenodioxazine chromophore was tested in almost every class of dyes, but only recently has it been introduced into reactive dyes. Until the 21st century, anthraquinone dyes were predominant in most applications requiring brilliant blue dyes, but the much stronger triphenodioxazine dyes now represent a less expensive choice in many applications (Hunger, 2003).

Phthalocyanine dyes

The water-soluble reactive phthalocyanine dyes yield brilliant turquoise and green shades not available in any other dye category. The most important reactive phthalocyanine dyes contain copper or nickel as their central atom; they are substituted with sulfonic acid groups and also with reactive groups joined via sulphonamide bridges, e.g. *C.I. Reactive Blue* 15 (Hunger, 2003).

2.1.4 Reactive dye reactivity

The reactive groups of various types of reactive dye have different chemical structures and show a wide range of reactivity. Reactive dyes reactivity is classified into the following:

- Alkali-controllable dyes, which have high reactivity and only moderate substantivity. They are applied at low temperatures and level dyeing requires careful control of the addition of alkali to initiate the fixation stage, e.g. dichlorotriazine, difluorochloropyrimidine and vinylsulphone reactive dyes.
- Salt-controllable dyes. These dyes have low reactivity towards cellulose under alkaline conditions and therefore the dyeing temperature will be as high as 80°C. They have appreciable substantivity and level dyeing requires careful addition of electrolyte to promote exhaustion, e.g. trichloropyrimidine, monochlorotriazine and monofluorotriazine reactive dyes.
- Temperature-controllable dyes, which undergo fixation at high temperatures even under neutral conditions, e.g. nicotinyltriazine (Broadbent, 2001).

2.1.5 Basic principle of dyeing cotton with reactive dyes

The relatively simple procedure for batch dyeing of cotton materials with reactive dyes, developed by Rattee and Stephen (Broadbent, 2001), is still used for all types of reactive dyes irrespective of their particular reactive group. Dyeing is commenced in neutral solution, in the presence of electrolyte to promote exhaustion of the dye onto the cotton. During this period, the dye does not react with the fibre and migration from fibre to fibre is possible. An appropriate alkali is added gradually to the dye bath to increase the pH, this initiates the desired dye-fibre reaction. The hydroxyl groups in cellulose are weakly acidic and absorption of hydroxide ions causes some dissociation, forming cellulosate ions, which react with the dye by nucleophilic addition or substitution. In general, the lower the reactivity of the reactive group of the dye towards alkaline cellulose, the higher the final dyeing temperature and the higher the final pH of the dye bath (Broadbent, 2001; Hunger, 2003). After dyeing, any unreacted and hydrolysed dye present in the cotton must be removed by thorough washing to ensure no colour bleed from the cotton on subsequent washing during use (Broadbent, 2001).

2.1.6 Reactive dye application and storage

Reactive dyes are water soluble anionic electrophiles, which react to a greater or lesser degree with nucleophilic fibres during dyeing. Fixation to cellulose presents a number of special problems. Application disadvantages of reactive dyeing of cellulose include the following:

- Hydrolysis accompanies fixation, resulting in incomplete utilisation of dye
- Relatively large amounts of electrolyte are required for exhaust and pad steam applications
- Laborious removal of unreacted and hydrolysed dye is required- often a longer operation than the dyeing step itself and not always entirely satisfactory
- Hydrolysed dye is discharged as coloured effluent

- Colour is not easily removed by effluent treatment processes and in many cases the dyes are not readily biodegradable
- Unhydrolysed, unfixed haloheterocyclic reactive dyes may pose an environmental hazard (Hunter and Renfrew, 1999).

Because most reactive dyes are prone to hydrolysis, their handling and use requires care. Once a dye is prepared, it cannot be stored for later use without some risk of hydrolysis of the reactive group. This decreases its fixation ability and is a particular problem with the most reactive types of dye. Many commercial reactive dyes are dusty powders but all physical forms must be handled with care. These dyes react with the amino groups in proteins in the skin and on mucous surfaces. Inhalation of the dust is dangerous and a dust mask is obligatory during handling. Reactive dye powders and grains are sometimes hygroscopic and drums must be carefully re-sealed. Most reactive dyes have a limited storage period, after which some deterioration can be expected (Broadbent, 2001).

2.1.7 Colour measurement

The colour from dyeing can be expressed on a scale developed by the American Dye Manufacturers Institute (ADMI). This scale uses a spectral or a tristimulus method to calculate a single colour value that is independent of hue (dominant wavelength). Therefore if two colours, A and B, are judged visually to differ from colourless to the same degree, their ADMI colour values will be the same (Allen et al., 1973; Greenberg et al., 1995). It is a very sensitive scale. For example the ADMI value for tap water is ~75.

2.1.8 Treatment of reactive dyeing effluent

The importance of colour and salinity pollution control has been significantly increased since the introduction of reactive dyes. Environmentalists are concerned with the presence of colour from reactive dyeing due to their incomplete exhaustion and high salt concentration used in reactive dyeing. Failure of conventional treatment processes for removal of colour from reactive dye baths with high salt content resulted in alternative treatment processes. Among all treatment processes for textile wastewater, activated carbon adsorption seems to be promising in the removal of reactive dyes from reactive dye bath effluent with high salt content and is explained in more detail in section 2.2. In the subsequent sections the failure of common conventional processes is explained.

Biological treatment

Biological treatments reproduce artificially or otherwise, the phenomena of self-purification that exists in nature. As a result of the low biodegradability of most of the dyes and chemicals used in the textile industry, their biological treatment by activated sludge does not always meet with great success: in fact most of these dyes resist aerobic biological treatment. Coagulation-flocculation treatment is generally used to eliminate organic substances. The products normally used have no effect on the elimination of soluble dyestuffs, even though this process is widely used in some countries. It makes it possible to effectively eliminate insoluble dyes (Allegre et al., 2004).

Evaporation

Evaporation is technically feasible when the water contains highly water-soluble compounds with low vapour pressure. High salinity of the dye-bath has been a limiting factor in evaporation for the test equipment, due to the increase of boiling point and the capacity of the vacuum pump. However, costs for evaporation are much higher than for membrane filtration. For the dye-bath treatment, evaporation does not allow the salt content to be re-used, as the activated carbon adsorption does, thus making evaporation economically unfavourable. The evaporation technique reclaims water and leaves a residue of salt, dye-stuffs and chemical oxygen demand together (Wenzel et al., 1996).

Chemical precipitation

Removal of reactive dyes by precipitation with various precipitants has been shown to be possible by other researchers. Precipitation has been found to leave a certain amount of impurities from precipitants and dyestuffs and in some case surplus precipitants, in the water phase. This increased the need for fresh water renewal in case of re-circulation, or activates the need for a secondary treatment such as activated carbon (Wenzel et al., 1996).

Membrane technology

The use of membrane filters in the textile industry was one of the most promising technologies available for the purification of process water for reuse but high salt concentrations resulting from reactive dyeing have limited its use. Membrane technology has emerged as a reliable and applicable technology in the treatment of various industrial process effluent streams with low salt concentrations (Dvarioniene et al., 2003). Care is needed when using membranes to avoid membrane clogging or fouling, which appears to occur rapidly (Marmagne and Coste, 1996). The problem associated with using membranes is that the higher the concentration of salt, the more important the osmotic pressure becomes and; therefore the greater the energy required (Allegre et al., 2004).

2.2 Activated Carbon

Removal of colour from reactive dye bearing wastewaters is one of the major environmental problems because of difficulty in treating such wastewaters by conventional treatment methods, as most of the reactive dyes are resistant to biological degradation and oxidizing agents. This section discusses the activated carbon adsorption as a remedial technique, which offers great potential for the removal of colour from reactive dye wastewaters and producing quality effluent. The type of carbon tests (equilibrium, column and regeneration) that will be evaluated for this study will be briefly explained in this section with their advantages and disadvantages. The adsorption experiments are detailed in **Chapter 4** for equilibrium, **Chapter 5** for column and **Chapter 6** for regeneration.

2.2.1 Background

Water insoluble dyes (e.g. disperse and vat dyes) generally exhibit good exhaustion properties, i.e. most of the dyes bonds to the fibre and have been reported to be removed by physical means such as flocculation (Shaul et al., 1986; 1988). Since the introduction of water soluble (reactive dyes), which are used extensively by the textile industries, conventional biological treatment processes are no longer able to achieve adequate colour removal. The use of adsorption as an alternative technique for removal reactive dyes is as a result of the failure of conventional physicochemical coagulation/flocculation methods (Juang et al., 1996).

Adsorption on porous carbon was described as early as 1550 BC in an ancient Egyptian papyrus and later by Hippocrates and Pliny the Elder, as an adsorbent for medicinal purposes (Bansal et al., 1988; Allen et al., 1998). In the 19th century, powdered carbons made from blood, wood and animals were used for the purification of liquids. At the beginning of the 20th century, the use of bone char available as granular material was used for decolourisation in the sugar industry, where the liquid to be treated was continuously passed through a column (Hassler, 1974). Currently, activated carbons are produced commercially from precursor materials such as coconut shells, coal, peat, nutshells, wood and lignite by either chemical or physical activation or a combination of both of these methods (Bansal et al., 1988).

Activated carbons are unique and versatile adsorbents because of their extended surface area, microporous structure (Allen and Koumanova, 2005), high adsorption capacity, and high degree of surface reactivity. They are extensively used to purify, decolourise, deodorise, dechlorinate, and detoxify potable waters; for solvent recovery and air purification in inhabited spaces such as restaurants, food processing and chemical industries. According to Bansal et al.(1988), the characterisation of activated carbon is carried out on the basis of several physical and chemical properties, commonly including their total surface, pore size distribution, impact hardness and ability to adsorb selected substances.

During the 20th century, the first processes were developed to produce activated carbons with defined properties on an industrial scale. The use of activated carbons in an adsorption process is increasing towards recycling and waste minimisation, thereby reducing the use of the water resources.

2.2.2 Characterisation of activated carbon

The effectiveness of activated carbon as an adsorbent is attributed to its unique properties. A given type or sample of activated carbon is usually quantified based on four primary criteria: total carbon surface area, carbon density, particle size distribution and adsorptive capacity. Of course, all these factors influence the adsorption rate and capacity.

Total carbon surface area and carbon density

Total surface area is measured by the adsorption of nitrogen gas onto carbon and is expressed in area per mass of carbon. Because the gas molecules used to measure adsorption are small, it should be noted that this measurement of surface area may be misleading when considering the adsorptive capacity of a carbon for large organic macromolecules (Ford, 1981; Patrick, 1995). Typical samples of activated carbon possess a high surface area in the range from 500 to 1 400 m^2/g (Hassler, 1974) and a well defined microporous structure (average pore opening is about 1.5 nm) (Streat et al., 1995).

Particle size distribution

Particle size distribution is important in carbon systems as it influences the handling of the activated carbon material. For example, in granular activated carbon (GAC), the particle size affects the hydraulic loading, backwash rates for a filter and adsorption rates (Patrick, 1995). The particle size distribution of GAC is best obtained by sieve analysis, whereas for the analysis of powdered activated carbon (PAC) a Coulter Counter is a suitable device (Zolfl et al., 2000)

Adsorptive capacity

Adsorptive capacity is characterised by the effectiveness of activated carbon in removing a given contaminant. For example, the commonly used *iodine number* describes the capacity of carbon to adsorb low-molecular mass substances, while *molasses number* characterises a capacity of carbon for more complex compounds (Patrick, 1995) and *methylene blue numbers* represent the amount of large micropores and mesopores in the activated carbon (Clements, 2002).

2.2.3 Adsorption on activated carbon

Each activated carbon has a unique set of physical and chemical characteristics that are dependent on the type of raw material and the processing methods (physical, chemical or a combination) employed in its manufacture (Allen et al., 1998). Adsorption is defined as a process where the adsorbate is attached to the surface of the adsorbent. The kinetics of adsorption onto the activated carbon are controlled by the process of diffusion. The transfer of the impurities from the bulk solution to the internal surface of the carbon proceeds through three stages:

- Bulk diffusion of the compound from the liquid to the film around the carbon particle
- Diffusion through this surface film, this is usually the rate determining step
- Diffusion through the internal structure to the adsorption sites in the carbon (van Lier, 1989).

Molecules can bind to the surface by two types of binding forces namely, physical and chemical forces. *Physiosorption* or physical adsorption is the result of intermolecular van der Waals forces or hydrogen bonds of attraction between molecules of the solid and the substance adsorbed. The physical adsorption is relatively weak and the adsorbed particles are assumed to be free to move on the surface of the adsorbent. There is no significant redistribution of electron density in either the molecule or at the substrate surface (Kumar et al., 2004). *Chemisorption* or activated adsorption is associated with the transfer and sharing of electrons between adsorbate and adsorbent resulting in a chemisorptive bond, a chemical bond stronger than van der Waals forces (Suffet and McGuire, 1981; Hunger, 2003). The process is irreversible and on desorption the original substance will often be found to have undergone a chemical change. In general, the adsorbability of a compound on activated carbon increases with

- Increasing molecular mass
- A higher number of functional groups such as double bonds or halogen compounds
- Increasing polarisability of the molecule. This is related to electron clouds of the molecule.

Table 2-1 : Typical characteristics of adsorption processes on activated carbon (Kumar et al., 2004)

Characteristics	Physical Adsorption	Chemical Adsorption
Binding force	Due to physical force of attraction, thus this process is also called as Van der Waal's adsorption	Due to chemical forces or bonding, thus this process is also called as activated adsorption.
Saturation uptake	Multilayer phenomena	Single layer phenomena
Activation Energy	No activation energy involved	May be involved
Temperature Range (over which adsorption occurs)	Adsorption is appreciable at lower temperature below boiling point of adsorbate	Adsorption can take place even at higher temperature
Nature of adsorbate	Amount of adsorbate removed depends more on adsorbate than on adsorbent	Depends on both adsorbent and adsorbate
Heat of adsorption	1 kcal/mole	50 to 100 kcal/mole

2.2.4 Factors affecting adsorption capacity

One of the factors that influences adsorption on activated carbon is the adsorptive capacity of a given amount of carbon for a particular solute. Factors that can affect adsorptive capacity are as follows: surface area of activated carbon, pore size of carbon, solubility of solute in aqueous solution, pH and temperature.

Branch-chain organics are more easily adsorbed than straight-chain organics, while the type of attached functional group affects adsorption. Double- or triple-carbon bond (unsaturated) organics are adsorbed more easily than single-carbon bond (saturated) organics. These phenomena are attributed to the influence of the molecular structure on the polarity and/or solubility of the compound of interest. The aqueous solubility of a solute is inversely related to its adsorption onto carbon. Less soluble compounds are adsorbed more easily than more soluble compounds (Pope, 1998).

The porosity of activated carbon, which is classified by the size of the diameter of the pores, varies from micropores (2 nm), to mesopores (2 to 50 nm), to macropores (greater than 50 nm). During treatment, particles of the same size as the pores tend to get stuck and retained by the carbon. Volatile organic chemicals, metals, and some non-polar inorganic chemicals are captured and held strongly by the activated carbon (Hassler, 1974). Less polar (or weakly ionized) organics are more easily adsorbed than polar (or strongly ionized) organics.

Adsorption reactions are usually exothermic. High temperatures would seem to inhibit or slow down adsorption but this is not usually found to be a factor in most systems. An explanation for this may be revealed by considering the rate-limiting factor for adsorption. In carbon, adsorption is limited primarily by the diffusion of solute onto the carbon particle. Higher temperatures may impede adsorption at the adsorption site, but they significantly speed up the pace of diffusion, offsetting any negative temperature effect (Mattson and Harry, 1971).

2.2.5 Factors affecting adsorption rate

Adsorption rate is limited by diffusion; variables that influence diffusion have a significant effect on adsorption rate. High concentration gradient across the surface of the carbon particle will increase the rate of adsorption, though a high concentration of solute can eventually have a negative effect on adsorptive capacity. Larger molecules are generally more easily adsorbed than smaller molecules. However, when pore diffusion governs the adsorption process, the adsorption rate decreases with molecular mass above values specific to each type of carbon and within a given class of organics (Parker and Hughes, 1998).

According to van Lier (1989), the rate of adsorption depends on:

- The nature and relative concentrations of the substances to be removed.
- The presence of compounds which are not to be removed, but interfere with adsorption of a compound to be removed.
- The pH and temperature of the solution containing compounds.
- The carbon type used.

2.2.6 Adsorption isotherms

Adsorption is most generally described in terms of isotherms which show the relationship between the adsorbate concentration and the amount of adsorbate adsorbed at a constant temperature (Osipow, 1962). An adsorption isotherm gives the concentration of a substance adsorbed on a surface in relation to its concentration in the surrounding fluid when the system is at equilibrium at a constant temperature (Broadbent, 2001). A liquid phase isotherm shows distribution of impurities between adsorbed phase and bulk solution at equilibrium. There are many liquid phase isotherm for adsorption but in these study only two (Freundlich and Langmuir isotherms) will be explained.

Freundlich isotherm

Freundlich, a German physical chemist, presented an empirical adsorption isotherm for non-ideal sorption on heterogeneous surfaces as well as multilayer sorption. A Freundlich isotherm can be used to determine the effect of solubility on the adsorptive capacity of activated carbon over a range of different concentrations. Under standard conditions, the adsorptive capacity of activated carbon will increase as the concentration increases, until the maximum saturation capacity is reached (Kumar et al., 2004).

A Freundlich isotherm is commonly used to describe the adsorption characteristics of activated carbon in water and wastewater treatment. The empirical derived equation of a Freundlich adsorption isotherm for this work is defined as:

$$\frac{\mathrm{X}}{\mathrm{M}} = k_F \mathrm{C}^{1/n}$$

where X/M is the amount of dye adsorbed per gram of carbon (mg dye/g carbon), C is the residual concentration (mg dye/L) and k_F and n are Freundlich parameters (Jusoh et al., 2005).

The adsorption isotherm model can be expressed in the linear form as:

$$\log\left(\frac{\mathrm{X}}{\mathrm{M}}\right) = \log k_F + \left(\frac{1}{n}\right)\log\mathrm{C}$$

Plotting log (X/M) against log (C) should give rise to a straight line to indicate the validity of the Freundlich model. The n and k_F values are obtained from the slope and intercept respectively. The constant k_F, partition coefficient in equilibrium, is positively related to the degree of adsorption or adsorption capacity, while constant, n, provides estimation of the intensity or strength of adsorption (Albanis et al., 2000).

Langmuir isotherm

A theoretical model for monolayer adsorption, which involves the assumption that forces acting in adsorption are of a similar kind to those involved in chemical combination, was proposed by Langmuir in the 20th century (Mantell, 1951). The model was originally developed to represent chemisorption on a set of distinct localized adsorption sites. The basic assumptions on which the model is based are:

- Molecules are adsorbed at a fixed number of well-defined localised sites
- Each site can hold one adsorbate molecule
- All sites are energetically equivalent
- There is no interaction between molecules adsorbed on neighbouring sites

The Langmuir model has a limited success in predicting mixture equilibria (Ruthven, 1984). The Langmuir adsorption isotherm is defined as:

$$\frac{\mathrm{X}}{\mathrm{M}} = \frac{ab\mathrm{C}}{1 + a\mathrm{C}}$$

where (X/M) is the amount of dye adsorbed per gram of carbon (mg dye/g carbon), C is the residual concentration and a, b are Langmuir parameters.

the model can also be expressed as:

$$\frac{1}{\left(\frac{X}{M}\right)} = \frac{1}{abC} + \frac{1}{b}$$

Plotting 1/(X/M) against 1/C should give rise to a straight line for the validation of the model. The a and b parameter values are obtained from the slope and intercept respectively. The parameter, a, is a constant related to the area occupied by a monolayer of adsorbate reflecting the adsorption capacity and b is a direct measure for the intensity of adsorption process (Al-Sarawy et al., 2005).

2.2.7 Breakthrough behaviour of activated carbon

Interstitial mass transfer in fixed beds is important for designing many column adsorbers. The mass transfer zone (MTZ) is the part of the bed of activated carbon where adsorption occurs. It also known as the adsorption wave zone, because it moves through the carbon bed as the carbon becomes spent. As long as the flow rate, impurity composition and concentration remain constant, the length of the MTZ remains fixed as it moves through the carbon bed. During the adsorption cycle in a column, the upper section of the bed will be saturated with impurities while the lower section is still free of impurity. Between these two extremes lies a zone in which the adsorption is actually occurring. This zone is referred to as the MTZ. As the column becomes saturated, this adsorption zone moves downwards through the bed and can be regarded as an adsorption wave front moving through the column. Breakthrough occurs when the leading edge of the MTZ, where impurity concentration is lowest, moves beyond the end of the carbon bed column.

2.2.8 System design

The two dominant factors that control the breakthrough in GAC columns are the adsorption capacity and adsorption kinetics. Pilot columns use the same reliable predictors of breakthrough behaviour used in full-scale columns in terms of both capacity and rate of adsorption. The Langmuir or Freundlich models are used to fulfil the maximum adsorption capacity of the adsorbent for designing. The shape of the breakthrough curve may decide the number of columns to be used in the system and the service time of columns (Jamode et al. 2004).

However, this approach may require time consuming and expensive studies. Rapid methods to design GAC columns from small columns have been developed to reduce study time and cost. Examples of methods using small columns are the short fixed bed, mini-columns, higher pressure mini-columns, dynamic mini-column adsorption technique, accelerated column tests, small-scale column tests and rapid small-scale column tests (RSSCT) (Eckenfelder, 2000). The use of the RSSCT, which does not require the use of complicated models, will be briefly explained and was used in this study.

Rapid small-scale column test

Rapid small-scale column testing is an inexpensive, accelerated testing method that can be used to determine the adsorptive characteristics for a large scale, fixed bed columns using small column studies. The primary advantage of using RSSCT over pilot testing is the time savings. Other major advantages are cost savings, reduced water requirements and the fact that extensive isotherm and kinetic studies are not necessary. Mass transfer models can be used to determine dimensional parameters. These parameters are used to maintain similitude between small and large-scale columns. Subsequent to determining similitude, the RSSCT can be scaled up to aid in the design of full-scale treatment operation.

2.2.9 Activated carbon adsorption as a reclamation technique

Activated carbons are the most important commercial adsorbents. Their high surface area together with their surface chemical structure allows them to be used in a wide variety of industrial applications, some of the most important dealing with the environment field and particularly with water purification and industrial wastewater cleaning (Jankowska et al., 1981; Gonzalez-Serrano et al., 2004). Most forms of activated carbon are non-polar in nature; they have the greatest affinity for other non-polar substances.

Powdered activated carbon (PAC) and granular activated carbon (GAC) are the forms of activated carbon used in water and wastewater treatment. PAC is added to the actual wastewater stream to adsorb contaminants, then removed later from the stream and discarded. PAC was often used in the past because of its faster adsorption rate, but disposal costs and handling concerns have made GAC a more popular alternative for most applications. GAC is used in water treatment, and then regenerated when it becomes less effective due to saturation with chemicals. GAC is also usually much easier to handle and transport than PAC (Ford, 1981; Brady and McKay, 1996).

Benefits of activated carbon treatment (Ford, 1981; Wagner and Jula, 1981) are:

- Highly effective at removing non-polar organic chemicals from water
- Applicable to a wide variety of organic compounds
- Very effective at removing colours from waste streams
- Effective at removing low levels (ppb range) of metal pollutants
- Thermal regeneration of the carbon destroys the adsorbed waste solute
- Very flexible system allows rapid start-up and shut down as needed
- System can be designed so that it is portable to be taken to waste sites

Limitations of activated carbon treatment (Ford, 1981; Wagner and Jula, 1981):

- Limited to wastes with low organic concentrations (<5%)
- Limited to wastes with very low inorganic concentrations (<1%)
- Unable to remove highly soluble organics, or those with low molecular weights
- Systems cannot tolerate suspended solids in the influent stream (due to clogging)
- High operating costs due to carbon costs and system requirements
- Disposal of contaminated carbon can be problematic if it is not regenerated

Regeneration of granular activated carbon

Activated carbons that are used for the removal of organic compounds from liquid phase systems will gradually become saturated, due to the concentration of contaminants on the surface of the adsorbent. When this occurs a decision must be made on how to deal with the spent material (Clark and Lykins, 1989). Due to the high manufacturing costs and the recovery of components adsorbed on the surface of activated carbon, regeneration is the preferred option. The possibility of regeneration is one of the main reasons for the wide-spread use of activated carbon as an adsorbent (Zolfl et al., 2000).

Regarding the regeneration of activated carbon, a careful distinction between reactivation and regeneration is of importance. Volatile components or substances with lower energy can be removed fairly easily, whereas non-volatile compounds or substances adsorbed with high energy and so-called irreversible residues resulting from polycondensation and polymerisation product formation can hardly be desorbed. Reactivation restores the activated carbon to a state where it is virtually identical to the properties of the virgin pre-cursor. Regeneration combines both the adsorptive regeneration and reactivation. However, for simplification all methods will be referred as regeneration methods (Zolfl et al., 2000).

There are three potential regeneration techniques: chemical, steam and thermal. Both chemical and steam are used primarily in industrial systems designed to recover the adsorbate (Clark and Lykins, 1989).

Thermal regeneration

The thermal reactivation of activated carbon is usually carried out in a multiple hearth furnace. Thermal regeneration is made up of four stages: drying, desorption, pyrolysis and gasification. Drying occurs in the entry zone of the furnace as the carbon is heated from ambient temperature to 100°C. The thermal desorption followed by pyrolysis of organic adsorbate occurs as the temperature increases beyond the drying temperature. Gasification occurs between 649°C and 1 038°C (Clark and Lykins, 1989).

The three main parameters influencing the regeneration success are the temperature gradient within the furnace, the retention time and the level of exhaustion of the activated carbon. A further increase in temperature would lead to an unacceptable and expensive burn-out of activated carbon which causes enlargement of micropores. Further carbon loss (up to 15 percent mass) occurs as a result of attrition caused by inevitable removal of the carbon from the column into the furnace. Another disadvantage of thermal regeneration is that the adsorbed compounds, which may be useful, are destroyed (Zolfl et al., 2000). Thermal regeneration is the most widely used regeneration method despite its energy demand which result high costs (Alvarez et al., 2004; Ferro-Garcia et al., 1993).

Activated carbon is a valuable commodity which is capable of being recycled using thermal reactivation or regeneration techniques. This process offers significant advantages:

- Removal of expensive waste disposal costs.
- Reduction in operating costs as regenerated material is often less expensive than virgin adsorbent.
- The regeneration of activated carbon makes it the less polluted environmental option (Clark and Lykins, 1989).

Chemical regeneration

Chemical regeneration is based on the transformation of the adsorbed components into water soluble salts by adding diluted acids or bases. Although this method is unharmful to the activated carbon, both the used chemicals and the desorbed substances need to be reprocessed in order to reduce chemical waste and costs (Zolfl et al., 2000). Chemical regeneration can be carried out by desorption of the adsorbates using specific solvents or by decomposition using oxidizing chemical agents (Alvarez et al., 2004). Desorption can take place by a pH change which allow the adsorbate to change their ionic nature and thus be released from the carbon surface. The desorption process needs to be followed by a neutralisation and rinsing stages (Santhy and Selvapathy, 2006).

2.3 Water Quality for Reuse

The required water quality used for textile processes depends on where it will be reused. The textile industry uses water of drinking quality although some processes do not require water of this quality. The use of reclaimed water for textile processes has been studied by various researchers and in their studies they proved that the use of reclaimed water for textile dyeing processes was possible. A study performed by Harker in 1980 showed that there was no difference observed between fabric processed with drinking water quality and fabric prepared with reclaimed water. Another research study by Inoue and co-workers (1977) and Tworeck (1984) showed that there was a slight difference which was observed when dyeing a fabric with reclaimed water and these effects were considered significant and were fully acceptable to the textile mill investigated.

For this study the acceptable limit (AL) for reuse were selected on basis that the textile industries are using water of drinking quality for their dyeing processes, i.e. the ADMI value of 75. When dyeing a medium shades such as Turquoise and dark shades such as Navy and Black, reclaimed water need not be of drinking water quality. According to studies mentioned on the previous paragraph, dyeing using reclaimed water with a very low colour produced acceptable results to the textile mills. Dyeing of light shades such as Beige with reclaimed water from dark shade effluent has to be of acceptable limit (thus 75 ADMI). Table 2.2 shows the summary of the acceptable limit for reuse with corresponding dye removed in percentages and dye concentration used for this study

Table 2-2 : Acceptable limit (AL) for reuse for the studied shades

Shades	**Navy**	**Black**	**Beige**	**Turquoise**
FEED ADMI	17 650	19 010	345	10 100
AL (ADMI)	75	75	75	75
% dye rem	99	99	78	99
AL dye conc (mg dye/L)	3	3	41	5

2.4 System Design

The design of a GAC pilot-scale involves time-consuming and expensive studies. The use of Rapid Small Scale Column Test (RSSCT), based on fixed-bed mass transfer models, which does not require use of complicated models, was developed by Frick and Crittenden et al to solve this problem of time-consuming and expensive methods. The three primary advantages of using RSSCT for design are:

- The RSSCT can be conducted in less time that is required for pilot studies.
- Extensive isotherm or kinetic studies are not required for the performance prediction of the pilot-scale, unlike predictive mathematical models.
- A small volume of water is needed for the test (Crittenden et al., 1991).

2.4.1 Scale-up and similitude

Scale-up is based on similitude between small and large-scale columns considering equilibrium capacity, bed volumes treated, particle densities and solute concentration. Results from RSSCT can be scaled up to predict the performance of full-scale treatment systems. Similarity of operation between small and large-scale column is assured by properly selecting the particle size, hydraulic loading rate and empty bed contact time (EBCT) for the RSSCT. Perfect similarity is achieved if the large and small systems have equal surface diffusivities, isotherm capacities, bulk densities, operating temperature and influent concentration. Then, the RSSCT and the full-scale plant will have identical breakthrough profiles (Crittenden et al., 1986; Crittenden et al., 1991). If the adsorption process is controlled by multi- adsorbate competition, then particular care should be given in estimating the following design parameters.

GAC particle size:

Smaller GAC particle sizes increase the rate of adsorption. But if the particles become very small, such as powdered activated carbon (PAC), then they could not be used in fixed-bed applications.

Type of GAC:

GAC with an appropriate pore size distribution suitable for the removal of identified target compound should be selected. Pore size distribution of GAC can be controlled by the degree of activation and choice of base materials (e.g. bitumen, wood, coconut, etc.)

Empty bed contact time

The empty bed contact time of the RSSCT is determined from intraparticle mass transfer resistances. If the void fractions, bulk densities and the capacities are identical for the carbons used in RSSCT and pilot-scale processes, the proper scaling between the small and large column EBCTs can be determined from the following equation:

$$\frac{EBCT_S}{EBCT_L} = \left[\frac{d_S}{d_L}\right]^{2-X} = \frac{t_S}{t_L}$$

Where $EBCT_S$ and $EBCT_L$ are the EBCTs, d_S and d_L are GAC particle sizes and t_S and t_L are the corresponding operational times for the small and large columns respectively. The dependence of the intraparticle diffusion coefficient on particle size is defined by X. If the intraparticle diffusion coefficient do not change with particle size ($X = 0$), then the exact similarity between RSSCT and pilot-scale effluent profiles can be maintained. If the intraparticle diffusion is assumed to cause most of the spreading in the mass transfer zone then the intraparticle diffusivity is proportional to particle size ($X = 1$).Columns with larger EBCTs will yield larger specific volumes of water treated per unit mass of GAC. This is because the ratio of length of active mass transfer zone to the length of the column decreases with increasing column length (Crittenden *et al.*, 1991).

2.5 Closure

In this chapter, the relevant literature on reactive dyes has been reviewed, to highlight the different reactive dye chemistries, classes and the basic principle of the reactive dyeing process. Different treatment technologies for the removal of colour from exhausted reactive dye bath have also been highlighted and the emphasis was on activated carbon adsorption. The incapability of the existing conventional treatment processes resulted in activated carbon adsorption being the promising technology in the removal of colour from exhausted reactive dye bath. Reactive dyeing of cellulose, such as cotton in this case study is performed at high temperatures, high salt concentration and high volumes of water (from dyeing, rinsing, etc.) and this results in high colour and high salt concentrations in the effluent. This is the main challenge that the textile industries are concerned about. Reactive dyeing of cotton and the parameters involved in the activated carbon adsorption process of reactive dyes will be evaluated in the subsequent chapters. The evaluating parameter such as different temperatures, pH values, salt concentrations in the removal of colour were necessary for recovery of water, salt and energy from reactive dye bath.

3 REACTIVE DYEING

As described in **Chapter 1**, reactive dyes will always have a significant place in textile dyeing because of their high colour fastness and the wide spectrum they possess. In the last decade the consumption of reactive dyes has been 4 to 5 times more than other dye groups. Cellulosic fibres such as cotton of a specific shade (colour) are produced by reacting the fibres with a mixture of reactive dyestuffs, salt and auxiliary chemicals. The reactive dyestuff can contain different functional groups (chemistries). Reactive dyeing of cotton was undertaken to estimate the amount of dye and salt that remains in the effluent before activated carbon studies. Laboratory reactive dyeing trials for different dye chemistries/classes operated at Dyefin Textile factory were undertaken. This chapter describe the selected dye chemistries and classes (section 3.1) used for this study with their dyeing process and recipes presented in sections 3.2 and 3.3.1. The discussion and conclusion of results are discussed.

3.1 Reactive Dye Chemistry

The reactive groups found in reactive dyes increase the molecular weight of a dye but do not enhance chromogenic strength. Four different reactive dye shades were used in this study; Navy, Black, Beige and Turquoise shades and were obtained using Drimarene HF, Cibacron S, Procion HE and Remazol L dye classes respectively. According to manufacturers' specifications (Table 3.1) the Drimarene HF (from Clariant) belongs to trifluoropyrimidine reactive chemistry, the chemistry for Cibacron S (from Ciba) is not divulged, while Procion HE (from Dystar) belongs to monochlorotriazine and Remazol (from Dystar) belongs to vinylsulphone reactive chemistry. Drimarene HF dyes are trifunctional reactive dyes with three halogens attached to a pyrimidine ring. Procion HE dyes are bifunctional reactive dyes which were launched in the late 1960s and early 1970s. Procion were designed to have substantially increased substantivity exhaustion and fixation values compared with corresponding products carrying one chlorotriazinyl. Remazol L dyes are also bifunctional reactive dyes which were established in mid 1980s. The synthesis involves a vinyl sulphone attached to a triazine ring (Hunter and Renfrew, 1999).

3.2 Principle of Reactive Dyeing

The preparation, dyeing and finishing of textile products with reactive dyes consumes large amounts of energy, chemicals and water. These wet-processing operations require the use of several chemical baths that are often at elevated temperatures to achieve the desired characteristics to the dyed fabric. Exhaust reactive dyeing of cotton has three consecutive distinct phases:

- The initial exhaustion phase – During this stage there is migration of reactive dye to the cotton fibre. The amount of dye absorbed by the fibre depends on substantivity. The salt such as sodium chloride and sodium sulphate are added to promote migration of dye to the fibre. This phase is usually performed by gradually increasing the temperature of the dye bath, this aids in the penetration and migration of dye into the fibre (Broadbent 2001). The increase in temperature allows swelling of the cotton fibre which leads to a higher dye uptake (El-Shishtawy et al., 2007)
- The fixation phase – At this stage the pH of the dye bath is increased by adding alkali, which causes dissociation of some hydroxyl group in the cotton fibre. This allows nucleophilic cotton

ions to react with the dye ions. Dye absorption reaction progresses until no further dye can be taken by the cotton fibre (i.e. reach equilibrium).

- The post-dyeing washing – The cotton fibre after dyeing contains unfixed dye as well as hydrolysed dye, residual alkali and salt that are bonded on the surface of fibre. The latter are removed by successive rinsing in cold and warm water. The cold rinse removes most of the electrolyte and the unfixed dyes. The removal of electrolyte shifts the dye equilibrium back to the aqueous phase and eases removal in the cold rinse. The hydrolysed dye which is adsorbed on the fibres is partially removed by warm rinse and more completely by hot soaping. Rinsing aims at removing hydrolysed and unfixed reactive dyes from the cotton fibre. Depending on the dye recipe of the reactive dye used, neutralisation can follow the cold rinse before warm rinse. Sodium hydroxide is adsorbed within the cotton fibres, a neutralisation step is needed to release the residual alkali as a neutral salt. The final last cold rinse removes the last traces of dye (Broadbent, 2001).

Several auxiliary chemicals are added to the bath during dyeing processes. These chemicals can be divided into two groups: commodity and specialty chemicals and will be discussed in the subsequent sections.

3.2.1 Specialty chemicals

Specialty chemicals are mixtures which have an unknown composition due to proprietary information. The mixtures are often developed to solve problems specific to the process and to counteract or enhance the effects of other chemicals (Hendrickx and Boardman, 1995). Examples of specialty chemicals used in this study are Dekol (from BASF plc), Tebolan (from Dr. Th. Bohme KG, Chem. Fabrik GmbH), Avcoson from (Avco Chemicals Ltd) and Subitol. In dyeing of cotton, Dekol is used as a dispersing agent and protective colloid, Avcoson is used for minimising primary fibre fibrillation and Tebolan to prevent unwanted reduction of sensitive dyestuffs. Avcoson, Subitol, Tebolan are used in the reactive dyeing dye bath. Dekol solution is used for soaping process of the cotton fibre and also in the reactive dyeing bath. Specialty chemicals can cause side effects that are detrimental to the overall process (This information was taken from Material Safety Data Sheet (MSDS). Their composition and chemistries were not divulged by the Manufacturer.

3.2.2 Commodity chemicals

Commodity chemicals are mixtures or chemical mixtures that have known composition. Examples of commodity chemicals used in this study are sodium hydroxide, sodium sulphate, sodium carbonate and acetic acid. The presence of hydroxide and sulphate ions opens the structure of the cotton and shifts the equilibrium of dye from the aqueous phase to the solid (fibre) phase thus controls or retards the rate of dyeing. The sodium carbonate (alkali) is necessary for the sufficient exhaustion of the dye bath to promote the dye-cotton reaction. The acetic acid is added to control the acidity of the dye bath.

3.3 Experimentation

Four different dye shades were evaluated (Table 3.1). Each shade consisted of three dyestuffs and associated auxiliaries. The dyeing recipes for the four shades are presented in section 3.3.1. The salt concentration and pH were measured using Jenway conductivity meter 4310 and pH meter 3310 by Jenway. The colour measurement of the dye solution presented in section 3.3.2 was performed using a Cary UV/Visible Spectrophotometer.

Table 3-1 : Characterisation of test dye solution

Shade	Dye			
	Class	**Chemistry**	**Supplier**	**Initial concentration (mg/L)**
Navy*	Drimarene HF	Trifluoropymidine	Clariant	3 850
Black**	Cibacron S	Not available	Ciba	3 912
Beige*	Procion HE	Monochlorotriazine	Dystar	945
Turquoise**	Remazol L	Vinylsulphone	Dystar	3 464

* - NaCl salt used, ** - Na_2SO_4 salt used

3.3.1 Preparation of dyeing solution

The dye recipes used for this study were taken from the unpublished WRC Project K5/1363 and are representative of the shades dyed at Dyefin Textile factory. Other reactive dyeing results for all reactive dyes used in Dyefin Textiles are presented under unpublished WRC Project reports. The reactive dyes used for the selected four shades are supplied as a powder form and the auxiliaries in liquid form were obtained from Dyefin Textile industry. Preparation of stock solution for the dyes and auxiliaries, and the shades dye solution was then subjected to the dyeing procedures outlined in **Appendix A.** The recipe for each shade is explained in the subsequent sections. Prior to the dyeing process, the textile was wetted to facilitate an even intake of dyestuff and dyeing water. For all the shades the exhausted dye bath effluent (**S1**) was set aside for later analysis.

Navy Shade

Dyeing liquor (**S0**) for 10 g fabric was prepared from the relevant stock solutions (**Appendix A**) according to a dyeing recipe: 30 mL Drimarene Navy, 6.6 mL Drimarene Red, 1.9 mL Drimarene Yellow, 2 mL Tebolan, 6 mL Dekol, 8 mL Avcoson, 7 g sodium chloride and 10 mL sodium carbonate into 100 mL volumetric flask and filled up to the mark with distilled water. The dye bath temperature was 60˚C with a pH value of 11. After dyeing the fabric (**S1**) was subjected to a cold (25˚C) water rinse (**S2**) followed with hot (100˚C) soaping with Dekol (**S3**) and lastly cold (25˚C) water rinse (**S4**). The dyeing procedure is shown in Fig A.1 of Appendices.

Black Shade

Dyeing liquor (**S0**) for 10 g fabric was prepared according to a dyeing recipe: 21 mL Cibacron Black R, 18 mL Cibacron Black G, 2 mL Tebolan, 6 mL Dekol, 8 mL Avcoson, 2.7 mL of 95% sodium hydroxide, 8 g sodium sulphate and 10 mL sodium carbonate into 100 mL volumetric flask and filled up to the mark with distilled water. The dye bath temperature was 60˚C with a pH value of 11. After dyeing the fabric (**S1**) was subjected to a warm (50˚C)water rinse (**S2**) followed by cold (25˚C) neutralisation (**S3**) then with hot (100˚C) soaping with Dekol (**S4**) followed by hot (75˚C)water rinse (**S5**), warm (50˚C)water rinse (**S6**) and lastly cold (25˚C) water rinse (**S7**). The dyeing procedure is shown in Fig A.2 of Appendices.

Beige Shade

Dyeing liquor (**S0**) for 10 g fabric was prepared according to a dyeing recipe: 5 mL Procion Yellow H-E4R, 1.5 mL Procion Red H-E7B, 2.9 mL Procion Blue H-ERD, 1.5 mL Tebolan, 2.5 mL Subitol, 60% Acetic acid to control pH between 5.5 to 6.5, 6 g sodium chloride and 7.5 mL sodium carbonate into 100 mL volumetric flask and filled up to the mark with distilled water. The dye bath temperature was 60˚C with a pH value of 11. After dyeing the fabric (**S1**) was subjected to a hot (100˚C) water rinse

(**S2**) followed by cold (25˚C) water rinse (**S3**) then with hot (100˚C) soaping with Dekol (**S4**) and lastly cold (25˚C) water rinse (**S5**). The dyeing procedure is shown in Fig A.3 of Appendices.

Turquoise Shade

Dyeing liquor (**S0**) for 10 g fabric was prepared according to a dyeing recipe: 0.24 mL Remazol Brilliant Yellow 3GL granules, 33 mL Remazol Turquoise Blue G 133%, 1.4 mL Levafix Blue CA granules, 1.5 mL Tebolan, 2.5 mL Subitol, 5 g sodium sulphate and 6.5 mL sodium carbonate into 100 mL volumetric flask and filled up to the mark with distilled water. The dye bath temperature was 60˚C with a pH value of 11. After dyeing the fabric (**S1**) was subjected to a hot (100˚C) water rinse (**S2**) followed by cold (25˚C) neutralisation (**S3**) then with hot (100˚C) soaping with Dekol (**S4**) and lastly cold (25˚C) water rinse (**S5**). The dyeing procedure is shown in Fig A.4 of Appendices.

3.3.2 Colour measurement

Transmittance values at each wavelength value were determined between 400 nm to 700 nm (visible range) at 10 nm intervals. The 1-cm absorption cell was thoroughly cleaned with detergent and rinsed with distilled water. The cell was rinsed twice with the sample to be analysed. The cell was filled with the sample to be analysed and the external surface of the cell was wiped clean using lens paper. The instrument was set to read 100% transmittance on the distilled water blank and the samples were analysed.

3.4 Results

This section (3.4.1) presents results obtained from the laboratory reactive dyeing of fabric for four different shades; Navy (trifloropyrimidine chemistry), Black (not divulged chemistry), Beige (monochlorotriazine chemistry) and Turquoise (vinylsulphone). The final section contains the mass balances for the total dyeing process of the selected shades. All results are discussed in the discussion section (Section 3.5). Experimental data is presented in **Appendix A** and the error analysis is presented in **Appendix C**.

3.4.1 Laboratory test dyeings

Figures 3.1 to 3.4 shows the dye and salt concentrations measured before and after laboratory dyeing trials of the four reactive dye shades. Dye and salt recovered after dyeing are presented in Figures 3.5 to 3.8.

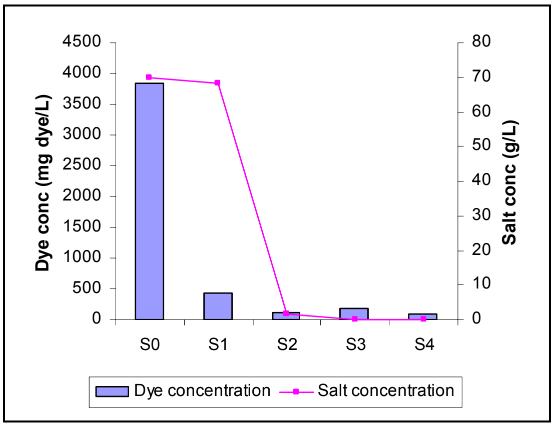


Figure 3-1: Dye and salt concentrations before and after dyeing of Navy shade. S0-

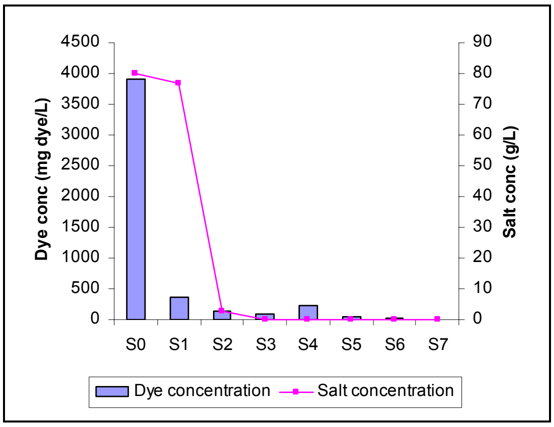


Figure 3-2 : Dye and salt concentrations before and after dyeing of Black shade. S0-

unexhausted dye bath, S1-exhausted dye bath, S2-warm water rinse, S3-cold neutralisation, S4-hot soaping

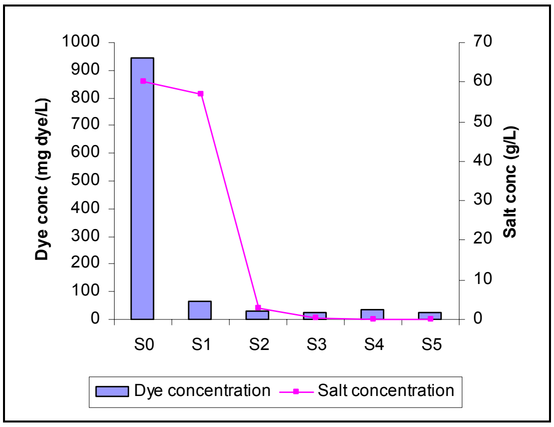


Figure 3-3 : Dye and salt concentrations before and after dyeing of Beige shade. S0-unexhausted dye bath, S1-exhausted dye bath, S2-hot water rinse, S3-cold water rinse, S4-hot soaping and S5-cold water rinse

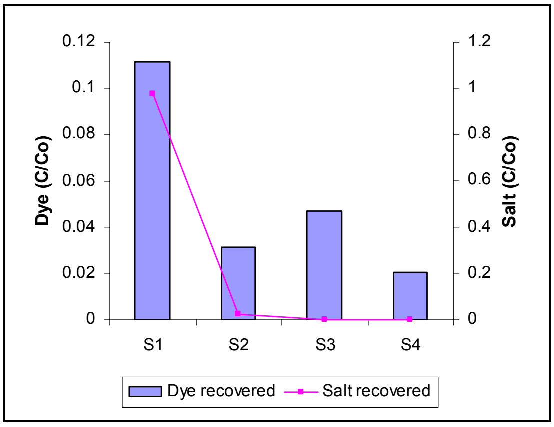


Figure 3-5 : Dye and salt ratios after dyeing of Navy shade. S1-exhausted dye bath, S2-cold water rinse, S3-hot soaping and S4-cold water rinse.

unexhausted dye bath, S1-exhausted dye bath, S2-warm water rinse, S3-cold neutralisation, S4-hot soaping and S5-hot water rinse, S6-warm water rinse and S7-cold water rinse

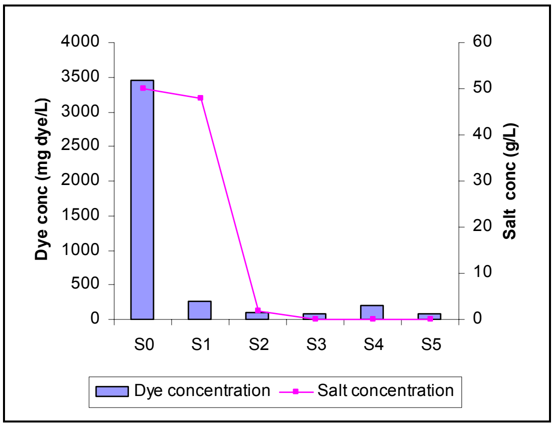


Figure 3-4 : Dye and salt concentrations before and after dyeing of Turquoise shade. S0-unexhausted dye bath, S1-exhausted dye bath, S2-cold water rinse, S3-cold neutralisation, S4-hot soaping and S5-cold water rinse

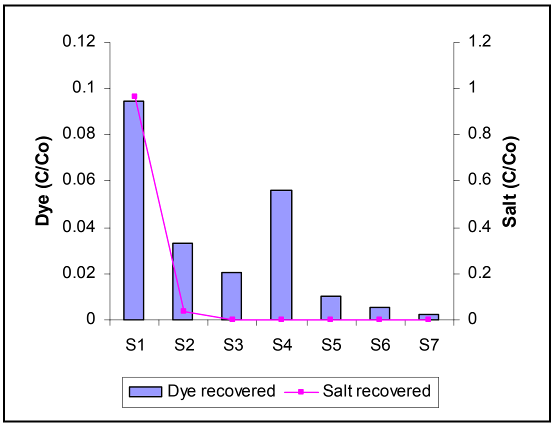


Figure 3-6 : Dye and salt ratios after dyeing of Black shade. S1-exhausted dye bath, S2-warm water rinse, S3-cold neutralisation, S4-hot soaping and S5-hot water rinse, S6-warm water rinse and S7-cold water rinse.

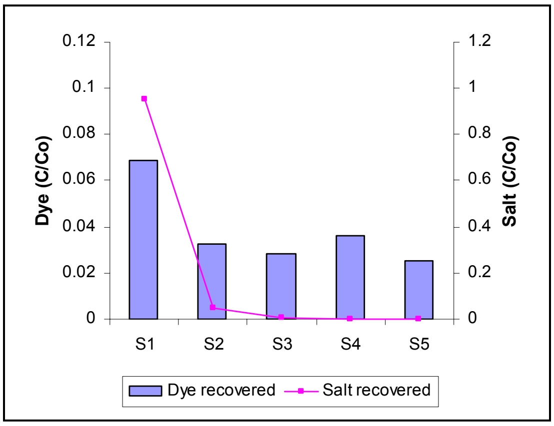


Figure 3-7 : Dye and salt ratios after dyeing of Beige shade. S1-exhausted dye bath, S2-hot water rinse, S3-cold water rinse, S4-hot soaping and S5-cold water rinse

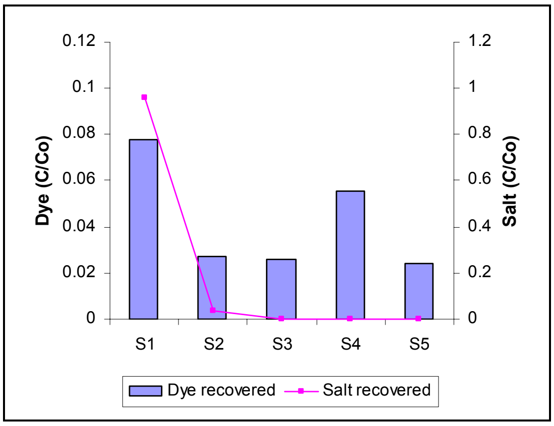


Figure 3-8 : Dye and salt ratios after dyeing of Turquoise shade. S1-exhausted dye bath, S2-cold water rinse, S3-cold neutralisation, S4-hot soaping and S5-cold water rinse.

3.4.2 Total dyeing process mass balance

The possibility for treatment of dye bath in terms of mass balance is shown in Tables 3.2 to 3.5 for all four shades. The flow diagrams of the mass balance for all four shades are listed in **Appendix A**, only Navy shade is presented in Fig 3.9.

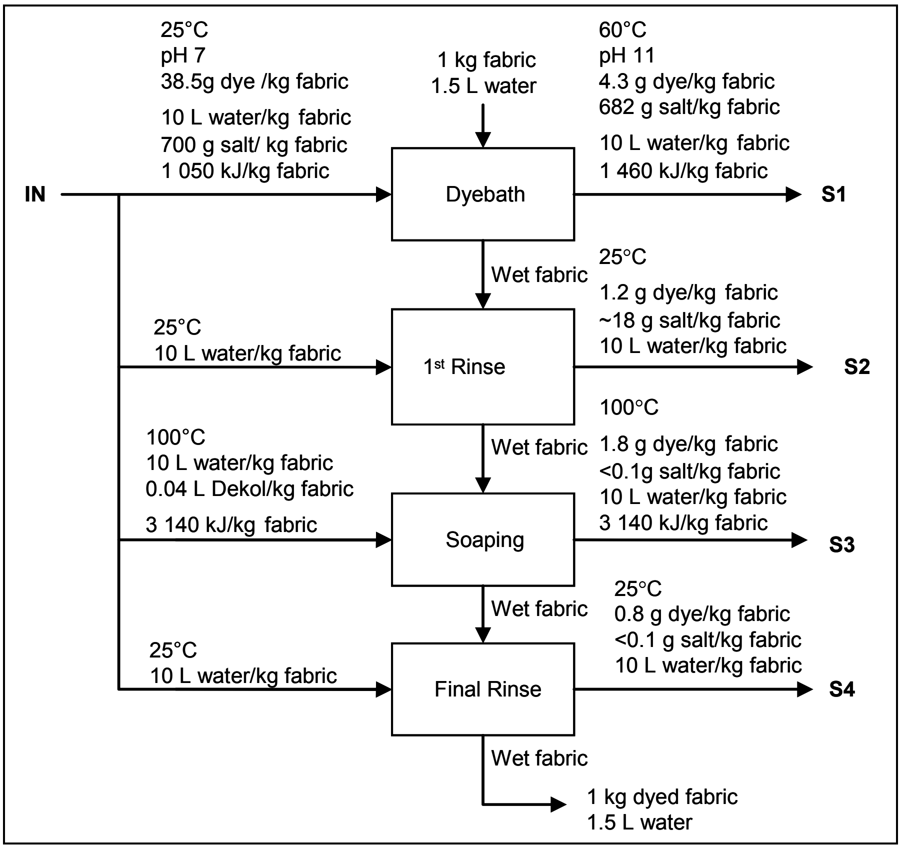


Figure 3-9 : Flow diagram and mass balance for dyeing of Navy shade

Table 3-2 : Total Navy shade effluent composition

Components	Units	Total composition (%)	Dye bath (%)
Water	L/kg fabric	40 (100)	10 (25)
Salt	g/kg fabric	700 (100)	682 (97)
Dye	g/kg fabric	8.1 (21)	4.3 (53)
Energy	kJ/kg fabric	4 600 (100)	1 460 (32)

Table 3-3 : Total Black shade effluent composition

Components	Units	Total composition (%)	Dye bath (%)
Water	L/kg fabric	70 (100)	10 (14)
Salt	g/kg fabric	800 (100)	770 (96)
Dye	g/kg fabric	8.7 (22)	3.7 (43)
Energy	kJ/kg fabric	8 800 (100)	1 460 (17)

Table 3-4 : Total Beige shade effluent composition

Components	Units	Total composition (%)	Dye bath (%)
Water	L/kg fabric	50	10 (20)
Salt	g/kg fabric	600	565 (94)
Dye	g/kg fabric	1.81	0.65 (36)
Energy	kJ/kg fabric	8 160	1 880 (23)

Table 3-5 : Total Turquoise shade effluent composition

Components	Units	Total composition (%)	Dye bath (%)
Water	L/kg fabric	50	10 (20)
Salt	g/kg fabric	500	480 (96)
Dye	g/kg fabric	7.31	2.7 (37)
Energy	kJ/kg fabric	4 600	1460 (32)

3.5 Discussion

This section discusses the experimental results in section 3.4 of **Chapter 3**, beginning with laboratory test dyeings, followed by mass balances for total dyeing process of all four selected shades.

3.5.1 Laboratory test dyeings

The reactive dyeing of four shades (Figs 3.1 to 3.4) was performed to estimate the amount of dye that remains in the effluent before adsorption tests were conducted. Fig 3.1 to 3.4 shows the reactive dyeing of Navy, Black, Beige and Turquoise shades, about 3 850, 3 912, 945 and 3 464 mg/L of dye concentrations and 70, 80, 60 and 50 g/L salt is used respectively when dyeing a fabric. According to the dye recipes higher salt concentrations were used for Navy and Black Shades than for Beige and Turquoise. This is because lower salt concentrations are required for dyeing light shades and higher salt concentrations for darker shades (Shu et al., 2005). Different dye chemistries used for this study exhibit different fixation ratios. This may be due to the types of reactive dyes used and their associated dye recipes. The efficiency of dyeing process for a specific shade is associated with various parameters such as substantivity and diffusion rate of dyes, auxiliaries, hardness of water, pH of the dye liquor, type and the concentration of reactive dye used.

According to results obtained from dye bath, high colour and high salt concentration are recovered for all the shades. Dye concentration recovered for all the shades after dyeing were in the following order dye bath > soaping > rinsing and neutralisation steps (Figs 3.5 to 3.8). The main source of residual colour in the reactive dye bath is the result of their incomplete exhaustion during the dyeing process (Golob et al., 2005). The remainder of most unfixed dye on the surface and inside of the fabric was eliminated by soaping using boiling detergent solution. The recovered dye concentration after dyeing (includes from dye bath effluent up until final rinse) ranged from 19% to 22% for the studied shades. According to Allegre et al., (2006), the hydrolysed and unfixed reactive dyes after dyeing represents 20 to 30% of the reactive dyes applied. This is the colour that is in the effluent and needs to be treated.

The salt concentration recovered was dye bath > 1st rinse> other dyeing processes (e.g. soaping, neutralisation, final rinse, etc.). All the salt used was found in the dye bath with traces of salt measured in the first rinse. The salts (NaCl and Na_2SO_4) used gave a better exhaustion of dye migration to fabric, the overall fixation ratio of reactive dyes ranged from 78% to 81% for the studied chemistries. NaCl and Na_2SO_4 are neutral salts that act as catalysts in the reactive dyeing; the need for alkali is for covalent bond fixation between dye and the fabric. From the study results obtained by Ahmed (2005), it was shown that both sodium chloride and sodium sulphate were effective exhaust agents in the presence of alkali.

3.5.2 Total dyeing process mass balance

Tables 3.2 to 3.5 (page 3-8 to 3-9) shows the mass balance for the dyeing of the four different shades. The effluent composition of the shades ranges from 19% to 22% of the dye with all the salt used for dyeing. The dye bath has the most dye of about 36% to 53% of the total colour in the effluent and almost all the salt ranging between 94% and 97% for all the selected shades. The most energy is used in dye bath, soaping and rinsing (depending on the desired shade) stages. The volumes of water used are the same for all stages of dyeing.

3.6 Conclusion

- Dye exhaustion to the fabric for Navy (trifloropyrimidine chemistry), Black (chemistry not divulged), Beige (monochlorotriazine chemistry) and Turquoise (vinylsulphone) shades was about 79%, 78%, 81% and 79% respectively. Therefore 19% up to 22% is discharged in the effluent resulting in high colour effluent from reactive dyeing operations. No significant relation was observed between the shade and fibre exhaustion for light as well as dark shades.

- High dye concentration liquor with all the salt used was obtained in the dye bath effluent. Treatment of dye bath with activated carbon compared to other treatment technologies is necessary because of high colour and high salt effluent.
- Moderate dye and low salt concentrations were found in the first rinse effluent. Thus treatment of the first rinse effluent with membrane filtration may be possible.
- Effluent with high dye concentrations and no salt were measured in the soaping process and traces of dye concentration with no salt were obtained in the neutralisation, second and final rinse effluents.
- Mass balance estimates show that the removal of colour for the studied reactive dye shades from the exhausted dye bath is necessary. Water recovery ranging from 14 to 25%, salt recovery of about 94 to 97% and energy savings of 17 to 32% could be achieved.

These results obtained from this chapter were able to provide the predictions of the amount of dye and salt remaining in the dye bath effluent before adsorption studies were undertaken.

4 CARBON EQUILIBRIUM TESTS

According to reactive dyeing studies performed (**Chapter 3**) reactive dye effluent consist of an average of 20% of the unexhausted dye bath with all the electrolyte. After dyeing, the exhausted dye bath contains about 53% of the discharged dye and 97% of the salt. The main aim of this part of the investigation was to evaluate the effect of different temperatures, pH values and electrolyte concentrations on the removal of reactive dyes using activated carbon. The possibility of using activated carbon for the removal of colour and the effect of dye equilibrium on different experimental conditions was evaluated. This chapter discusses the carbon equilibrium test for this study, beginning with a brief introduction on adsorption models and experimental methods used, followed by experimental details and the discussion of the results obtained, and lastly the conclusion.

4.1 Introduction

Equilibrium studies are used to determine the capacity of the activated carbon adsorbent. The equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms, usually the equilibrium ratio between the quantity adsorbed and that remaining in solution at a fixed temperature. The adsorption equilibrium data can be correlated with various adsorption isotherm models mentioned in the literature (**Chapter 2**). The equilibrium adsorption isotherms are of importance in the design of adsorption system (**Chapter 7**).

Chapter 2 introduced the two adsorption models for which the experimental data was interpreted; Langmuir and Freundlich adsorption isotherms respectively. The two parameter models, namely Freundlich and Langmuir, can be readily linearised and hence the parameter values can be easily obtained. When performing the adsorption process the characteristics of the adsorbent are of fundamental importance and characteristics of the granular activated carbon used for this study are explained in Section 4.1.1.

4.1.1 Characteristics of activated carbon

The selection of suitable activated carbon is of fundamental importance when designing a carbon treatment plant. The activated carbon can be classified by adsorption capacity and physical properties. Table 4.1 lists the F-400 specifications which illustrate the adsorptive character of the activated carbon selected for this study. Some of the important characteristics are explained in the subsequent paragraph.

Iodine number provides an indication of the amount of micropores in the carbon, i.e. indicate adsorption capacity for smaller molecules. Molasses number represents the amount of larger pores in the carbon, i.e. indicate adsorption capacity for larger molecules. Methylene blue numbers represent the amount of large micropores and mesopores in the activated carbon. Apparent density is the mass of carbon per unit volume, which can be packed in an empty column (Clements, 2002). Discussion with the supplier indicated that the Chemviron F-400 has a high adsorption capacity and would be the most appropriate quality and it is readily available in South Africa. The F-400 has amphoteric properties (Allen and Koumanova, 2005), which is an advantage for the adsorption of dyes which may exist in solution as either anions or as cations.

Table 4-1 : Some chemical and physical specifications for F-400 compared to other activated carbons as supplied by the manufacturers (Clements, 2002)

Adsorptive character	F-400	F-200	Norit 1240	Diahope DC 106
Origin	Bituminous coal	NA	NA	NA
Iodine number (mg/g)	1 050	850	1 020	1 050
Molasses number	243	177	230	280
Methylene blue numbers (mg/g)	260	200	200	190
Apparent density (kg/m^3)	425	500	440	475
Moisture content (%)	2	2	2	2
Ash content (%) (on dry basis)	10	10	7	5
Surface area (m^2/g) based on BET	1 100	NA	NA	NA

Note: NA- unknown

4.2 Experimentation

The experimentation design for the carbon equilibrium study is explained in Section 4.2.1 and the procedure followed is discussed in Section 4.2.2.

4.2.1 Experimental design

The dye solution is made up under neutral conditions so as to reduce the degree of dye hydrolysis. Alkali, to pH 11, is added just prior to dyeing. Thus if the salt solution is to be reused, it will need to be at a neutral to acidic pH value. Thus three pH conditions were investigated (pH 11; 7 and 4). Under certain conditions reactive dyeing can be undertaken at 100˚C although for the dyes considered for this study, 60˚C is more usual. As the proposed system may cool down to room temperature, additional temperatures of 40˚C and 20˚C were investigated. The recommended salt concentrations for the different shades were all different (Navy - 70 g/L; Black – 80 g/L; Beige – 60 g/L; Turquoise – 50 g/L). Higher salt concentrations would result in greater dye exhaustion hence dye concentrations about 30 g/L above and below the recommended values were investigated. A matrix of experimental conditions is given in Table 4.2. Each condition was evaluated (in duplicate) for 5 different ratios of carbon/dye.

Table 4-2 : Experimental design for the equilibrium trials

Temperature [˚C]	Salt [g/L]	pH		
		low	neutral	Recipe
100	low			X
	recipe	X	X	X
	high			X
80	low			
	recipe			X
	high			
60	low			
	recipe			X
	high			
20	low			
	recipe			X
	high			

Note: X represents conditions under which a test was conducted

4.2.2 Procedure

A representative sample of the F-400 granular activated carbon was pulverised so that 95% passed through a 45 µm screen. The pulverised sample was oven dried for 3 h at 150°C. A representative sample of the unexhausted dye bath solution to be tested was prepared (according to **Chapter 3**) in order to obtain similar condition to the textile process. Different weights of the oven dried pulverised carbon sample of 1; 2; 3; 4 and 5 g (using a MonoBloc AB204-5 Balance accurate to 0.001 g) were transferred to separate metal flasks (*see* Figure 4-1 for metal flasks). Duplicates of each weight of the activated carbon were prepared. To each metal flask containing oven dried pulverised carbon, 80 mL of the unexhausted dye solution was added using a graduated measuring cylinder and the metal flask was clamped on the stirring device (*see* Figure 4-2 and Figure 4-3 for the stirrers). A constant temperature in the water bath was maintained using a ±1C˚ temperature controller by Julabo; the stirring device was designed to permit immersion of the lower part of the flask containing the carbon-solution mixture in the bath (see Figure 4-4 for the stirrers). A series of tests were undertaken at 60˚C for different time periods and 2 h was found to be adequate for equilibrium (see Figure 4-5 to Figure 4-8). The mixture was agitated for 2 h. The same volume of dye solution was added to a container without carbon and subjected to the same procedure in order to obtain a blank reading. After the 2 h contact time had elapsed, the contents of the flask were filtered under gravity with No 2 Whatman filter paper. The first and the last portions of the filtrate were discarded and the middle portion was saved for analysis. The blank was filtered in the same manner as the other samples. The pH was adjusted to 7.6 by using sulphuric acid (Greenberg *et al.*, 1995) and safety glasses were worn all the time. The colour of the effluent was measured using American Dye Manufacturer Institute colour method and determined by scanning the sample from 400 nm to 700 nm using a Cary UV/Visible spectrophotometer. The salt concentration and pH were measured using conductivity meter 4310 and pH meter 3310 both by Jenway.

Figure 4-1 : Metal flasks where test dye solution was poured

Figure 4-2 : Front view of the stirrers with a temperature controller used

Figure 4-3 : Back view of the shaker

Figure 4-4 : Stirrers view where metal flasks are clamped

4.3 Results

This section presents results obtained from the decolourisation equilibrium tests of four different shades; Navy, Black, Beige and Turquoise using powdered activated carbon. The section begins with different time interval to reach equilibrium followed by the adsorption isotherms obtained using the Freundlich model (Section 4.3.1) at different temperatures, pH values and electrolyte concentrations. Section 4.3.2 presents parameters obtained from Freundlich and Langmuir to give indication why Freundlich was the selected model. Section 4.3.3. contains mass balances for the dyeing of the four shades of which the mass balance diagrams are presented in **Appendix B**. All the results of this section are discussed in Section 4.4 and the error analysis is presented in **Appendix C**.

4.3.1 Adsorption isotherms

Adsorption isotherm data for the different time interval for all the shades at 60˚C are presented in Figure 4-5 to Figure 4-8. Experimental data is presented in Table B.1 of **Appendix B**. Figure 4-9 to Figure 4-20 show the Freundlich model isotherms plotted from the mass of dye adsorbed per gram of carbon [log (X/M)] against residual dye concentration [log (C)]. The straight lines were plotted at four different temperatures (20, 60, 80 and 100˚C), three different pH values (basic, neutral and acidic conditions) and three different electrolyte concentrations for all the four shades and presented in Figure 4-9 to Figure 4-12, Figure 4-13 to Figure 4-16 and Figure 4-17 to Figure 4-20 respectively. Experimental data is presented in **Appendix B**. Each graph was constructed from 10 data points (5 duplicates)

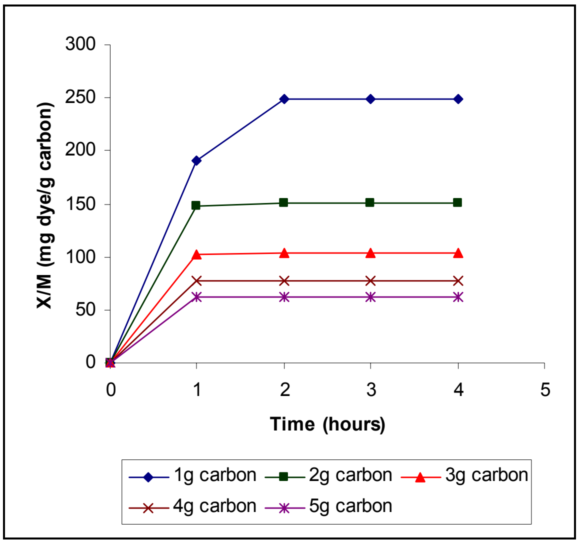


Figure 4-5 : Different time interval at 60˚C- Navy shade

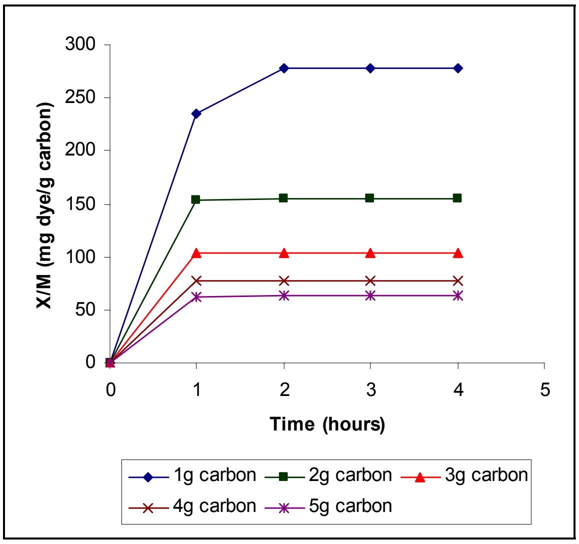


Figure 4-6 : Different time interval at 60˚C- Black shade

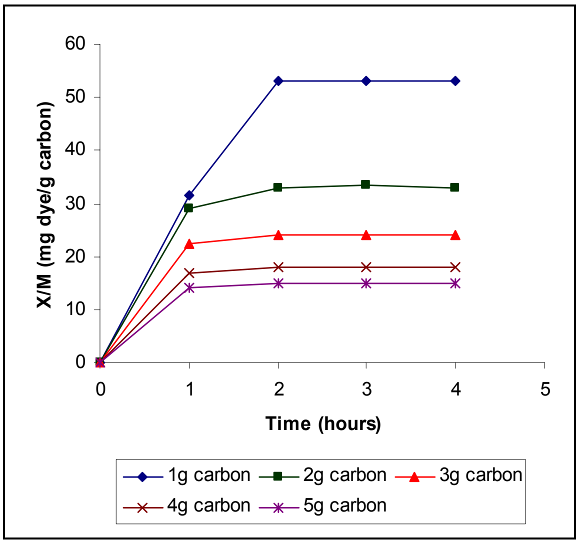


Figure 4-7 : Different time interval at 60˚C- Beige shade

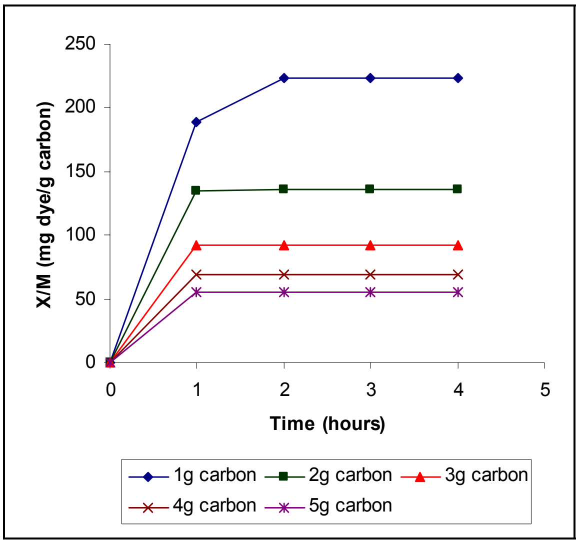


Figure 4-8 : Different time interval at 60˚C- Turquoise shade

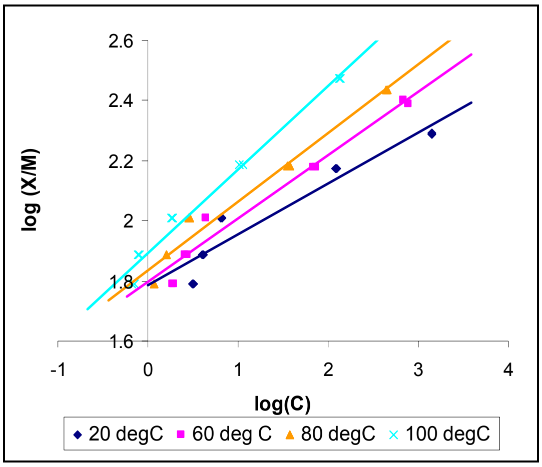


Figure 4-9 : Effect of temperature on adsorption of Navy shade at pH 11 and 70 g/L NaCl

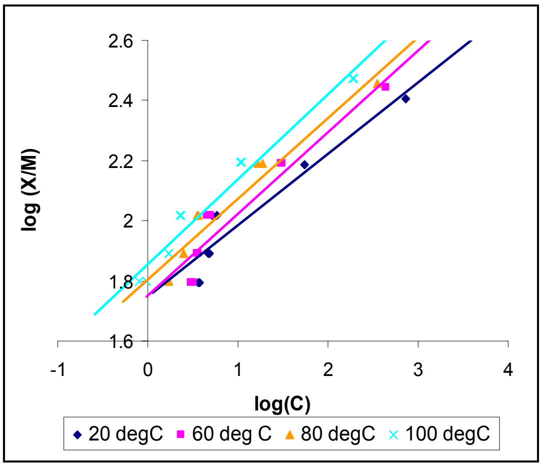


Figure 4-10 : Effect of temperature on adsorption of Black shade at pH 11 and 80 g/L Na_2SO_4

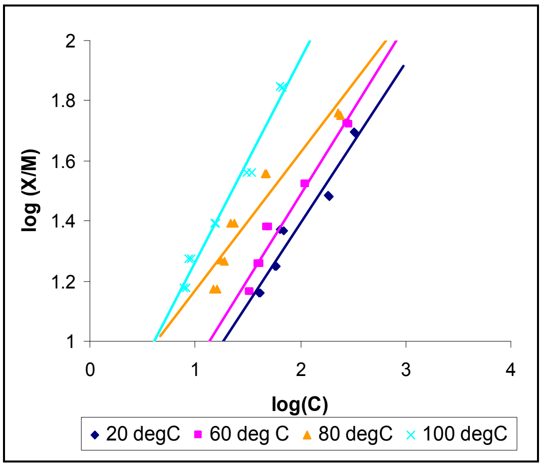


Figure 4-11 : Effect of temperature on adsorption of Beige shade at pH 11 and 60 g/L NaCl

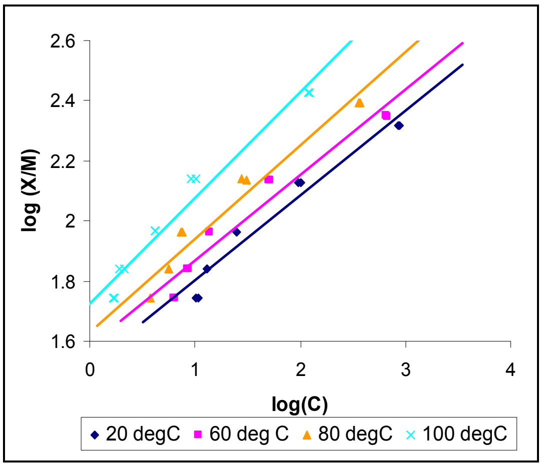


Figure 4-12 : Effect of temperature on adsorption of Turquoise shade at pH 10 and 50 g/L Na_2SO_4

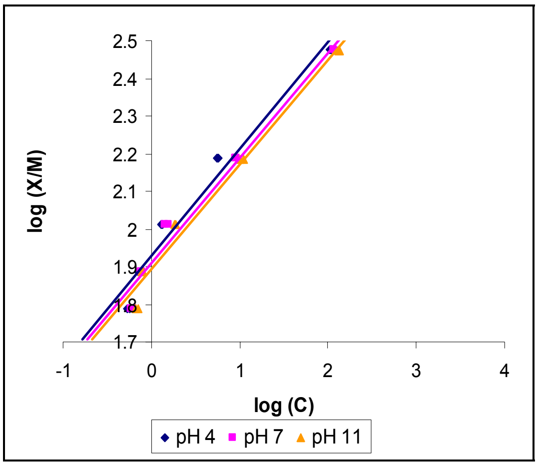


Figure 4-13 : Effect of pH on adsorption of Navy shade at 100°C and 70 g/L NaCl

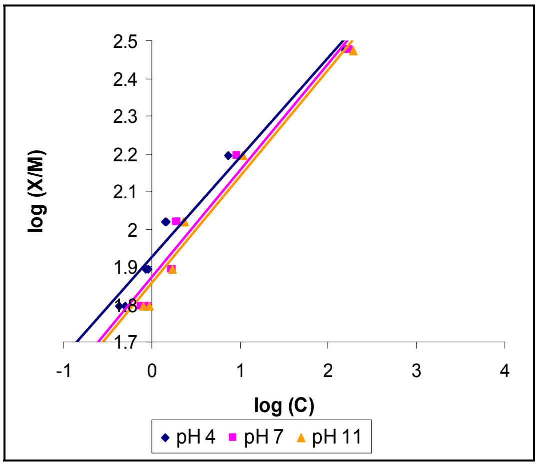


Figure 4-14 : Effect of pH on the adsorption of Black shade at 100°C and 80 g/L Na_2SO_4

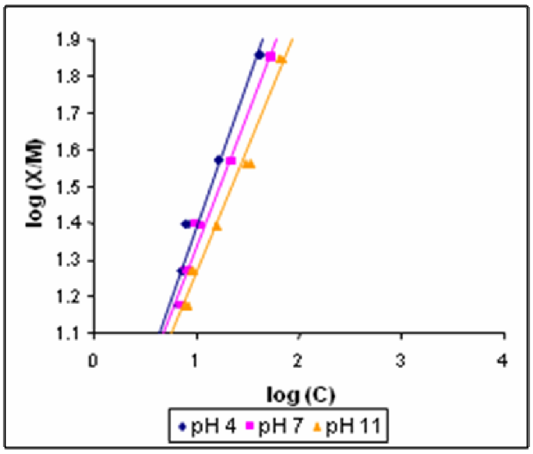


Figure 4-15 : Effect of pH on the adsorption of Beige shade at 100ºC and 60 g/L NaCl

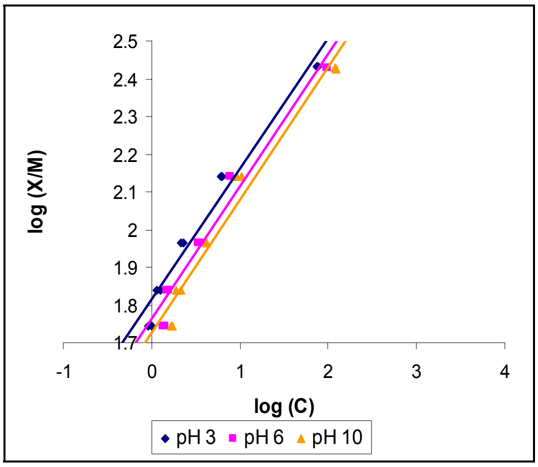


Figure 4-16 : Effect of pH on the adsorption of Turquoise shade at 100ºC and 50 g/L Na_2SO_4

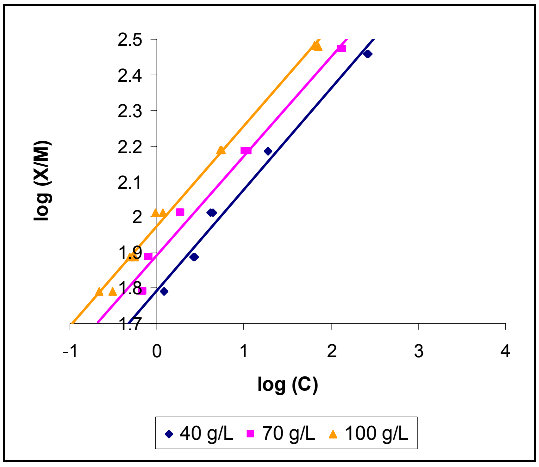


Figure 4-17 : Effect of electrolyte concentrations on adsorption of Navy shade at 100°C and pH 11

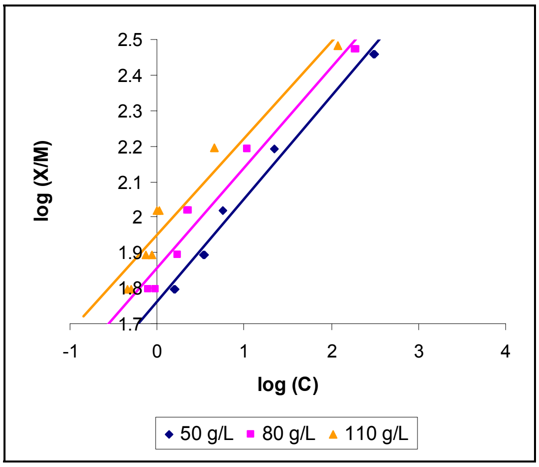


Figure 4-18 : Effect of electrolyte concentrations on the adsorption of Black shade at 100°C and pH 11

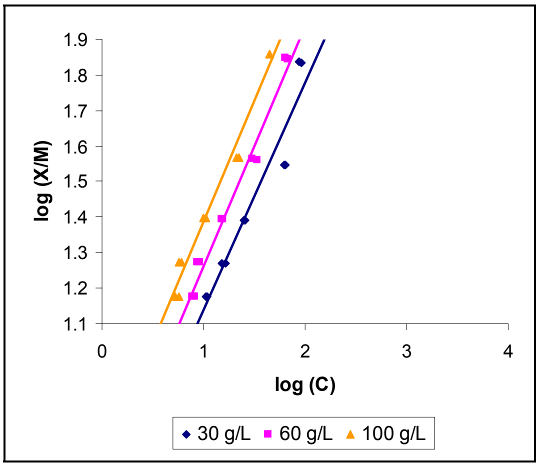


Figure 4-19 : Effect of electrolyte concentrations on the adsorption of Beige shade at 100°C and pH 11

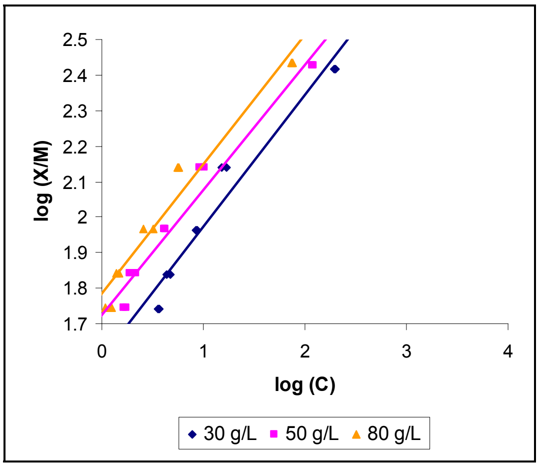


Figure 4-20 : Effect of electrolyte concentrations on the adsorption of Turquoise shade at 100°C and pH 10

4.3.2 Adsorption isotherm model parameters

The coefficients of determination obtained from Freundlich and Langmuir models are presented in Table 4.3 and the Freundlich model parameters are listed in Table 4.4 for all the four shades at different temperatures, pH values and electrolyte concentrations. The curves showing the validation calculated and experimental data of Freundlich model are presented in **Appendix B**.

Table 4-3 : Coefficients of determination in Freundlich and Langmuir isotherm models (number of samples per condition =10)

Shades	Temp (°C)	Salt (g/L)	pH	Freundlich model	Langmuir model
				r	r
Navy	20	70	11	0.747	0.591
	60	70	11	0.924	0.671
	80	70	11	0.973	0.699
	100	70	11	0.995	0.734
	100	70	4	0.981	0.826
	100	70	7	0.992	0.771
	100	70	11	0.995	0.734
	100	40	11	0.993	0.603
	100	70	11	0.995	0.734
	100	100	11	0.997	0.549
Black	20	80	11	0.964	0.876
	60	80	11	0.981	0.851
	80	80	11	0.983	0.840
	100	80	11	0.984	0.723
	100	80	4	0.986	0.682
	100	80	7	0.978	0.742
	100	80	11	0.984	0.723
	100	50	11	0.994	0.616
	100	80	11	0.984	0.723
	100	110	11	0.966	0.835
Beige	20	60	11	0.949	0.521
	60	60	11	0.978	0.586
	80	60	11	0.922	0.638
	100	60	11	0.978	0.392
	100	60	4	0.983	0.446
	100	60	7	0.991	0.451
	100	60	11	0.978	0.392
	100	30	11	0.865	0.331
	100	60	11	0.978	0.392
	100	100	11	0.977	0.385
Turquoise	20	50	10	0.796	0.602
	60	50	10	0.862	0.713
	80	50	10	0.924	0.771
	100	50	10	0.954	0.786
	100	50	3	0.959	0.812
	100	50	6	0.954	0.764
	100	50	10	0.954	0.786
	100	30	10	0.938	0.872
	100	50	10	0.954	0.786
	100	80	10	0.949	0.819

Table 4-4 : Parameters in Freundlich isotherm model (number of samples per condition =10)

Shades	Temp (°C)	Salt (g/L)	pH	k_F (mg dye/g carbon) / (mg dye/L)	n	r
Navy	20	70	11	61.54	5.941	0.747
	60	70	11	62.43	4.716	0.924
	80	70	11	68.35	4.364	0.973
	100	70	11	78.16	3.594	0.995
	100	70	4	84.83	3.521	0.981
	100	70	7	81.09	3.580	0.992
	100	70	11	78.16	3.594	0.995
	100	40	11	61.85	3.518	0.993
	100	70	11	78.16	3.594	0.995
	100	100	11	94.20	3.547	0.997
Black	20	80	11	55.99	4.222	0.964
	60	80	11	56.28	3.681	0.981
	80	80	11	63.79	3.734	0.983
	100	80	11	72.02	3.543	0.984
	100	80	4	84.53	3.785	0.986
	100	80	7	74.09	3.516	0.978
	100	80	11	72.02	3.543	0.984
	100	50	11	57.94	3.455	0.994
	100	80	11	72.02	3.543	0.984
	100	110	11	89.04	3.672	0.966
Beige	20	60	11	2.096	1.866	0.949
	60	60	11	2.282	1.772	0.978
	80	60	11	3.100	2.175	0.922
	100	60	11	3.873	1.480	0.978
	100	60	4	3.950	1.263	0.983
	100	60	7	4.085	1.391	0.991
	100	60	11	3.873	1.480	0.978
	100	30	11	3.129	1.559	0.865
	100	60	11	3.873	1.480	0.978
	100	100	11	5.061	1.468	0.977
Turquoise	20	50	10	33.13	3.542	0.796
	60	50	10	38.51	3.524	0.862
	80	50	10	42.34	3.203	0.924
	100	50	10	53.18	2.840	0.954
	100	50	3	64.79	2.886	0.959
	100	50	6	57.61	2.840	0.954
	100	50	10	53.18	2.840	0.954
	100	30	10	39.93	2.696	0.938
	100	50	10	53.18	2.840	0.954
	100	80	10	60.74	2.738	0.949

Table 4-5 : Possible treatment of dye bath with PAC using Freundlich parameters

Shades	Temp (°C)	Salt (g/L)	pH	X/M (mg dye/g carbon) /	kg fabric/ g carbon	L effluent/ g carbon
Navy	20	70	11	171	0.04	0.40
	60	70	11	226	0.05	0.53
	80	70	11	274	0.06	0.63
	100	70	11	422	0.10	1.00
	100	70	4	475	0.11	1.11
	100	70	7	441	0.10	1.00
	100	70	11	422	0.10	1.00
	100	40	11	347	0.08	0.83
	100	70	11	422	0.10	1.00
	100	100	11	521	0.13	1.25
Black	20	80	11	227	0.06	0.63
	60	80	11	281	0.08	0.78
	80	80	11	311	0.08	0.83
	100	80	11	382	0.10	1.00
	100	80	4	403	0.11	1.11
	100	80	7	398	0.11	1.11
	100	80	11	382	0.10	1.00
	100	50	11	321	0.08	0.83
	100	80	11	382	0.10	1.00
	100	110	11	446	0.13	1.25
Beige	20	60	11	20	0.03	0.30
	60	60	11	24	0.04	0.37
	80	60	11	21	0.03	0.32
	100	60	11	65	0.10	1.00
	100	60	4	108	0.16	1.67
	100	60	7	82	0.13	1.25
	100	60	11	65	0.10	1.00
	100	30	11	46	0.07	2.50
	100	60	11	65	0.10	1.00
	100	100	11	87	0.14	1.43
Turquoise	20	50	10	161	0.06	0.59
	60	50	10	189	0.07	0.71
	80	50	10	243	0.09	0.91
	100	50	10	382	0.14	1.43
	100	50	3	451	0.16	1.67
	100	50	6	414	0.14	1.43
	100	50	10	382	0.14	1.43
	100	30	10	319	0.13	1.25
	100	50	10	382	0.14	1.43
	100	80	10	469	0.16	1.67

4.3.3 Mass balance

The possibility for treatment of dye bath with activated carbon in terms of mass balance which could result in cost savings is shown in Table 4.6 to 4.9 for all the four shades. The flow diagram of the mass balance of the Navy shade is shown in Figure 4-21 and the other three shades are listed in **Appendix B**. The sample calculation for energy savings is presented in **Appendix B**.

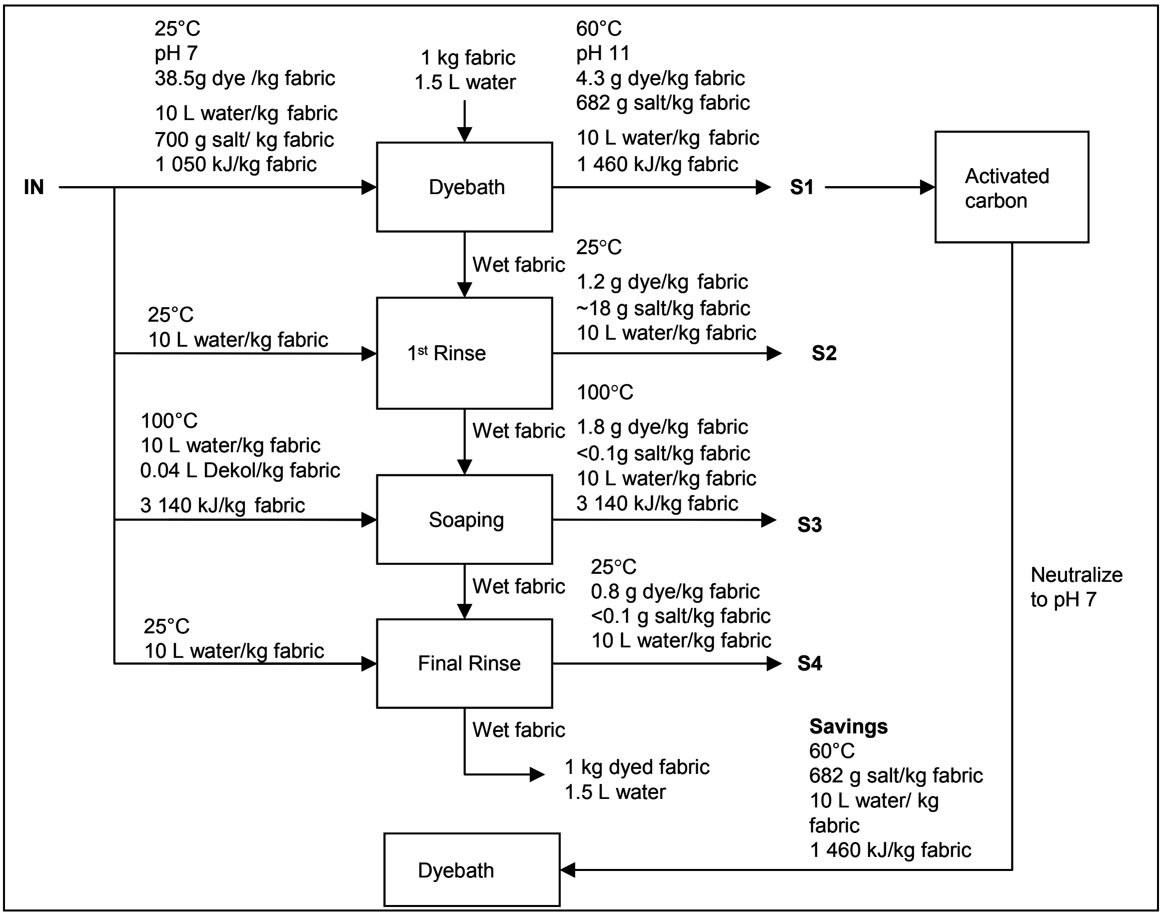


Figure 4-21 : Flow diagram and mass balance for dyeing of Navy shade

Table 4-6 : Total Navy Shade Effluent composition without and with the activated carbon recycle system

Components	Units	No recovery	Activated carbon recovery	Savings (%)
Effluent 25˚C	L/kg fabric	20	20	25
Effluent 60˚C	L/kg fabric	10	0	
Effluent 100˚C	L/kg fabric	10	10	
Salt	g/kg fabric	700	18	97
Dye	g/kg fabric	8.1	3.8	53
Energy	kJ/kg fabric	4 600	3 140	32

Table 4-7 : Total Black Shade Effluent composition without and with the activated carbon recycle system

Components	Units	No recovery	Activated carbon recovery	Savings (%)
Effluent 25˚C	L/kg fabric	20	20	14
Effluent 50˚C	L/kg fabric	20	20	
Effluent 60˚C	L/kg fabric	10	0	
Effluent 75˚C	L/kg fabric	10	10	
Effluent 100˚C	L/kg fabric	10	10	
Salt	g/kg fabric	800	30	96
Dye	g/kg fabric	8.7	5.0	43
Energy	kJ/kg fabric	8 800	7 340	17

Table 4-8 : Total Beige Shade Effluent composition without and with the activated carbon recycle system

Components	Units	No recovery	Activated carbon recovery	Savings (%)
Effluent 25˚C	L/kg fabric	20	20	20
Effluent 80˚C	L/kg fabric	10	0	
Effluent 100˚C	L/kg fabric	20	20	
Salt	g/kg fabric	600	35	94
Dye	g/kg fabric	1.81	1.16	36
Energy	kJ/kg fabric	8 160	6 280	23

Table 4-9 : Turquoise Shade Effluent composition without and with the activated carbon recycle system

Components	Units	No recovery	Activated carbon recovery	Savings (%)
Effluent 25˚C	L/kg fabric	20	20	20
Effluent 80˚C	L/kg fabric	10	0	
Effluent 100˚C	L/kg fabric	20	20	
Salt	g/kg fabric	500	20	96
Dye	g/kg fabric	7.31	4.61	37
Energy	kJ/kg fabric	4 600	3 140	32

4.4 Discussion

The adsorption tests were conducted to determine the degree of adsorption of different reactive dye chemistries onto powdered activated carbon. Figs 4.5 to 4.9 presents the different time intervals were evaluated to determine the time for dye carbon equilibrium to be reached, 2 h to 4 h were found to be adequate (see **Appendix B**). Studies on adsorption of reactive dyes performed by Namasivayan and co-workers (1998), Ahmad and co-workers (2006) and Santhy and Selvapathy (2006) showed that 70 min to 4 h is sufficient to reach dye carbon equilibrium adsorption.

From Figure 4-9 to Figure 4-12, the influence of temperature at constant recipe pH and salt concentration for the four different shades on activated carbon adsorption was examined and it was observed that the mass of dye adsorbed increased as the temperature increases. The adsorption capacity [(mg dye/g carbon)/(mg dye/L)] from 20 to 100˚C ranged from 61.54 to 78.16 for Navy shade; 55.99 to 72.02 for Black shade; 2.096 to 3.873 for Beige shade and 33.13 to 53.18 for Turquoise shade This may be due to that the increase in temperature allowed the swelling of the activated carbon pores, which led to a higher dye-uptake (Kim, 2004). For 20˚C isotherms may not be at equilibrium due to slow kinetics of low temperatures.

Figure 4-13 to Figure 4-16 show the influence of pH at 100˚C and recipe salt concentration of the four shades on activated carbon adsorption and it was observed that the mass of dye adsorbed increased slightly as the pH decreases from pH 11 to 4. The adsorption capacity (pH 4 to pH 11) [(mg dye/g carbon) / (mg dye/L)] decreased from 84.83 to 78.16 for Navy shade; 84.53 to 72.02 for Black shade; 3.950 to 3.873 for Beige shade and 64.79 to 53.18 for Turquoise shade. A possible reason for the dye adsorption behaviour with pH is that at lower pH values, the surface charge of the carbon will be positive thus attracting the negatively charged functional groups on the reactive dye causing an increase in amount of dye adsorbed (Al-Degs et al., 2000; Santhy and Selvapathy, 2006; Vadivelan and Kumar, 2005).

Figure 4-17 to Figure 4-20 presents the influence of electrolyte concentration at 100˚C and recipe pH value of the shades on activated carbon adsorption and it was observed that the mass of dye adsorbed increased as the electrolyte concentration increases. The increase in adsorption capacity [(mg dye/g carbon) / (mg dye/L)] ranged from 61.85 to 98.20 for Navy shade; 57.94 to 89.04 for Black shade; 3.129 to 5.061 for Beige shade and 39.93 to 60.74 for Turquoise shade. NaCl and Na_2SO_4 are neutral salts that act as catalysts in the reactive dyeing; the need for pH change to basic (pH 11) for higher adsorption between dye and the carbon is necessary (Ahmed, 2005).

High amount of dye uptake by powdered activated carbon was observed at high temperature, high electrolyte concentration and low pH values.

Table 4.3 showed that in every case the r-value for the Freundlich model was greater than the corresponding value for the Langmuir model. The r value for Freundlich model was greater than 0.90 for 87% of the tests and greater than 0.95 for 72% of the tests; while for the Langmuir model the highest r value was 0.88. According to Arslanoglu and co-workers (2004) and Kim (2004) higher coefficients of determination of isotherm are used to determine the best fit model. The Freundlich adsorption parameters and r values using linear regression analysis for the different shades are presented in Table 4.3 for different temperatures, pH values and electrolyte concentrations respectively. In the Freundlich isotherm model, the parameter k_F is a measure of adsorption capacity, whereas the parameter n is a measure of adsorption bond strength. A large k_F value [(in mg dye per gram of carbon) / (mg dye per litre)] indicates a larger adsorption capacity and a higher n value indicates a stronger adsorption bond (Kim, 2004). According to the results obtained in Table 4.4 similar results were observed in all the four shades; the k_F values obtained increased as the temperature increases, increased as the pH value decreases (from pH 11 to pH 4) and increased as the electrolyte increases). Large k_F values of about 94, 89, 5 and 61 [(mg dye/g carbon)/(mg dye/L)]for Navy, Black, Beige and Turquoise shades respectively, were observed at 100˚C, pH 4 and high electrolyte concentrations. There was not much difference in bond strength between activated carbon and reactive dyes at different temperatures, pH values and electrolyte concentrations. Bond strength for Navy, Black and Turquoise (ranged from 2.738 to 5.941) were higher that Beige (ranged from 1.263 to 2.175). All the n values obtained for all the studied shades were between 1 and 10, this indicated favourable adsorption (Arslanoglu et al., 2004; Santhy and Selvapathy, 2006). The adsorption results obtained for the removal of the four shades showed the possibility of decreasing the pH or using higher concentrations of salt to achieve higher dye removals. If the pH value were to be decreased to around a value of 4, it would have to be neutralised to a value of 7 before reuse. The amount of salt discharged to drain would need to be evaluated before dyeing in higher salt concentrations could be considered. The use of dyeing at higher temperatures (above 60˚C) need to be carefully considered due to the adverse effect on the ability to control shade consistency.

The treatment of dye bath with activated carbon is presented in Table 4.5. From Chapter 3 it was shown that the dye bath effluent contains about 430 mg/L for Navy shade, 370 mg/L for Black shade, 65 mg/L for Beige shade and 270 mg/L for Turquoise shade. In all the selected shades the dye bath effluent is at 60˚C. The treatment of the 60˚C Navy shade effluent with a gram activated carbon will treat 0.05 kg fabric, i.e. about 0.53 L effluent. For treatment of Black, Beige and Turquoise shades effluent, a gram of carbon will treat about 0.08 kg fabric, i.e. 0.78 L effluent; 0.04 kg fabric, i.e. 0.37 L effluent and 0.07 kg fabric, i.e. 0.71 L effluent respectively. A colour removal of above 95% was observed starting from 3 g to 5 g carbon for all the studied shades in the adsorption equilibrium tests undertaken.

Tables 4.6 to 4.9 and Fig 4.21 show the mass balance for the dyeing and adsorption of the four different shades. The treatment of dye bath with activated carbon showed dye bath effluent can be reclaimed. The possibility exist for re-use of 97% salt, 25% water and 32% energy (Table 4.5); 96% salt, 14% water and 17% energy (Table 4.6); 94% salt, 20% water and 23% energy (Table 4.7); and 96% salt, 20% water and 32% energy (Table 4.8) for Navy; Black; Beige and Turquoise shades respectively. The removal of colour from dye bath using activated carbon of all the shades represents 36% up to 53% of the total colour in the effluent. First rinse stream (**S2)** has a low salt concentration. The possibility exists for the further concentration of the **S2** effluent by a membrane process. The permeate from membrane process can be re-used for the first rinse and the concentrate can join exhausted dye bath effluent (**S1**) (see figs B.1 to B.4, Appendix B).

4.5 Conclusion

- The best adsorption for the four reactive dye shades studied occurred at high temperature, low pH and high electrolyte concentration.
- Based on determination of coefficients, the adsorption of the reactive dyes studied was better fitted by the Freundlich isotherm model.
- Hot decolourised water with salt was recovered after adsorption of the reactive dyes and this implies significant water, salt and energy savings.

From the textile industry perspective the discharged dye is at 60˚C and high pH of about 11. Advantage of neutralising the effluent and heating to 100˚C with high salt concentrations is needed for best possible adsorption of the reactive dyes shades studied. The results obtained in this chapter predicted the performance of PAC in the removal of colour from reactive dye bath for re-use purposes. The adsorption kinetics of the selected reactive dye shades were subsequently evaluated using GAC in a packed column (**Chapter 5**). The temperature had to be evaluated since it was the major factor that influenced the adsorption of the reactive dyes studied in this chapter. The results obtained form a basis for evaluating the temperature effect on column systems, which is presented in the subsequent chapter.

5 COLUMN TESTS

As stated in the previous chapter temperature and salt concentration were the major factors that influenced adsorption equilibrium with pH a minor factor. The possibility of reuse of recovered hot decolourised water with salt was observed from **Chapter 4**. Due to poor handling, transport and disposal concerns of PAC, GAC has been used for column plants because of its advantages. The carbon of the same type as in **Chapter 4** was used in this chapter; the only difference was that the carbon used in **Chapter 4** was in powder form. The performance of GAC on column system was evaluated to determine the reactive dye kinetics involved in the adsorption process. The study of column adsorption behaviour and kinetics is necessary for the information required for the design and operation of adsorption equipment for wastewater treatment. Column adsorption behaviour is a prerequisite during modelling of the adsorption kinetics and the behaviour of the adsorbent. This was done to determine the breakthrough conditions for a dye solution. This chapter discusses the adsorption behaviour of F-400 granular activated carbon studied in column test. The experimental methods used, followed by experimental work and the discussion of the results obtained and lastly the conclusion of the experimental results are presented in this chapter.

5.1 Experimentation

A representative sample of the appropriate granular activated carbon was sieved with -1 mm and +0.95 mm screen. The average 1 mm GAC sample was oven dried for 3 h at 150°C. The 30 g sample of oven dried GAC was boiled for 2 h, to ensure removal of air and then closely packed into a jacketed glass column of 200 mm length and 26 mm internal diameter. The bed was supported and closed off with glass wool, which also ensures good liquid distribution. The column was sealed with rubber bungs and silicone sealer to avoid leaking of liquid. The column was clamped to a burette stand and water from the water bath was pumped through the outer walls of the column to maintain a constant temperature. A temperature controller with an accuracy of ±3 C˚, manufactured by Labcon was used. Polystyrene chips were distributed on top of the water bath to avoid loss in heat. A representative dye solution to be tested was continuously fed into a column at a constant flow rate. A digital flow control peristaltic pump (Watson- Marlow 101U/R) was calibrated and used to feed the column. The pump flowrate was measured before and after each test. The difference never exceeded 0.003 mL/min. The pump has a maximum flow of up to 53 mL/min at 32 rpm (maximum recommended speed). The 102R pump head accept continuous tubing or elements. The dye solution was fed through a bed of granular activated carbon in down flow. Samples of the effluent were collected periodically and analyzed for the remaining dye concentration using a Cary UV/Visible spectrophotometer (model with curvette of 1 cm). The salt concentration and pH were measured using Jenway conductivity meter 4310 and a Jenway pH meter 3310. Fresh carbon was used for each experiment.

Two experiments were undertaken in parallel, first Navy and Black and then Turquoise and Beige. A single batch (20 L) of dye solution was made for each test. It was stored in plastic buckets with lids a cold room (4˚C). The column loading took between 10 and 14 days and the column was immediately regenerated. Effluent samples were analysed for colour (ADMI) on the day of sampling. Regeneration took 1 day. After standing overnight the next loading cycle commenced.

A schematic diagram of the experimental set-up is shown in Figure 5-1. Column calculations (specifications) for this study are explained in Section 5.2.1.

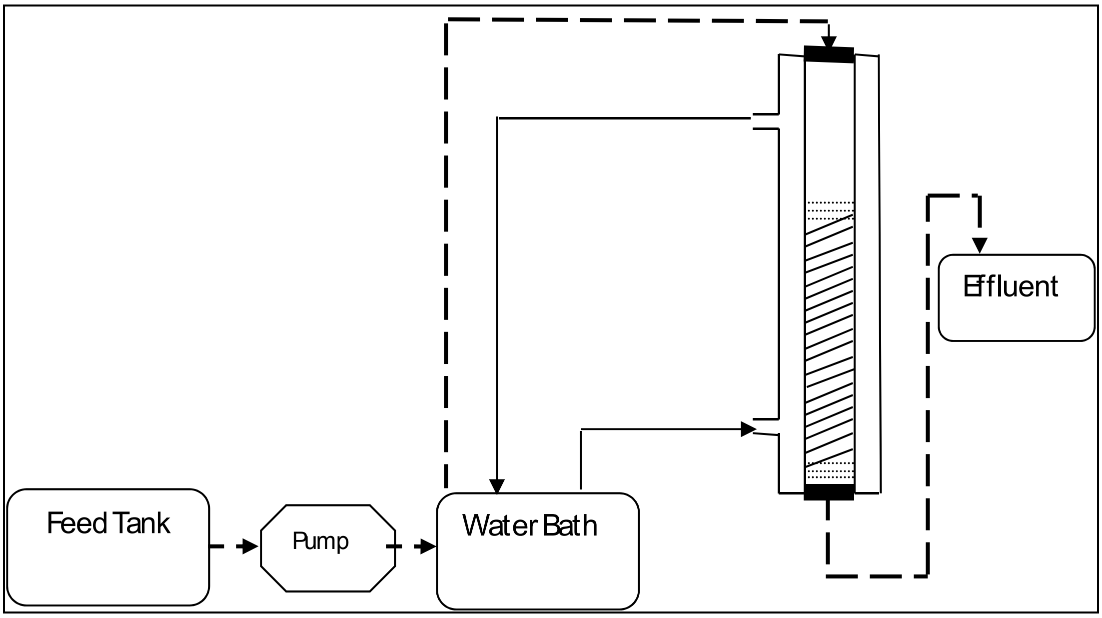


Figure 5-1 : Schematic set-up diagram of column experiment

5.1.1 Column calculations

Column calculation parameters for the four shades are presented in this section.

Column parameters

ID_S (small column internal diameter) $= 0.026$ m

L_S (small column length) $= 0.2$ m

d_S (particle diameter-small column) $= 1$ mm

pb (carbon bulk density) $= 0.425$ g/mL

ε (bed void) $= 0.4$

Q_S (flow rate-small column) $= 0.625$ mL/min

M_{CS} (mass of carbon-small column) $= 30$ g

Cross sectional area of column (A_S)

$$\begin{aligned} A_S &= \frac{\pi {ID_S}^2}{4} \\ &= \frac{\pi(0.026)^2}{4} \\ &= 531 \text{ cm}^2 \end{aligned}$$

Volume of carbon bed (V_{Bs})

$$\begin{aligned} \mathrm{V_{bS}} &= \frac{M_{CS}}{pb} \\ &= \frac{30\ \mathrm{g}}{0.425\ \mathrm{g/mL}} \\ &= 70.59\ \mathrm{mL} \end{aligned}$$

Hydraulic loading rate (V_S)

$$\begin{aligned} \mathrm{V_S} &= \frac{Q_S}{A_S} \\ &= \frac{0.625\times10^{-6}\ \mathrm{m^3/min}}{0.000531143\ \mathrm{m^2}} \\ &= 0.1177\ \mathrm{cm/min} \end{aligned}$$

Wall effect (column internal diameter: carbon particle diameter)

$$\begin{aligned} &= \frac{ID_S}{d_S} \\ &= \frac{26}{1} \\ &= 26 \end{aligned}$$

Empty bed contact time ($EBCT_S$)

$$\begin{aligned} \mathrm{EBCT}_S &= \frac{V_{bS}}{Q_S} \\ &= \frac{70.588\ \mathrm{mL}}{0.625\ \mathrm{mL/min}} \\ &= 113\ \ \mathrm{min} \end{aligned}$$

5.2 Results

Section 5.2.1 presents results obtained from column test studied. Experimental data for this chapter is presented in **Appendix D.**

5.2.1 Column breakthrough curves

The breakthrough curves obtained at different temperatures and different flowrates are presented in Figure 5-2 to Figure 5-9 for the four shades studied. The results of the breakthrough curves and exhaustion are listed in Tables 5.1 to 5.2 respectively. The sample calculation for exhaustion data is presented in **Appendix D**.

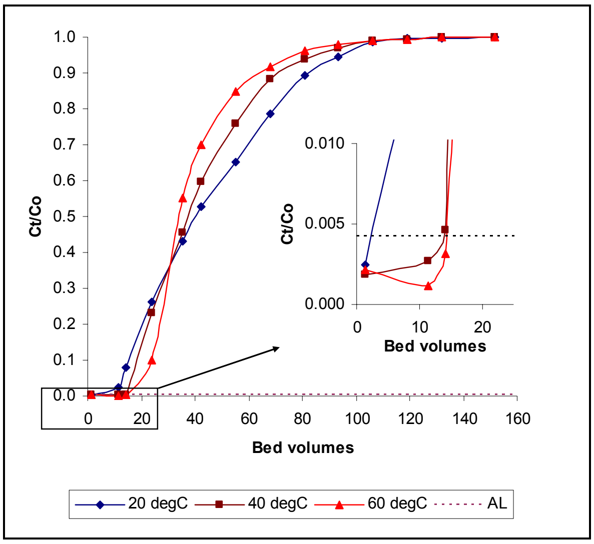


Figure 5-2 : Navy breakthrough curve at different temperatures

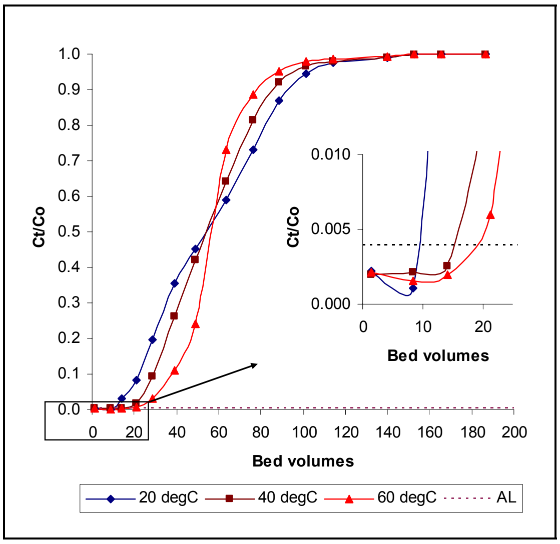


Figure 5-3 : Black breakthrough curve at different temperatures

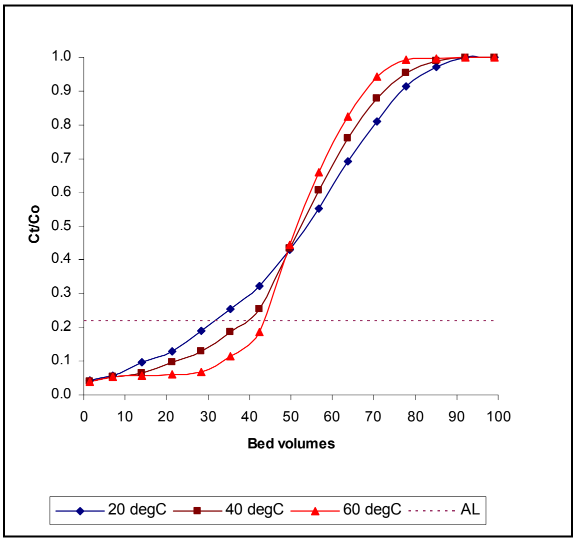


Figure 5-4 : Beige breakthrough curve at different temperatures

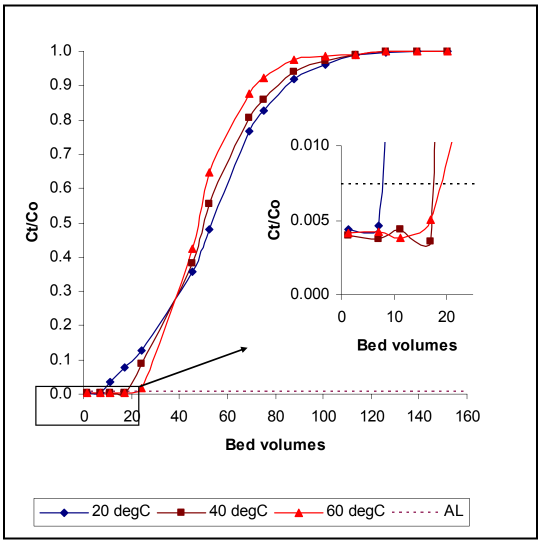
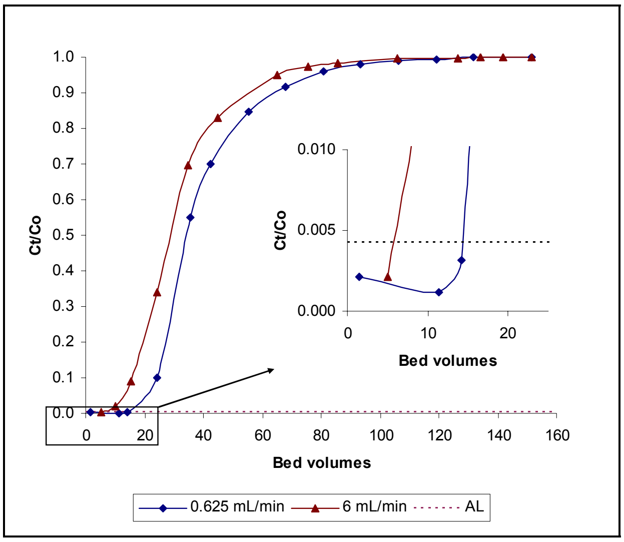


Figure 5-5 : Turquoise breakthrough curve at different temperatures

AL-Acceptable Limit for reuse



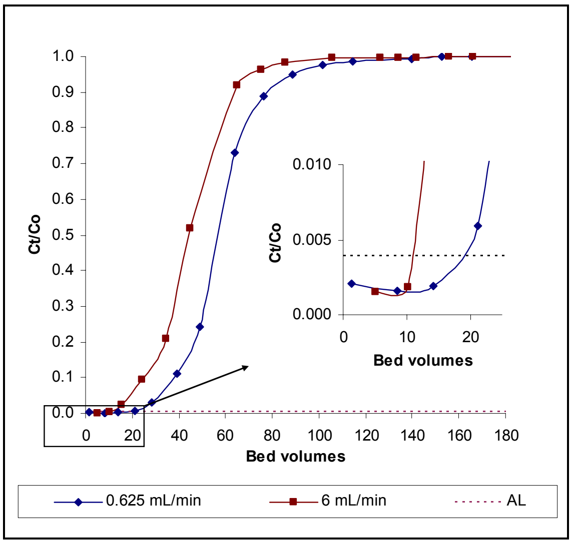
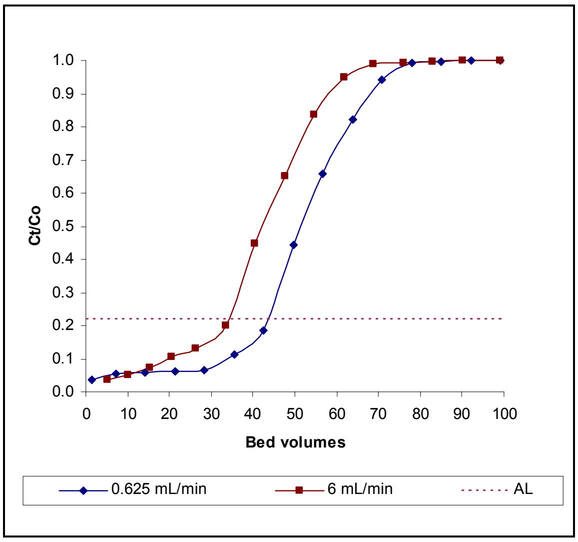


Figure 5-6 : Navy breakthrough curve at different flowrates and 60˚C

Figure 5-7 : Black breakthrough curve at different flowrates and 60˚C



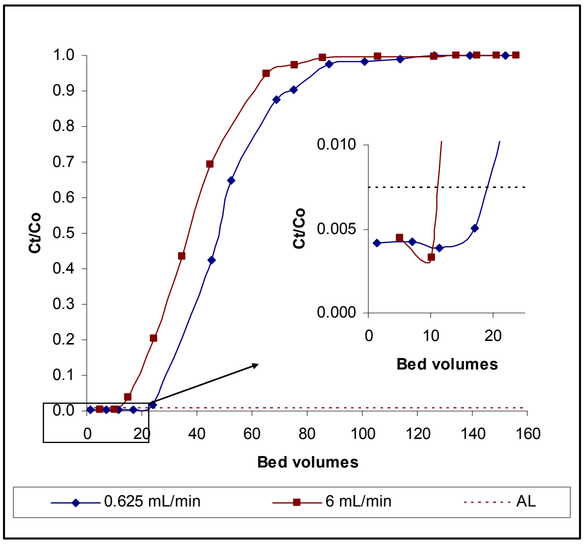


Figure 5-8 : Beige breakthrough curve at different flowrates and 60˚C

Figure 5-9 : Turquoise breakthrough curve at different flowrates and 60˚C

AL-Acceptable Limit for reuse

Table 5-1 : Column breakthrough effect of the shades to acceptable limit for reuse

Shade	Temp (˚C)	Flow rate (mL/min)	Acceptable Limit for reuse (V/Vo)	Acceptable Limit for reuse (mg dye/g carbon)	Acceptable Limit for reuse (kg fabric/g carbon)
Navy	20	0.625	1	2	0.02
	40	0.625	11	20	0.25
	60	0.625	14	25	0.33
	60	6	11	20	0.25
Black	20	0.625	8	15	0.20
	40	0.625	14	26	0.33
	60	0.625	21	37	0.50
	60	6	10	18	0.25
Beige	20	0.625	35	16	1.00
	40	0.625	40	18	1.00
	60	0.625	45	20	1.00
	60	6	34	15	1.00
Turquoise	20	0.625	7	11	0.16
	40	0.625	17	28	0.50
	60	0.625	24	39	0.50
	60	6	10	16	0.25

Table 5-2 : Column exhaustion effect (CO=95%)of the shades at different temperatures

Shade	Temp (˚C)	Flow rate (mL/min)	V/Vo	X/M (mg dye/g carbon)	kg fabric/ g carbon
Navy	20	0.625	94	72	1.69
	40	0.625	94	70	1.65
	60	0.625	81	65	1.54
	60	6	65	52	1.22
Black	20	0.625	102	92	2.17
	40	0.625	102	97	2.28
	60	0.625	89	97	2.29
	60	6	75	78	1.83
Beige	20	0.625	85	21	0.47
	40	0.625	78	21	0.47
	60	0.625	71	20	0.47
	60	6	62	17	0.38
Turquoise	20	0.625	101	80	1.88
	40	0.625	88	75	1.76
	60	0.625	88	76	1.79
	60	6	65	57	1.35

5.3 Discussion

Breakthrough curves of C_t/C_0 versus volume treated were obtained at constant flowrate (0.625 mL/min) for all four shades at different temperatures (20, 40, 60˚C) and are shown in Figs 5.2 to 5.5. The two temperatures 20˚C and 40˚C were evaluated to check the effect of column temperature but only 60˚C temperature results will be discussed in terms of breakthrough and exhaustion of the column (see Table 5.1 and 5.2). The reason for choosing 60˚C is that all the dyeing of the four shades selected is performed at 60˚C. Thus the effluent to be treated will be at the same temperature, provided it is treated immediately as there might be a possibility of a drop in temperature if it is not treated immediately (thus the reason for evaluating 20˚C and 40˚C).

The breakthrough time and volume increased as the temperature increased and it was observed that the exhaustion point decreased as the temperature increased. This may be due to that the increase in temperature allowed the swelling of the activated carbon pores, which led to a higher dye-uptake. The acceptable limit (AL) (75 ADMI) for reuse for all the shades in terms of concentrations are summarised in Table 2.2 of Chapter 2. The acceptable concentrations based on 75 ADMI for Navy and Black shades are 3 mg dye/L, for Beige and Turquoise are 41, 5 mg dye/L respectively. For treatment at 60˚C for Navy and Black shades, the AL was at 14 and 21 bed volumes respectively. Treatment of Beige and Turquoise shades, the AL was at 45 and 24 bed volumes respectively. The flow through the test column was continued until the dye concentration of column effluent (C_t) was about $0.95C_0$, which indicated the exhaustion point (Eckenfelder, 2000) and exhaustion capacity results are shown in Table 5.2.

Changes in flowrates were evaluated at 0.625 and 6 mL/min flowrates at 60˚C and the breakthrough curves are shown in Figure 5-6 to Figure 5-9. It is evident from the results obtained in Tables 5.2 to 5.3 that as the flow rate increased, the service times were shortened. As the flowrate decreased, the breakthrough time increased and longer service times were achieved. The AL for reuse for Navy, Black, Beige and Turquoise shades were at 11, 10, 34 and 10 bed volumes respectively. The variation in the breakthrough curve and adsorption capacity may be explained on the basis of mass transfer zone. Increase in flowrates caused the increase in zone speed, which resulted in decrease in time required to achieve breakthrough (Perry and Chilton, 1973).

At 60˚C and a flowrate of 0.625 mL/min to AL, a gram of activated carbon, will treat 0.33 kg fabric of Navy shades, 0.50 kg fabric of Black shade, 1 kg of Beige shade fabric and 0.50 kg fabric Turquoise shade before breakthrough occurs. The values of carbon capacity per kg of fabric (Table 5.1) and exhaustion capacity (Table 5.2) obtained from column test (ranged from 17 to 97 mg dye per gram carbon) are much lower than those of adsorption equilibrium tests (ranged from 20 to 521 mg dye per gram carbon) (see **Chapter 4**). This indicates that the column tests were not run under equilibrium conditions.

An important factor that had affected the column test results was the influence of the wall effect (ratio of column inner diameter to average particle diameter). According to Couteau and Mathaly (1997), the minimum value of 39 was considered to be sufficient to eliminate the wall effect problem although Crittenden and co-workers (1991), the minimum value to avoid channelling was 50. For the column tests evaluated the wall effect ratio was too low (26). Small particles of activated carbon are appropriate for the operation but some operational requirements such as ease of handling and low pressure drop in adsorption bed define the lower limit of particle size. For the system design discussed in **Chapter 7** one column test was repeated correcting the shortcomings of the methodology used in this Chapter. The wall effect ratio was taken into account following Crittenden and co-workers design model (Crittenden et al., 1991).

5.4 Conclusion

- For a fixed flow, higher temperatures delay the breakthrough for all the selected shades. High adsorptive capacities for AL ranging from 20 to 39 mg dye per gram carbon were observed for 60˚C (highest temperature for this column study) for all the shades evaluated. For low temperature (20˚C), the adsorptive capacity ranged from 2 to 16 mg dye per gram carbon.
- Higher temperatures exhaust the carbon quicker than low temperatures. The dye volumes for 95% exhaustion ranged from 81 to 89 bed volumes for high temperature (60˚C) while for low temperature (20˚C) was 85 to 102 bed volumes.
- A decrease in flow rate increases the adsorption capacity of the column for AL. The carbon capacity at low flow rate ranged from 20 to 37 mg dye per gram carbon while at high flow rate ranged from 15 to 20 mg dye per gram carbon.

In this chapter the adsorption dye kinetics on activated carbon were investigated and the effect of temperature on breakthrough curve and exhaustion point was observed. The advantage of using granular activated carbon for treatment of wastewater is the possibility of regeneration. The granular activated carbon exhausted with reactive dye was chemically regenerated for re-adsorption processes. The information from column test was useful for the design of column for pilot-scale use, which is presented in **Chapter 7**.

6 REGENERATION

The main objective of the regeneration treatment process is to re-establish the adsorptive capacity of the carbon for the adsorption of reactive dye, increase the usefulness of GAC and reduce costs for GAC and waste treatment. Regeneration of the adsorbent material is of crucial importance in the economic development. The saturated granular activated carbon which was used for dye removal in **Chapter 5** was subjected to regeneration. This chapter discusses the chemical regeneration of saturated F-400 granular activated carbon used in the column tests. A brief background on regeneration, experimental methods used, followed by discussion of the results and lastly conclusion that can be drawn from the experimental results are presented in this chapter.

6.1 Background

Activated carbons that are used for the removal of organic compounds from liquid phase systems will gradually become saturated, due to the concentration of contaminants on the surface of the adsorbent. When this occurs a decision must be made on how to deal with the spent material (Clark and Lykins, 1989). Due to the high manufacturing costs and the recovery of components adsorbed on the surface of activated carbon, regeneration is the preferred option. The possibility of regeneration is one of the main reasons for the wide-spread use of activated carbon as an adsorbent (Zolfl et al., 2000). There are three potential regeneration techniques: chemical, steam and thermal. Advantages of having a regeneration system are as follows:

- System is reliable from a process standpoint
- Reduces solid waste handling problems caused by disposal of spent carbon
- Saves up to 50% of the carbon cost (EPA, 2000)

Thermal regeneration is the mostly common applied regeneration method but due to high costs resulting from energy used and effluent gas treatment further alternative regeneration processes have been investigated. Thermal regeneration studies performed by Abdul and Campbell (1996) showed that a significant deterioration of the GAC pore structure resulted in reduced adsorption surface area. Due to this, many chemicals have been tested for the regeneration of activated carbon to treat wastewater. Studies by Huling and co-workers (2005) concluded that chemical regeneration of activated carbon was not an economically viable process and the overall feasibility of the process was based on chemical costs and disposal of concentrated effluent. Studies performed by Sorlini and Collivignarelli (2005) proved that base-acid regeneration for granular activated carbon system was the best amongst base, acid and thermal regeneration process for the removal of organics. The removal efficiency ranged from 50% to 60% for base-acid regeneration, 40% to 50% for thermal regeneration and about 20% for base and acid regeneration

6.2 Experimentation

The chemical regeneration procedure used for this study was developed by Santhy and Selvapathy (Santhy and Selvapathy, 2005). Experiments were carried out for the desorption of the four shades studied using 1 M NaOH as the eluent. The influent was allowed to percolate through the saturated carbon bed of 70.6 mL at a flow rate of 0.625 mL/min (see Figure 6-1 for first regeneration). From these results it was assumed that 3 bed volumes of 1 M NaOH would be sufficient. After the desorption of the shades, the carbon bed was washed with volumes of distilled water three times to remove the free alkali. A volume of 50 mL of 1 M HCl at a flow rate of 0.625 mL/min was washed through the column to neutralize any residual alkalinity. The carbon bed was finally washed with distilled water and the next cycle of operation of removal of dye from solution was performed. The process of adsorption and regeneration of carbon beds were repeated over 4 cycles of operation. The adsorption process was performed as described in **Chapter 5**.

6.3 Results

This section presents results obtained from the chemical regeneration of granular activated carbon tests for four different shades; Navy, Black, Beige and Turquoise. Figure 6-1 presents elution using 1 M NaOH. The column breakthrough curves obtained using regenerated granular activated carbon is shown in Figure 6-2 to Figure 6-5. Table 6.1 presents the exhaustion time for the regenerated carbon for the 1st, 2nd, 3rd and 4th cycles. Experimental data for regeneration is presented in **Appendix E.**

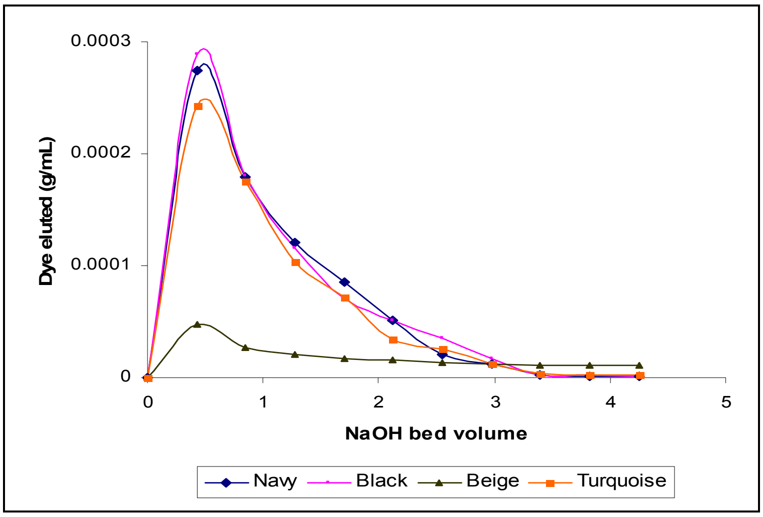
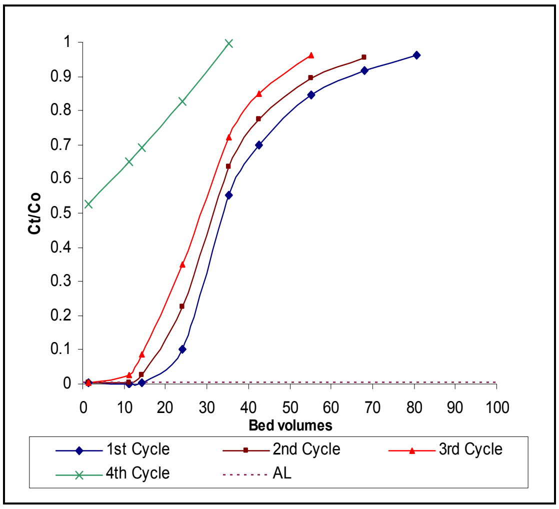


Figure 6-1 : Desorption of shades from granular activated column using NaOH



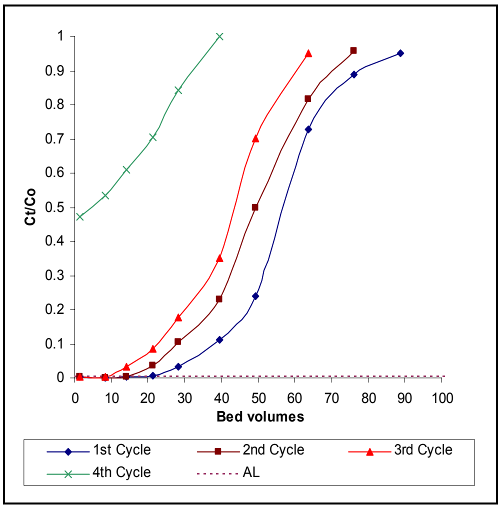
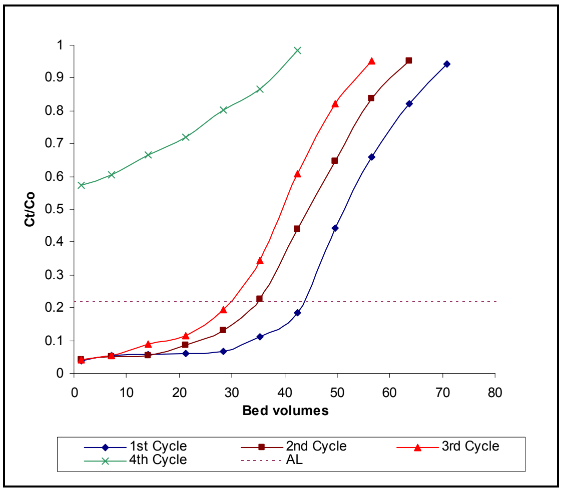


Figure 6-2 : Regeneration of GAC-Navy shade at 60˚C

Figure 6-3 : Regeneration of GAC-Black shade at 60˚C



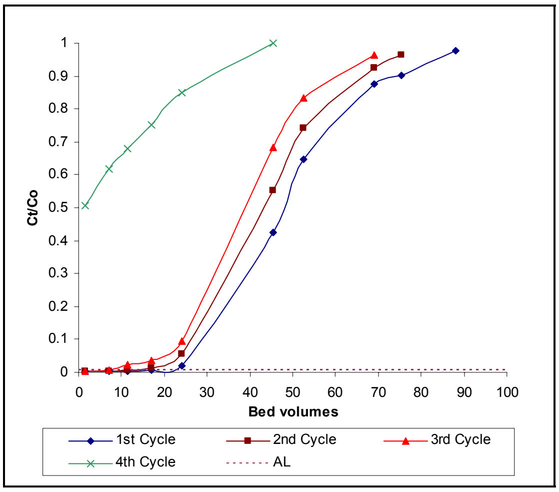


Figure 6-4 : Regeneration of GAC-Beige shade at 60˚C

Figure 6-5 : Regeneration of GAC-Turquoise shade at 60˚C

AL-Acceptable Limit for reuse

Table 6-1 : Effect of shades bed volume treated for regeneration cycles at 60˚C

Shades	Regeneration cycles	AL (V/Vo)	AL (mg dye/g carbon)	AL (g carbon/kg fabric)
Navy	1st cycle	14	25	3
	2nd cycle	11	20	4
	3rd cycle	1	2	42
	4th cycle	—	—	—
Black	1st cycle	21	55	39
	2nd cycle	14	39	28
	3rd cycle	8	29	22
	4th cycle	—	—	—
Beige	1st cycle	45	20	1
	2nd cycle	35	16	1
	3rd cycle	30	13	1
	4th cycle	—	—	—
Turquoise	1st cycle	24	39	2
	2nd cycle	15	24	3
	3rd cycle	7	11	6
	4th cycle	—	—	—

6.4 Discussion

The flow through the tested column was continued until the dye concentration of column effluent (C_t) was about $0.95C_0$, which indicated the exhaustion point (Eckenfelder, 2000).The elution of granular activated carbon was achieved using 1 M NaOH followed by 1 M HCl (Figure 6-1). About 3 bed volumes were sufficient for almost complete desorption of the four shades. From the results shown in **Appendix E**, the dye recovery for Navy, Black, Beige and Turquoise shades was 748, 765, 187 and 675 mg dye/L respectively. The percent recovery for the first cycle at 60˚C for Navy, Black, Beige and Turquoise was 97, 98, 99 and 97 % respectively. The column tests with regenerated carbon were performed at 60˚C. According to Table 6.1, the bed volumes treated for Navy and Black shades, the AL were at 14; 11 and 1; and 21, 14 and 8 for the first, second and third cycles respectively. The bed volumes treated for AL for Beige shade were at 45; 35 and 30 for the first, second and third cycles respectively. The AL for reuse for Turquoise shade were at 24, 15 and 7 bed volumes treated for the first, second and third cycles respectively.

At least three cycles of regeneration were carried out within the standard limit for reuse. Significant deterioration of the carbon was observed at the fourth cycle. A small decline in GAC adsorption capacity was observed from the first to the third regeneration cycles. The role of dye auxiliaries on the activated carbon were not evaluated in the study and it is possible that they could have major effects that are detrimental on the performance of activated carbon. The auxiliary mixtures are often developed to solve problems specific to the process and to counteract or enhance the effects of other chemicals (Hendrickx and Boardman, 1995). According to Huling et al. (2005) there are two general mechanisms that could adversely affect the adsorption capacity of the regenerated carbon. The first mechanism is the change in physical and chemical characteristics of GAC because of oxidative treatment. The second mechanism is the accumulation of by-products caused by incomplete transformation of the target compounds at adsorption sites. The change in adsorption capacity of regenerated carbon was postulated to be due to the accumulation of reactive dyes and possibly reaction by-products, which may have blocked adsorption sites.

6.5 Conclusion

- NaOH elution can regenerate the spent F-400 granular activated carbon exhausted with reactive dyes up to 3 regeneration cycles.
- Fewer bed volumes were treated as the regenerated carbon was used. As regenerated carbon was used less carbon capacity was observed.
- The removal of dyes with regenerated carbon within the limit for reuse was observed up to 3 cycles of operation.

The effectiveness of chemical regeneration of saturated carbon using NaOH was not satisfactory in terms of industrial application because of the number of cycles achieved. The results obtained showed that the use NaOH compared to other chemical regenerants need to be investigated for the implementation of activated carbon for removal of reactive dyes. The overall results from **Chapter 3** to **6** showed the possibility of designing a pilot scale system, which is presented in **Chapter 7**.

7 SYSTEM DESIGN

From **Chapter 4** and **Chapter 5**, the possibility of recovery of hot decolourised water with salt from reactive dye bath was shown to be possible by adsorption studies and chemical regeneration (**Chapter 6**). A laboratory-scale column with a small diameter, filled with carbon was tested and the dye solution was run through the column to obtain data that were used for adsorption and design. The rapid small-scale column test methodology which uses mass transfer similarity criteria to allow scale up of the test results to the full size column was evaluated for design purposes. The design of adsorption systems requires column tests similar to the actual operation of full-scale systems.

In **Chapter 5** the wall effect of the particle diameter to column diameter ratio was not taken into account, thus before designing an adsorption column for this study. One column test for Navy shade at 60˚C was performed with column internal diameter to particle diameter ratio of 50. The main objective of this chapter is to design an adsorption plant using the information obtained from the improved column (column: particle ratio of 50) adsorption study.

The column effluent was monitored for the contaminant of interest. For water treatment applications, the attainment of a specific effluent concentration is more critical than breakthrough. Thus, both the dye effluent and initial breakthrough are employed to analyze the data. The first information from the breakthrough curve is the cumulative number of bed volumes to breakthrough. In this chapter; mostly comparison of small-scale to full-scale operation will be made. A brief introduction on scaling up using RSSCT was presented in **Chapter 2** and the design methodology using the information collected is shown in Section 7.1.

7.1 Design

The RSSCT design of one of the four shades is presented in section 7.1.1 and the design is shown in section 7.1.2.

7.1.1 Small column design

The calculations presented are for the Navy shade only. Design calculations for the other three shades can be done using a similar method. The breakthrough curve for design obtained at 60˚C Navy Shade is shown in Figure 7-1 and the experimental data presented in **Appendix E**.

Navy Shade

Column parameters

$$
\begin{aligned}
ID_S &= 0.026 \text{ m} \\
d_S &= 0.2 \text{ mm} \\
pb &= 0.425 \text{ g/mL} \\
\varepsilon &= 0.4 \\
EBCT_S &= 120 \text{ min} \\
tb_S &= 952 \text{ min} \\
\mathrm{T} &= 60 \text{ degC} \\
\frac{ID_S}{d_S} &= \frac{26}{0.2} = 52
\end{aligned}
$$

The minimum column-diameter-to-particle-size ratio should be 50 to avoid channelling (i.e. ID=26 mm) (Crittenden et al., 1991).

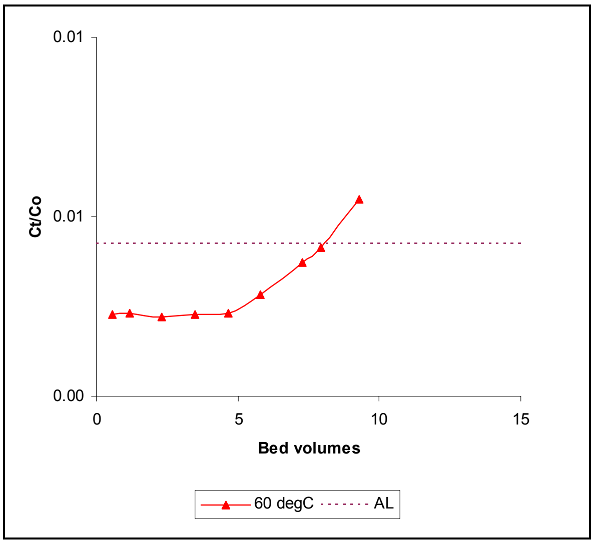


Figure 7-1 : Navy breakthrough curve at 60˚C for column design

Small-scale: Column surface area

$$
\begin{aligned}
A_S &= \frac{\pi ID_S^{\ 2}}{4} \\
&= \frac{\pi (2.6 \text{ cm})^2}{4} \\
&= 5.309 \text{ cm}^2
\end{aligned}
$$

In this study the minimum value of superficial Reynolds number (Re_S) of 1 was selected. According to Crittenden and co-workers (1991), a value of 1 for Re_S usually yields good results but lower values can be selected if head loss and column length are unacceptable. The minimum Reynolds number guarantees the effects of dispersion and the external mass transfer of the large column must be greater than in the RSSCT

Small-scale: Hydraulic loading rate (superficial velocity) using $\mathrm{Re}_s = 1$

Water viscosity (ν)= 0.89 cP

$$\begin{aligned}\mathrm{Re}_s &= \frac{g V_{\mathrm{S}} d_S}{\nu} \\ V_{\mathrm{S}} &= \frac{\mathrm{Re}_s \, \nu}{g d_S} \\ &= \frac{1 \times 0.00089}{996 \times 0.02} \\ &= 0.0045 \text{ cm/s} \\ &= 0.27 \text{ cm/min}\end{aligned}$$

Small scale: Flowrate

$$\begin{aligned}Q_S &= V_S A_S \\ &= 0.27 \text{ cm/min} \times 5.31 \text{ cm}^2 \\ &= 1.43 \text{ cm}^3\text{/min}\end{aligned}$$

Small-scale: Volume of the carbon bed

$$\begin{aligned}V_{\mathrm{bS}} &= EBCT_S \times Q_S \\ &= 120 \text{ min} \times 1.43 \text{ cm}^3\text{/min} \\ &= 172 \text{ cm}^3\end{aligned}$$

Small-scale: Mass of carbon

$$\begin{aligned}M_{CS} &= V_{bS} \times pb \\ &= 172 \text{ cm}^3 \times 0.425 \text{ g/cm}^3 \\ &= 73 \text{ g}\end{aligned}$$

7.1.2 Full-scale design

Suppose a column with 1 m internal diameter (assumption) packed with 500 kg granular activated carbon of 2 mm particle diameter was used for pilot-scale study.

Pilot-scale for Navy shade

The diffusion of adsorbate onto GAC was assumed to be controlled by proportional diffusivity where most of the mass transfer zone spreading was caused by intraparticle diffusion ($X = 1$) (Crittenden *et al*. 1991)

Pilot-scale: Empty bed contact time

$$\frac{EBCT_S}{EBCT_L} = \left[\frac{d_S}{d_L}\right]^{2-X} = \frac{t_S}{t_L}$$

$$\frac{EBCT_S}{EBCT_L} = \left[\frac{d_S}{d_L}\right] = \frac{t_S}{t_L}$$

$$\frac{d_S}{d_L} = \frac{EBCT_S}{EBCT_L}$$

$$\begin{aligned} EBCT_L &= EBCT_S \frac{d_L}{d_S} \\ &= 120 \text{ min} \frac{2 \text{ mm}}{0.2 \text{ mm}} \\ &= 1\ 200 \text{ min} \end{aligned}$$

Pilot-scale: Volume of the carbon bed

$$\begin{aligned} V_{bL} &= \frac{M_{CL}}{pb} \\ &= \frac{500 \text{ kg}}{425 \text{ kg/m}^3} \\ &= 1.176 \text{ m}^3 \end{aligned}$$

Pilot-scale: Flow-rate

$$\begin{aligned} Q_L &= \frac{V_{\text{bL}}}{EBCT_L} \\ &= \frac{1.176 \text{ m}^3}{0.833 \text{ day}} \\ &= 1.412 \text{ m}^3\text{/day} \end{aligned}$$

Pilot-scale: Feed volume for a week

$$\begin{aligned} Vo_L &= 1.412 \text{ m}^3 \times 7 \\ &= 9.880 \text{ m}^3 \text{ per week} \end{aligned}$$

Pilot-scale: Column surface area

$$\begin{aligned} A_L &= \frac{\pi {ID_L}^2}{4} \\ &= \frac{\pi (1 \text{ m})^2}{4} \\ &= 0.785 \text{ m}^2 \end{aligned}$$

Pilot-scale: Hydraulic loading rate (superficial velocity)

$$\begin{aligned} V_L &= \frac{Q_L}{A_L} \\ &= \frac{1.412 \text{ m}^3\text{/day}}{0.78 \text{ m}^2} \\ &= 1.798 \text{ m/day} \\ &\therefore 0.125 \text{ cm/min} \end{aligned}$$

Pilot-scale: Reynolds number

$$\begin{aligned} \frac{V_S}{V_L} &= \frac{d_L}{d_S} \cdot \frac{\mathrm{Re}_S}{\mathrm{Re}_L} \\ \mathrm{Re}_L &= \mathrm{Re}_S \frac{V_L}{V_S} \cdot \frac{d_L}{d_S} \\ &= 1 \frac{0.126}{0.27} \cdot \frac{0.2}{0.02} \\ &= 4.7 \end{aligned}$$

The breakthrough time of the small column and the large column should be the same.

Pilot-scale: Time to breakthrough

$$\begin{aligned} \frac{tb_S}{tb_L} &= \frac{EBCT_S}{EBCT_L} \\ tb_L &= tb_S \frac{EBCT_L}{EBCT_S} \\ &= 952 \frac{1\ 200}{120} \\ &= 9\ 520 \text{ min} \\ &\therefore 6.6 \text{ days} \end{aligned}$$

Thus the granular activated carbon will be regenerated every week.

8 CONCLUSIONS AND RECOMMENDATIONS

In this study four different dye classes were investigated (Drimarene HF, Cibacron S, Procion HE and Remazol Levafix using four standard shades (Navy, Black, Beige and Turquoise). The reactive dyestuffs contained different functional groups (chemistries). Reactive dye exhaustion to the fibre for the four reactive dye classes was about 80%, i.e. 20% remains in the effluent. Reactive dyeing of the four studied shades resulted in salt concentrations over 90% and hot coloured water remaining in the dye bath effluent. The efficiency of the dyeing process for a specific shade is associated with various parameters such as substantivity and diffusion rate of dyes, hardness of water, pH and temperature of the dye liquor, type and concentration of reactive dye used. The use of granular activated carbon for the adsorption of reactive dyes has been examined and results obtained indicated that activated carbon could effectively remove colour from exhausted reactive dye bath effluent and allow re-use of hot decolourised water with high concentration of salt.

From the adsorption results obtained using activated carbon it was concluded that the most important factor influencing the adsorption rate and capacity for the reactive dye shades studied is the adsorption temperature. Textile processes require hot water for reactive dyeing of cotton. There is great potential in the textile industry for hot water recovery. The use of heat exchangers to transfer heat to the incoming dyeing feed water can be eliminated when using granular activated carbon columns. The pH values and electrolyte concentration also played a vital role in the whole adsorption process and particularly in adsorption capacity. Colour removal of 100%, salt recovery of 94 to 97% and energy savings 17 to 32% in the dye bath effluent were achieved. Reactive dyeing of cotton is performed at high temperatures and in this study the results were discussed based on 60˚C, which was the common temperature used for dyeing for all four shades selected.

The breakthrough time from column breakthrough curves for 60˚C were at 14, 21, 45 and 24 bed volumes for Navy, Black, Beige and Turquoise shades respectively. The exhaustion or saturation times for the granular activated carbon were at 24, 41, 45 and 35 bed volumes for Navy, Black, Beige and Turquoise shades respectively. The variation in the slope of the breakthrough curve may be explained on the basis of mass transfer fundamentals of adsorption capacity of granular activated carbon. Increase in flowrate caused an increase in zone speed, resulting in decrease in the time required to achieve breakthrough, while a decrease in flowrate resulted in an increased breakthrough time. This was due to decreased contact time between the dye and carbon at higher flow rates.

From the column test results shown, the values of carbon capacity per kilogram of fabric obtained from the column test were much lower than those of the adsorption equilibrium test. The reason is that more of the adsorption sites are exposed in PAC than in the GAC and the process is faster when using PAC. The Freundlich isotherms measured in the adsorption equilibrium experiments do not apply to the column tests, perhaps due to that the equilibrium is not reached in column tests. One of the advantages of using GAC in the column test is the possibility of regeneration. From studies presented in the literature; it was shown that the required water quality for textile process is not stated. The textile industries are using drinking water quality for dyeing, therefore the 75 ADMI could be used as the standard limit when treating water for reactive dyeing reuse. Dyeing of the same shades or dyeing of a darker shade with treated light shade effluent would not need drinking water quality.

The regenerated carbon for this study was found to be effective up to 3 cycles of operation within the acceptable limit for reuse. Significant deterioration of the carbon was observed at the fourth cycle. The poor performance could be associated with role of dye auxiliaries in the overall adsorption process because of their unknown composition and chemistry (this was not divulged by the manufacturer for confidentiality. This led to the activated carbon not economically feasible for industrial application. Fewer bed volumes were treated when using regenerated carbon compared to virgin carbon. The possibility of savings exists when using regenerated GAC for treatment. Regeneration should also ensure that the eluted solution is not posing any disposal problems in terms of high acidity and high colour concentration. A further investigation of thermal regeneration of the spent granular activated carbon for the removal of reactive dyes is needed to determine its advantages and disadvantages over chemical regeneration. The design, operation and maintenance of carbon adsorption and regeneration processes depend on costs and characteristics of textile water to be treated and the capacity of the plant. Therefore the designer is responsible for selecting a system that will meet the discharge permit requirements at the lowest cost possible. Once the optimum flowrate, bed depth and operating capacity of GAC is determined, the carbon contactors configurations can be estimated. The use of RSSCT method for designing in this study has the major potential advantage over other methods in predicting the performance of pilot-scale. The carbon particle must be at least 1/50 of the column diameter to overcome the wall effect problem. Small particles of activated carbon are appropriate for the operation but some operational requirements such as ease of handling and low pressure drop in adsorption bed define the lower limit of particle size.

Further research in this area should concentrate on evaluating different activated carbons and role of auxiliaries in activated carbon adsorption studies. When implementing the laboratory-scale plant in textile industry, the effect change in temperature, pH and electrolyte concentration should be noted and the chemical parameters should also be researched. The first rinse stream has a moderate colour with low salt concentration effluent. If further colour removal is required, this stream could be treated by reverse osmosis. The permeate can be used for the first rinse and the concentrate can join dye bath effluent. The further investigation should also be expanded to the evaluation of other chemical regenerants and thermal regeneration of saturated activated carbon. The use of GAC adsorption and the regeneration of GAC should also be taken into account for water, salt and energy savings for the textile industry. This study proved that the activated carbon adsorption technique is the solution in reactive dyeing textile industries because of the possibility for re-use of water, salt and energy; thus enabling environmental improvements with savings in salt, energy and water.

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