

**REACTIVE DYE EFFLUENT TREATMENT USING A MIXTURE OF
SUGARCANE BAGASSE AND WATER HYACINTH**

BY

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DECLARATION

DECLARATION BY STUDENT

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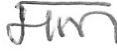
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DEDICATION

To mum and dad who have been there to provide most if not all the necessities needed for my education, may the LORD JEHOVAH bless you and give you long life. To my lovely wife Abigail and daughter Nezhah, thumbs up for always being by my side and encouraging me in my studies. To my brothers and sisters (Judith, Christine, Stacy, Dan, Beryl, Pauline, Ivy and Gynnel) thanks a lot for the support and encouragement in my academic journey. Lastly, to all my friends for the helping hand you lent at the time most needed.

ABSTRACT

Water pollution remains a major problem in developing countries. Textile industries contribute to this problem by producing large amounts of wastewater during dyeing and finishing processes. The dye that remains in the wastewater is a disturbance to the ecological system besides being a health hazard. Therefore, the main objective of this project was to develop an adsorbent material from a blend of sugarcane bagasse and water hyacinth for removal of reactive red 198 dye, commonly used on cellulosic fibers, from textile effluent. The specific objectives of the study were to develop adsorbent materials from sugarcane bagasse and water hyacinth through chemical modification, to blend modified sugarcane bagasse and water hyacinth at different ratios and analyze their dye adsorption at varied conditions (dye concentrations, particle sizes) and to optimize dye adsorption of the blend by varying adsorbent dosage, blend ratio and initial dye concentration. Sugarcane bagasse treated with 0.1M hydrochloric acid and water hyacinth treated with 0.1M sodium hydroxide were blended together and used to treat wastewater containing reactive red 198 dyes. Batch experiments were carried out varying the initial dye concentration from 5 mg/l to 50 mg/l, adsorbent particle sizes from 280 μm to 2000 μm and blend ratios of 0:100, 25:75, 50:50 and 100:0. The absorbance of the samples was measured using UV Vis spectrophotometer and percentage dye removal determined. Minitab statistical tool was used in experimental optimization based on the rotatable central composite design. A full quadratic regression equation that related the variables and the response was developed. A two-way interaction of the regression model was investigated. From the regression model, initial dye concentration and blend ratio had significant effect on adsorption since P-value was less than 0.005. Adsorption of reactive red 198 dye was optimal at initial dye concentration of 50.23 mg/l, particle size of 745.87 μm and at a blend ratio of 100:0. At these optimum conditions, the dye removal percentage was found to be 89%, with the chemical oxygen demand (COD) reduction of 95%. From the current result, it was concluded that chemically modified sugarcane bagasse could serve as adsorbent materials for removing reactive red 198 dyes from textile wastewater. Treatment of the adsorbents enhances their dye adsorption compared to non-modified adsorbents. Adsorption process may therefore be employed as a clean technology in wastewater treatment.

However, the two adsorbents should be used separately to obtain better results unless an optimal blend is established.

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LIST OF ACRONYMS

3D -	Three-dimensional
AC -	Activated carbon
ANOVA -	Analysis of variance
APHA -	American public health association
ATU -	Acute toxicity unit
BOD -	Biological oxygen demand
BSS -	British standard size
CAC -	Commercial activated carbon
CI -	Colour Index
COD -	Chemical oxygen demand
DP -	Durian peel
DRP -	Dye removal percentage
EC -	Electrical conductivity
EMCA -	Environmental management and co-ordination authority
IOC -	Inorganic chlorinated compounds
MB -	Methylene blue
NEMA -	National environment management authority
SB -	Sugarcane bagasse
SS -	Suspended solids
TDS -	Total dissolved solids
TOC -	Total organic carbon
TS -	Total solids
TSS -	Total suspended solids
VIF -	Variance inflation factor

CHAPTER ONE

1.1 Introduction

The chapter covers background information, problem statement and justification of the study, objectives to be achieved and scope of the research.

1.2 Background information

Industrialization and urbanization are taking the world to new horizons. Among the consequences is environmental disorders and the production of hazardous materials leading to environmental pollution (Sarker, Golam, Azam, El-gawad, et al., 2017; Tahir, Sultan, Akhtar, Hameed, & Abid, 2012). This is felt particularly in the developing countries. The textile industry concerned with meeting clothing demand, which is a necessity of life (Reza & Abedin, 2011) emits huge amounts of effluents. The effluents are a major source of water pollution including the ground water due to penetration in rocks and soil of the outlet streams (Profile, 2018b). Among the textile processes, dying is the most pollutant producing process. Discharge of pollutants cause widespread pollution such as organic pollution, toxic pollution and eutrophication, along with serious ecological destructions.

The effluent may contain organic compounds, which are unused or partially used, Biological Oxygen Demand (BOD), strong color and Chemical Oxygen Demand (COD). The pollution intensity depends on the fabric. Besides, dyeing sequence, dyeing equipment and liquor ratio also affect the pollution intensity.

The high population growth rate and simultaneous growth in industries has increased pollution rate in Africa.

The urban population without proper sanitation services increased from 88 million in 1990 to 175 million in 2008, and the number of people without access to drinking water rose from 29 million in 1990 to 57 million in 2008 (Gleick, 2014; Wang & Omosa, 2019).

Textile industries consume large amounts of water mainly from the dyeing and finishing operations. This wastewater from industries consists of organics, toxic materials and some other additives that result in deterioration of ecology and damage to the aquatic life. Almost 3 decades ago, disposal of wastewater into water sources or land without treatment was problematic (Ammayappan, Technology, Jose, Sheep, & Raj, 2016). In the recent years, the problem has been on the spotlight due to the increasing number of industries and their untreated discharges.

Discharge of dye effluents affects the people who may use the polluted water streams for domestic purposes such as bathing, washing and drinking. It is therefore very important to verify the water quality, even when just 1.0 mg/L of dye concentration gets its way into the drinking water because this could cause a significant color change, making it unfit for human consumption (Adegoke & Solomon, 2015).

The dyes cause various diseases and these include dermatitis, allergy, and skin irritation and provoke mutations and cancer in human beings.

1.3 Problem statement

Textile effluents have very complex structures because they contain surfactants, salts, metal ions and their metal complexes, biocides, toxic anions and toxic organic chemicals.

Textile industries generate huge volumes of effluent with extreme variation in composition and pollution load. The variability comes from the diversity in the transformation processes and the wide range of chemicals used.

Different methods have been recommended to improve the quality of textile effluent including filtration, biosorption, electromechanical treatment, solvent extraction, chemical precipitation, membrane separation and flocculation. However, the methods have disadvantages such as incomplete ion removal, production of other waste products and toxic sludge that require further disposal. Therefore, the methods do not fit the needs of the developing countries. Processes such as trickling filters and activated sludge require energy input for wastewater treatment. In rural areas, it is very difficult to practice such processes due to space and economic concern. In addition, skilled labors are required to operate such treatment processes. Moreover, the dyes are non-biodegradable in nature making them stable to light and oxidation.

Conventional methods that have been used in textile wastewater treatment are expensive and less efficient against other dyes. This project proposes adsorption treatment using a mixture of sugarcane bagasse and water hyacinth for removal of dyes from textile wastewater. The method is envisaged to be economical and able to remove both organic and inorganic components without generating other wastes.

1.4 Justification of the study

As the world population grows, there is a simultaneous rise in demand for clean water. The wastewater released from textile industries pollute water bodies and pose health concerns to living organisms.

Dyes and their precursors are well known for their high toxicity and are carcinogens as they form toxic aromatic amines (Gomes & Lu, 2003). The dyes are difficult to break down biologically due to the complex nature of their chemical structures.

Reactive dyes are important class of textile dyes experiencing significant losses during processing operations and their treatment is problematic. During the washing process, reactive dyes exhausted are about 10-50%. The rest are lost to the environment in their hydrolyzed and unfixed form hence contaminating it with about one million tons of the compounds (S. Kaur & Singh, 2007).

It is noteworthy that some of the dyes in the textile effluents are highly toxic and mutagenic and decrease the penetration of light and photosynthetic activities of aquatic plants leading to oxygen deficiency and limiting beneficial activities such as recreation, irrigation and drinking water.

From studies, about 40,000 dyes and pigments are listed, consisting of more than 7000 different chemical structures. Most of these dyes and pigments are completely resistant to biodegradation processes.

Of all the industrial wastewaters, effluents from textile plants are considered the most polluting considering the volume and the composition of the effluents (Profile, 2018a).

In addition, there are increased demands for textile products and proportional increase in their production. The use of synthetic dyes has contributed to dye wastewater becoming a serious environmental pollutant in the current times.

Agricultural wastes such as sugarcane bagasse are available in large amounts, renewable, and less expensive as compared to other materials used as adsorbents. Water hyacinth is the most problematic weed in the world (Williams, 2017). According to data by Albright et al. (2004), the plants covered tens of thousands of hectares of water surface in Lake Victoria. The infestation reduced levels of fishing, posed a threat to the biodiversity of the lake and hampered water transport. Instead of the plant being a nuisance in Lake Victoria

(Wilson, Ajuonu, Hill, Julien, & Katagira, 2018), it can be combined with sugarcane bagasse and used as adsorbent which is a value addition process. Adsorption using the two adsorbents is better than other adsorbents because they can be used without or with a minimum processing (washing, drying, grinding) and thus reduce production costs because the raw material is cheap and energy costs associated with thermal treatment are eliminated (Franca, Oliveira, & Ferreira, 2009).

According to National Environment Management Authority (NEMA) regulations, any production process undertaken should incorporate environmental concerns in the design, process and disposal of a product and done in a way to reduce toxic emissions. If wastes are generated, no person shall dispose of the wastes on a public highway, street, road, recreational area or in any public place except in a designated waste receptacle. Therefore, employing these agricultural wastes as adsorbents encourages NEMA compliance and environmental conservation.

The desorption capacity of sugarcane bagasse is also another factor that highlights the biosorbent potential of the sugarcane bagasse. These characteristics plus the availability of low cost sugarcane bagasse highlights the material as a key biosorbent for green economy. The pollutant removal capacity of bagasse not only depends on the chemical composition but also the morphological organization (the irregular structure and the different levels of porosity). Furthermore, sugarcane bagasse is easily treatable and modifiable.

1.5 Objectives

1.5.1 Main objective

Development of an adsorbent material from a blend of sugarcane bagasse and water hyacinth for optimal removal of reactive red 198 dye from textile effluent

1.5.2 Specific objectives

1. To make adsorbent materials from sugarcane bagasse and water hyacinth through chemical modification
2. To form a blend of modified sugarcane bagasse and water hyacinth at different ratios and analyze their dye adsorption at varied dye concentration and particle sizes
3. To optimize dye adsorption of the blend by varying adsorbent dosage, blend ratio and initial dye concentration

1.6 Scope of the study

The study was confined to the following areas:

- i. Adsorption of reactive red 198 using chemically modified sugarcane bagasse and water hyacinth
- ii. Sugarcane bagasse was chemically modified using 0.1M hydrochloric acid while water hyacinth modified using 0.1M sodium hydroxide
- iii. A sample wastewater prepared in the laboratory and industrial wastewater from Rivatex East Africa Limited jigger dyeing machine were used
- iv. Adsorption experiment using a mixture of sugarcane bagasse and water hyacinth was used
- v. Parameters investigated were initial dye concentration, blend ratios and particle sizes because of their influence on the adsorption of the mixture
- vi. Minitab statistical tool based on rotatable central composite design was used to optimize the adsorption process

CHAPTER TWO

2 LITERATURE REVIEW

2.1 Introduction

The chapter presents description of the dyes, activation process, effluent characterization and the adsorbent biosorption processes.

2.1.1 Description of dyes

Dyes are substances, which provide color when applied on a substrate by at least temporarily, modifying the crystal structure of the colored substance. Dyeing is a wet process of color incorporation into different fibrous forms such as loose fibre, yarn, fabric, and nonwoven in a suitable dyeing machine (Ammayappan, Jose, Sheep, & Raj, 2016; Sharma, 2020). Dyes are widely applied in cosmetics, pharmaceutical, food, textile, photographic, plastics and paper industries. The adherence of the dyes onto the compatible surfaces is through the following processes: solution, formation of covalent bonds or complexes with metals or salts, mechanical retention or physical absorption. The classification of dyes is based on their application and chemical structure.

Dyes are composed of chromophores, which are a group of atoms responsible for the dye color. The chromophores have diverse functional groups such as azo, nitro, anthraquinone, carbonyl, aril methane, methane, and others. Additionally, auxophores, the electron donating or withdrawing substituents generate and intensify the color of the chromophores. Most common auxochromes are amine, sulfonate, carbonyl and hydroxyl.

There are over 10,000 different dyes and pigments available for industrial application worldwide and over 700,000 tons of synthetic dyes are produced annually (Ammayappan, Technology, et al., 2016).

In textile, materials can be dyed using batch, semi-continuous or continuous. The process used depends on many factors including material type such as fiber, yarn, fabric, fabric construction and garment. In addition, generic type of fiber, dye size lot and dyed fabric quality requirements. Among the processes, the batch process is the most common method.

2.1.2 Textile dyes used in dyeing and printing

Textile dyes can be classified based on their chemical structures (Azo dyes, Nitro dyes, Indigo dyes, Anthraquinone dyes, Phthalein dyes, Triphenyl methyl dyes, Nitrated dyes, etc.) or their industrial application (Benkhaya, Harfi, & Harfi, 2018a).

I. Azoic dyes

The annual global production of azo dyes is about 1 million tons. The dye is found in diverse forms and natures and more than 2,000 different types of azo dyes are currently in use. According to the Azo bond linkage ($-N=N-$) there are mono azo dyes having one azo linkage, diazo dyes having two azo linkages and triazodyes having three azo linkages respectively.

Azo dyes constitute the largest portion of synthetic dyes. It is estimated that 70% of all the dyes used in industry are azo dyes. They are widely used in food industries, cosmetic, textile and leather, pharmaceutical, paper and paint. Figure 2.1 shows molecular structure of an azo dye.

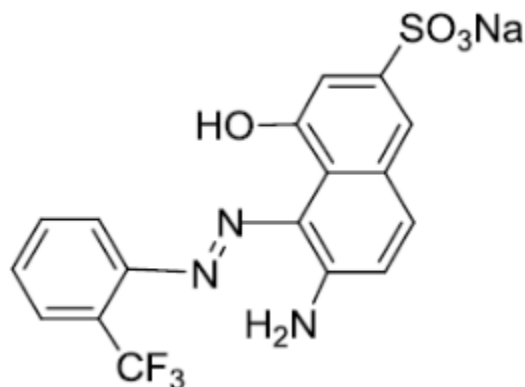


Figure 2.1: Molecular structure of azo dye

II. Vat dyes

Vat dyes are applied on cellulosic fibers, notably cotton, on which they display unparalleled levels of fastness (i.e. washing, bleach, light, etc.), due to their water insolubility. Vat dyes are not widely used because of their low substantivity coupled with the pale depths of shades that arise from their limited diffusional behavior within the fibers. Examples are vat blue 5 and acid blue 74 shown in Figure 2.2.

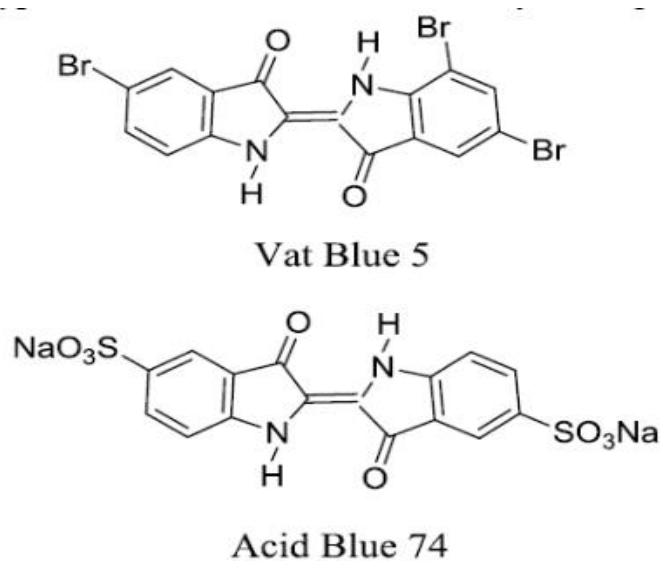


Figure 2.2: Molecular structures of Vat dyes

III. Sulphur dyes

Sulfur dyes are mainly applied in dyeing cellulosic materials or blends of cellulosic with synthetic fibers. They are also used in dyeing of silk and paper in limited quantities and on certain types of leathers. Among synthetic dyestuff classes, sulfur dyes are known to have the dullest range of colors. However, they exhibit excellent washing and good light fastness and are inexpensive. These properties combined with ease of application still make the consumption of sulfur dyes to remain high (Nguyen & Juang, 2013). Examples of Sulphur dyes are shown in Figure 2.3.

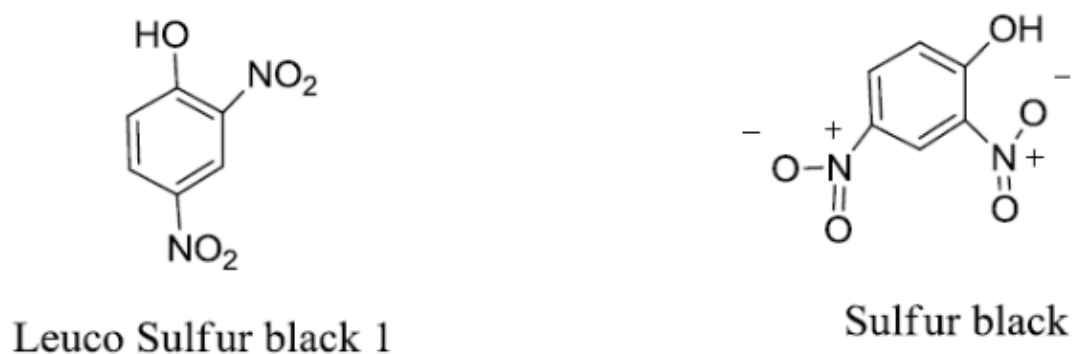


Figure 2.3: Molecular structures of commonly used two types of Sulphur dyes

IV. Acid dyes

Acid dyes can be applied to nylon, wool or silk in the pH range 3.0 - 7.0. The wet-fastness of this class of dyes range from moderate to good and their lightfastness from 5.0 to 6.0, which is the blue-scale range. Their application is under acidic conditions using either acetic or formic acid and the degree of acidity depends on individual dye properties. Acid dyes have variable fastness to washing and are generally bright.

Their molecular structures vary greatly and include some metal complexes. The defining characteristic of acid dyes is the presence of sulphonated groups responsible for water-solubility.

When these dyes are applied on wool, partial bonding occurs due to interaction between the sulphonate groups and ammonium groups on the wool fibre. Van der Waals forces provide additional bonding interaction. The degree of interaction, and hence, the degree of colorfastness varies in direct proportion with dye molecule size. An example of acid dye is C.I. Acid Blue 25 in Figure 2.4.

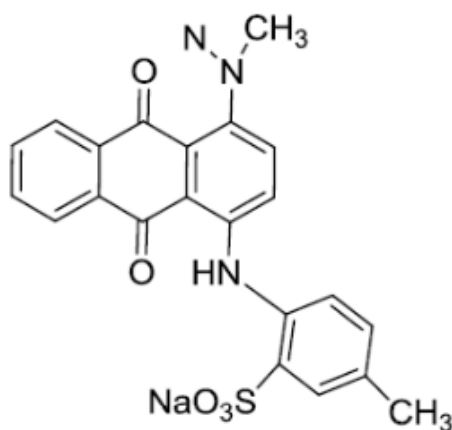


Figure 2.4: Molecular structure of C.I. Acid Blue 25

V. Disperse dyes

These are synthetic colorants for hydrophobic substrates and commonly applied as commercial mixtures in textile coloration. These dyes are frequently insoluble or sparingly soluble in water, non-ionic in character and applied to hydrophobic fibers from an aqueous dispersion.

They are mainly used on polyester but have found application to nylon, cellulose acetate and acrylic fibers. The dyes are applied to polyester at the boil with a carrier introduced to

the dye bath to facilitate diffusion of the dye into the substrate. An example of disperse dyes is C.I. Disperse Red 8 shown in Figure 2.5.

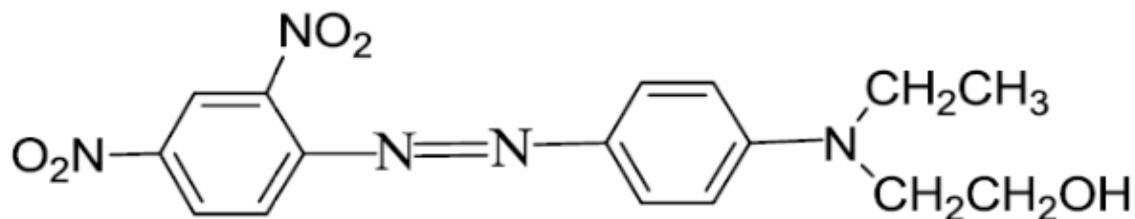


Figure 2.5: Molecular structure of C.I. Disperse Red 8

VI. Basic dyes

These dyes are usually applied to acrylic, paper and nylon substrates, but can also be used in some modified polyester substrates. Basic dyes are applied with retarders due to their poor migration properties at the boil. This poor migration is due to the rapid increase in diffusion at high temperatures and high substantivity of the dye for the substrate.

The dyes are water-soluble and produce colored cations in solution; these cations are attracted electrostatically to substrates with a negative charge (Benkhaya, Souad, & Harfi, 2020). Either the dyes can have the positive charge localized on an ammonium group or it can be distributed as a delocalized charge over the dye cation. Basic blue 24 in Figure 2.6 is an example of basic dyes.

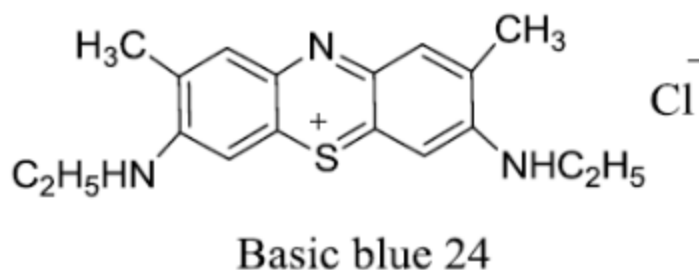


Figure 2.6: Molecular structure of Basic blue 24

VII. Direct dyes

Direct dyes have a wide shade gamut and are easy to apply. They have moderate wash-fastness performance that has led to their replacement somewhat by reactive dyes, which have much higher wet, and washing fastness properties on cellulosic substrates.

Direct dyes are classified according to many parameters such as chromophore, application characteristics or fastness properties (Benkhaya, Harfi, & Harfi, 2018b). The major chromophore types are azo, stilbene, phthalocyanine, dioxazine and other smaller chemical classes such as formazan, anthraquinone, quinolone and thiazole. An example of molecular structure of direct dyes is C.I. Direct Red 2 shown in Figure 2.7.

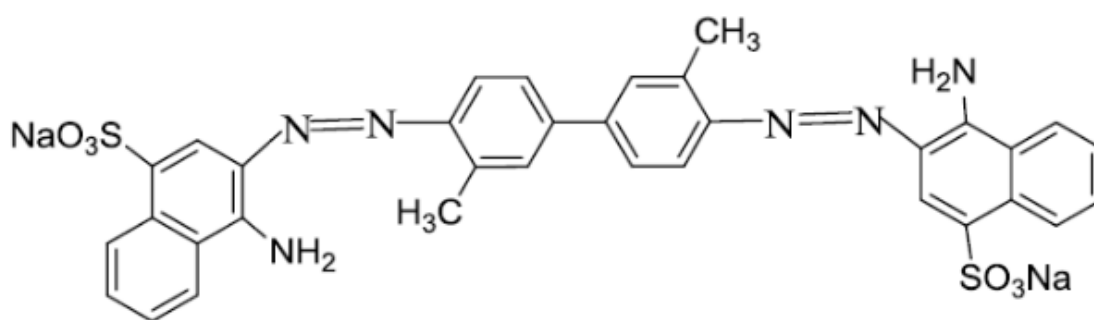


Figure 2.7: Molecular structure of C.I. Direct Red 2

VIII. Reactive dyes

These dyes have a chromophore, one or two auxophores, and a solubilizing agent. They form covalent bonds with the functional groups of the fiber through either substitution or addition reaction and is mainly applied to cellulosic fibers in the presence of an electrolyte for exhaustion and an alkali for fixation (Ammayappan, Technology, et al., 2016).

Reactive dyes can be applied either in their hydrolyzed or unhydrolyzed form. In their hydrolyzed form, the covalent bond is formed between the reactive group of the dye molecules and -OH group of cellulosic fibers.

With polyamides or wool fibers on the other hand, the bond is formed between $-NH_2$ group of the fibers and the dye molecules (Indi & Hulle, 2020; Lewis, 2011).

To overcome the low exhaustion properties due to hydrolysis of reactive dyes, Cold pad batch dyeing method is used. The method consumes small amount of water and little energy with the addition of salt eliminated. However it takes longer batching time close to 12 hours (Gopalakrishnan, Punitha, & Saravanan, 2019; Khatri, Hanif, Khatri, & Tanwari, 2011).

The dyes furnish excellent wash fastness and a wide gamut of shades of good light fastness on cotton. Such properties place this class of dyes at the quality end of the market.

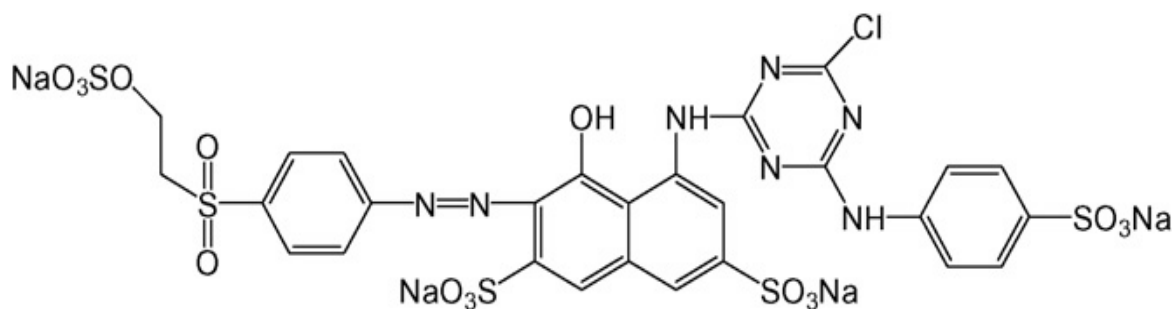


Figure 2.8: Molecular structure of Reactive Red 198

Reactive red 198 in Figure 2.8 has a chemical formula of $C_{27}H_{18}ClN_7Na_4O_{16}S_5$ with a molecular weight of 984.21 and its peak adsorption bands at 234, 392, 518 nm with the maximum wavelength on 518 nm (S. Kaur & Singh, 2007).

2.2 Sugarcane Bagasse

Sugarcane bagasse is the fibrous residue that remains after crushing and extraction of juice from sugarcane stalk.

Sugarcane originated from Asia and is found mostly in tropical and subtropical climates.

Saccharum spontaneum species of sugarcane is prevalent in eastern and northern Africa,

through the Middle East, from Malaysia, Taiwan, and China to India through the Pacific to the New Guinea.



Figure 2.9: Sugarcane bagasse treated in water and sun dried

Source: (Jorge, Silva, Antonio, Lahr, & Christoforo, 2012)

Figure 2.9 shows the sugarcane bagasse washed in water and sun dried. The washing removes dirt and other soil components that can be removed by water. Globally (mostly Latin America and Asia), approximate bagasse production was 1,900 million metric tons between 2013 and 2018 with Brazil taking the lead as indicated in Table 2.1. Brazil is the world's largest sugarcane producer with around 740 million-ton cane (43% global production) crushed in 2010/2011 harvest season (Mokhena et al., 2018).

It is estimated that about 54 million dry tons of bagasse are annually produced worldwide (Kumar, Negi, Choudhary, & Bhardwaj, 2014).

Table 2.1: Sugarcane production from different countries between 2009 and 2013

Country	Year	Average production (million metric ton yr ⁻¹)	Average annual yield of sugarcane (metric ton ha ⁻¹)
Brazil	2013	743.0	120.0
Mexico	2012	42.5 – 44.6	65.0
Colombia	2013	21.5	108.0
Argentina	2010	19.0	56.0
Cuba	2009	11.6	22.4
India	2012 - 2013	350.0	70.0
Thailand	2013	100.1	62.6
China	2013	125.5	-
South Africa	2013	20.3	-

Source: (Mokhena et al., 2018)

2.3 Sugarcane bagasse composition

The bagasse is composed of components including cellulose, hemicelluloses, lignin, ash and a small amount of extractives as shown in Figure 2.10.

Lignocellulosic matter provides a strong attractive force for the binding of the pollutant ions because of the numerous and varied functional groups.

Bioadsorbents from sugarcane bagasse are composed of macromolecules containing humic and fulvic substances, cellulose, hemicelluloses, lignin and proteins having different functional groups such as carbonyl, carboxylic, amine and hydroxyl groups, which act as adsorptive sites.

The functional groups include $-OH$, $CONH_2$, $-COOH$, $-NH_2$, $-OCH_3$ and $-SH_2$. The sites work by attracting and binding the pollutant ions by donation of electron pairs (complexation) or through ion exchange by replacing with hydrogen ions.

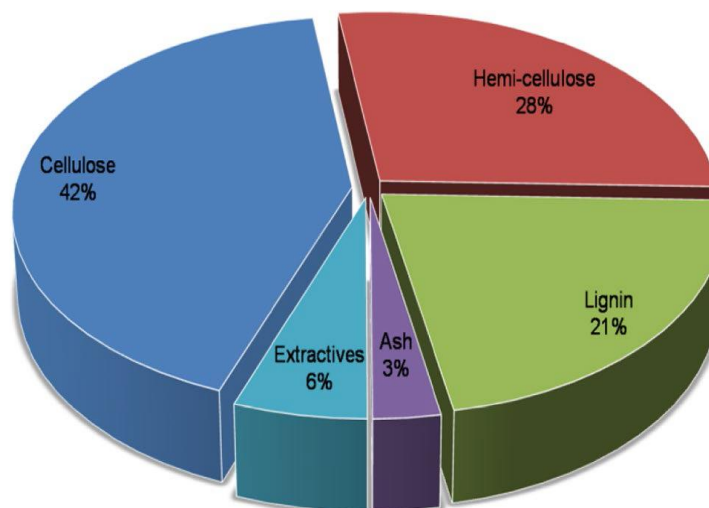


Figure 2.10: Chemical composition of sugarcane bagasse (mean value of 60 bagasse samples)

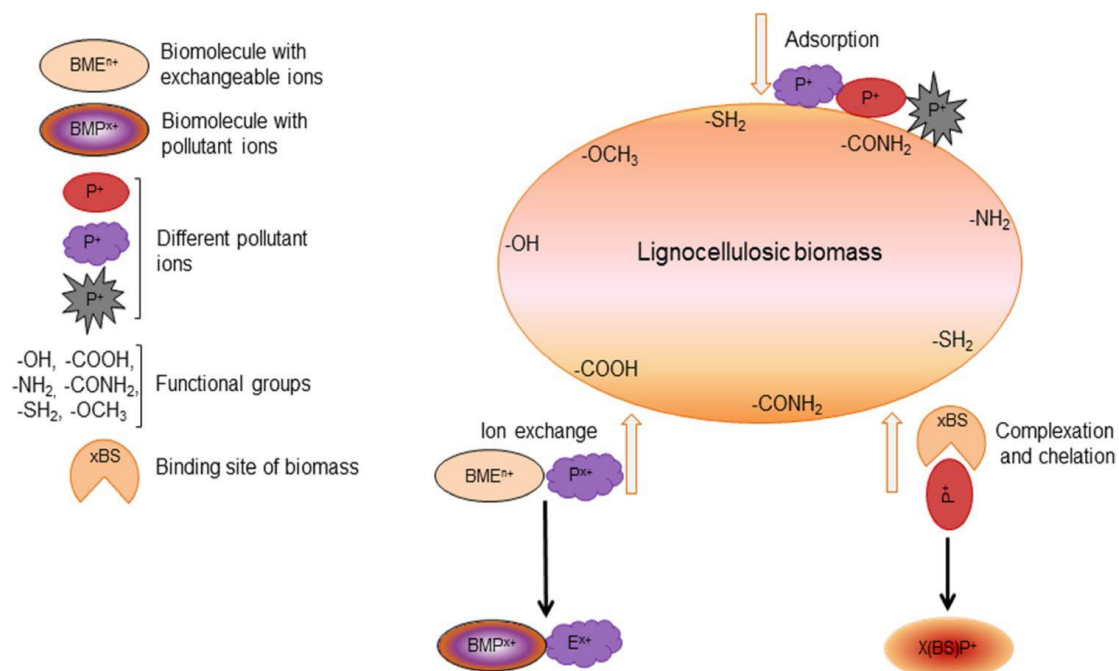


Figure 2.11: Mechanisms of biosorption using low-cost biosorbents

Source: (Sarker, Golam, Azam, El-gawad, et al., 2017)

From 2.11, the lignocellulosic chemical composition varies depending on the plant type, the soil where it is grown and the analysis conditions (if either washed or dried) (Teixeira, Souza, & Freire, 2015).

The presence of the binding sites and high level of silica make sugarcane bagasse and its derivatives effective in pollutant removal. The biological polymers such as cellulose and lignin also provide additional properties to the developed adsorbent materials.

2.4 Water hyacinth

Water hyacinth is a free-floating perennial aquatic plant that has its nativity from tropical and sub-tropical South America. Figure 2.12 is a water hyacinth plant.

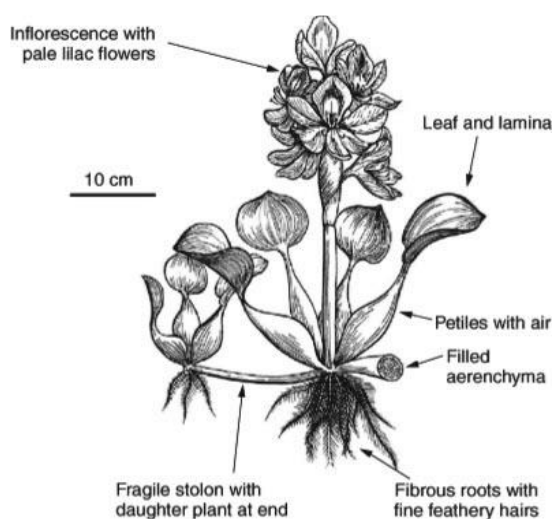


Figure 2.12: Water hyacinth plant

Source: (Williams, 2017)

- Scientific name: *Eichhornia crassipes*
- Order: Commelinales
- Family: Pontederiaceae
- Genus: Eichhornia
- Species: Crassipes

The water hyacinth plant shown in Figure 2.13 has broad, glossy, thick and ovate leaves that flatten out to make a mat on the water surface. It can arise above the surface of water as high as 1 meter in height. The leaves are 10 – 20 cm across and float above the surface of water.

The plant has long, spongy and bulbous stalks and feathery, freely hanging roots, which are thick and dense, purple – black in color and used by many macro and micro invertebrates and small or juvenile fish as a home. The erect stock supports a single spike of 8 – 15 conspicuously attractive flowers, mostly lavender to pink in color with six petals. The reproductive organs are located with the flowers on top of the mat (Ellis, 2011). Water hyacinth is considered one of the fastest growing plants, which reproduces, primarily by runners or stolons which later become daughter plants. The plant produces many seeds that are viable up to thirty years.

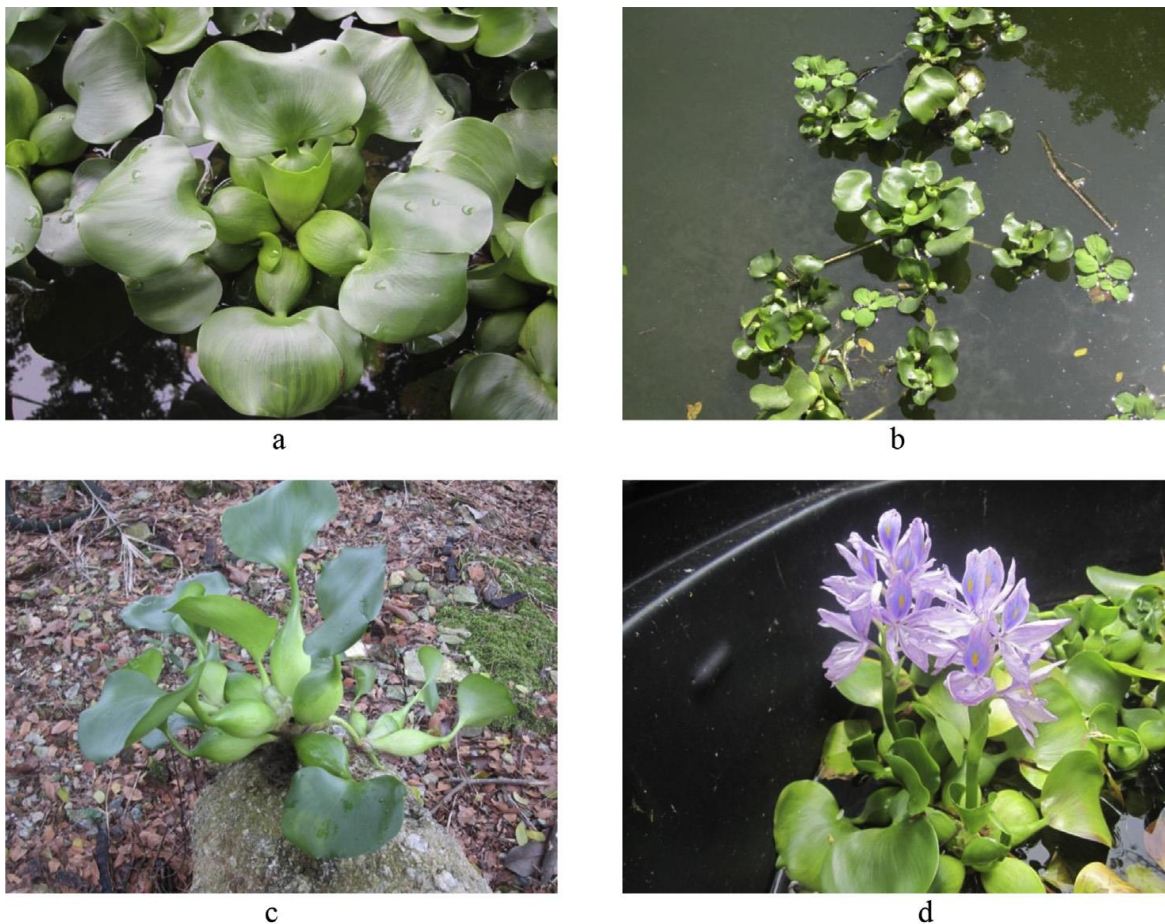


Figure 2.13: Different parts of water hyacinth (*Eichhornia crassipes*). a) Leaves b) Baby plant c) Rhizome d) Flower

Source: (Rezania, Ponraj, Talaiekhosani, Sabbagh, & Sairan, 2015)

The common category of water hyacinth (*Eichhorniacrassipes*) is a vigorous grower known to double its population in two weeks. Water hyacinth creates colonies and it is very likely that one will never see *E. crassipes* as a single standing plant. The plant has extreme tolerance with a high capacity for the uptake of heavy metals, including Cr, Cd, Co, Ni, Pb and Hg making it suitable for bio cleaning of industrial wastewater (Ellis, 2011).

Besides the heavy metals, *Eichhorniacrassipes* can also remove other toxins such as cyanide, which is environmentally beneficial in areas that have endured gold mining operations. From arsenic contaminated water, water hyacinth can remove arsenic.

2.5 Textile Effluent treatment

The removal of dyes from dye effluents is a serious environmental challenge and government legislation requires that the wastewater from textile industries should be treated.

As a result, there is a constant need of an effective process that can efficiently remove the dyes. Adsorption by agricultural byproducts has proven to be both economical and realistic method for removal of the many types of pollutants found in textile waste water such as heavy metals (Argun, Dursun, Ozdemir, & Karatas, 2007; Kheireddine, Leong, Teo, & Yang, 2008), COD, phenol, gasses and dyes.

Textile wastewater is a mixture of total dissolved solids, dyes, heavy metals, organic compounds, surfactants, salts, chlorinated compounds, biological oxygen demand (BOD), chemical oxygen demand (COD). Some studies have therefore tested the agricultural wastes as adsorbents for these pollutants.

Ahmad and Hameed used bamboo activated carbon to study the reduction of color and COD, and their results were 91.84% and 75.21% for maximum reduction of color and COD respectively (Adegoke & Solomon, 2015).

2.6 Chemical modification of the adsorbents

Chemical modification is the process of impregnating the adsorbent with chemicals such as HCl, NaOH, KOH, ZnCl₂, H₃PO₄, or K₂CO₃ followed by heating in a nitrogen atmosphere at temperatures in the range of 450 - 900 °C, or under room conditions depending on the

chemical used. In this process, carbonization and activation are achieved simultaneously. Chemical modification offers several advantages such as it can be carried out in a single step under lower temperatures.

Moreover, it results in the development of a better porous structure as shown in Figure 2.14. Besides, part of the added chemicals (such as zinc salts and phosphoric acid), can be easily recovered (Royer et al., 2009; Zhang et al., 2004). Physical activation do not give satisfactory characteristics of the adsorbents (Ioannidou & Zabaniotou, 2007).

Modification of sugarcane bagasse significantly improves the sorption potential. A study by Yu et al. (2012) on methylene Blue removal using pyromellitic dianhydride modified sugarcane bagasse gave a 12 - fold higher adsorption capacity than the unmodified sugarcane bagasse. Fasoto et al. (2014) also found that unmodified sugarcane had lower adsorption capacity for Cr (VI) and Zn (II) than modified sugarcane bagasse (Sarker, Golam, Azam, El-gawad, et al., 2017).

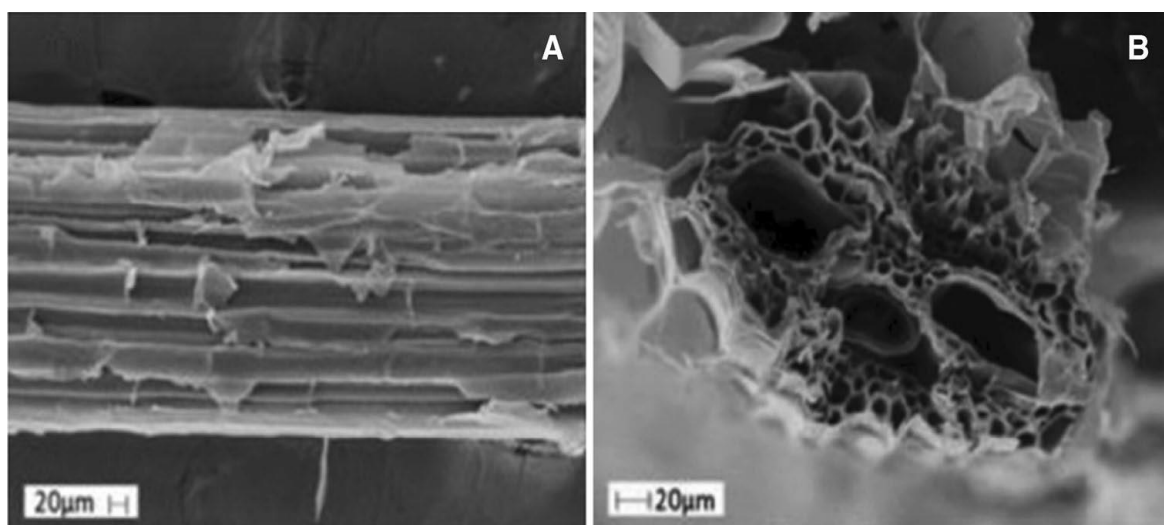


Figure 2.14: Scanning electron micrographs of modified sugarcane bagasse fiber surface in

A and Fiber cross-section in B

2.7 Review of adsorbents used in textile effluent treatment

Activated carbons (AC) of corncob wastes with surface area in the range of 538 - 943 m²/g were able to remove 432 - 790 and 230 - 1060 mg/g of Basic Red 22 (telon blue) and Acid Blue 25 (astrazon red), respectively.

Compared to AC prepared from plum kernel (surface area 1162 m²/g) and bagasse (surface area 607 m²/g), the removal capacity of AC from corncob for acid blue 25 was the highest (“Adsorption of Dyes and Phenols from Water on the Activated Carbons Prepared from Corncob Wastes,” 2010; Juang, Wu, & Tseng, 2002).

Namasivayam et al. used coir pith, an agricultural residue, for the adsorption of rhodamine B and acid violet dyes. The starting material was dried, sieved and carbonized at 700 °C. The results showed that rhodamine B adsorption reached equilibrium stage at 5, 7, 10, and 10 min for dye concentration 10, 20, 30 and 40 mg/L, respectively while crystal violet had equilibration time of 40 minutes for all concentrations studied (Namasivayam, Radhika, & Suba, 2001). The low adsorption capacities of 8.06 mg and 2.56 mg/g of the adsorbent for acid violet and rhodamine B, respectively, make coir pitch a poor adsorbent for the removal of dyes.

Wool carbonizing waste investigated by Perineau et al. for the adsorption of dyes reported that the surface properties of the material tended to adsorb solutes of ionic nature. The adsorption of basic dyes was found to be 6 to 10 times higher than that of acid dyes (Adegoke & Solomon, 2015).

Hakimi and Hameed utilized durian peel (DP) to remove acid dye from aqueous solutions. The adsorption equilibrium and kinetics of acid green 25 (AG25) from the aqueous solutions at initial dye concentrations of (50–500 mg/L), pH (2–10), and temperature (30 -

50 °C) were studied in a batch mode operation. The equilibrium data by Langmuir isotherm model with maximum monolayer adsorption capacity of 63.29 mg/g at 30 °C indicated the potential of DP as adsorbent for the removal of acid dye from aqueous solution (Hameed & Hakimi, 2008).

Rice husk ash a waste from rice mills was used as an adsorbent for removal of acidic dyes namely acid violet 17, acid violet 54, acid violet 49, acid blue 15, and acid red 119 and their COD from aqueous solutions. The adsorption capacity varied from 99.4 to 155 mg/g, with a period of 30 - 120 minutes as the optimum for attaining equilibrium (Adegoke & Solomon, 2015).

In a study to investigate the efficiency of carbonaceous adsorbent in removing dyes and phenols, the authors compared carbonaceous adsorbent with slag, blast furnace, dust and sludge (steel industry waste) and found carbonaceous adsorbent to be the most efficient among them.

Further, comparison of the carbonaceous adsorbent with an activated carbon showed it to be 45% efficient for acid dyes (ethyl orange, metanil yellow and Acid Blue113) and 70 to 80% efficient for basic dyes (chrysoidine G, crystal violet, and meldola blue) as compared to a commercial activated carbon (Jain, Gupta, & Jain, 2004). Tables 2.2 summarizes dye removal efficiencies of different adsorbents.

Table 2.2: Removal of Dyes using different adsorbents

Dyes	Adsorbent	pH values	Temperature (°C)	% of Removal
Food azo dye	Glass beads coated with chitosan	3.5, 4.5 & 6	50	40.9 - 74.7
Methyl Orange	Montmorillonite	4	60	76
Methyl blue	Phoenix tree leaf powder	4 - 10	50 - 110	60.7
Toluenediamine	Activated carbon	4 - 10	30 - 50	72.43
Benzaldehyde	Granular activated carbon (Coconut husk)	8.4	20.15	88
Acid dye	Pristine & acid activated clay	3.5 - 9	65	78.42
Reactive azo dye	Argano-zeolite	3 - 10	85 - 125	81.24
Tectilon blue	Granular activated carbon	7.4	140	85.2
Crystal violet dye	Surfactant modified alumina	3.5, 8 & 11.5	44 - 85	74.6
Acid dye	Activated carbon	3.5 - 9	74	86.8
Methylene blue and red 22	Beech saw dust	3 - 5	23 & 100	68 - 74
Methylene blue	Rice husk	7.5 & 9	70 - 140	84.6
Methylene blue	Jack fruit leaf powder	3.9 - 10	50 - 120	87.4
Pentachloro phenol	Alginate-encapsulated pillared clay	5.3	35	70.25

Source: (Karthik, Kamal, V, & Mannarthippusulthan, 2015)

2.8 Amalgamation of sugarcane bagasse with other agricultural wastes

The bagasse easily amalgamates with other agro-industrial wastes such as corncobs, tea waste, grape stalks, saw dust and apple peel. Water hyacinth has extreme tolerance with a high capacity for the uptake of heavy metals, including Cr, Cd, Co, Ni, Pb and Hg making it suitable for bio cleaning of industrial wastewater (Rezania et al., 2015).

Besides the heavy metals, water hyacinth can also remove other toxins such as cyanide, which is environmentally beneficial in areas that have endured gold mining operations. From arsenic contaminated water, water hyacinth can remove arsenic. Appendix 2 is a summary of the removal of heavy metals from different types of wastewater.

Sugarcane bagasse with a high adsorption and desorption capacity when combined with water hyacinth having very high affinity for heavy metals and other toxins can best form a hybrid adsorbent for textile waste water treatment.

2.9 Textile dyeing effluent characterization and the adsorption process

2.9.1 Textile industry effluent

Textile industries use large quantities of water and chemicals especially in the finishing and dyeing processes. On average, 60 - 90% of total water consumption is spent in washing processes. Therefore, it is estimated that around 10 - 15% of the dyes are lost during the dyeing process. The wet processing operations have very high water demand (Table 2.3) more than 5000 m³ per day for a large mill. Approximately, 120 liters of water are needed for each kilogram of cotton produced (Ammayappan, Technology, et al., 2016).

Table 2.3: Typical water usage for 1kg of woven fabrics in textile wet processing

Subcategory	Minimum	Median	Maximum
Simple processing	12.5	78.4	275.2
Complex processing	10.8	86.7	276.9
Complex processing plus desizing	5.0	113.4	507.9

Source: (Union, 2002)

The industries use both natural (cotton, wool and silk) and synthetic fibers (polyester, acrylics and nylon). The production of the natural and synthetic fibers is approximately equal. However, in the synthetic materials, polyester accounts for about half. Pollutants in wastewater vary greatly and depend on the chemicals and treatment processes used. The likely pollutants include suspended solids, biodegradable organic matter; toxic organic compounds e.g. Phenols and heavy metals (Tufekci & Toroz, 2007).

Textile industries are distinguished based on their raw materials, which determines the volume of water used as well as the wastewater generated (Dey & Islam, 2015b). During each stage as shown in Figure 2.15, different chemicals and other additives are used such as strong alkalis, strong acids, inorganic chlorinated compounds (ICO), hypochlorite of sodium, organic compound such as dyestuff, bleaching agent, finishing chemicals, thickening agents, starch, wetting and dispersing agents, surface-active chemicals, and salts of metals. Various dyes are used for coloring purposes and multicolor to improve the products. Figure 2.15 presents the processing steps and associated pollutants.

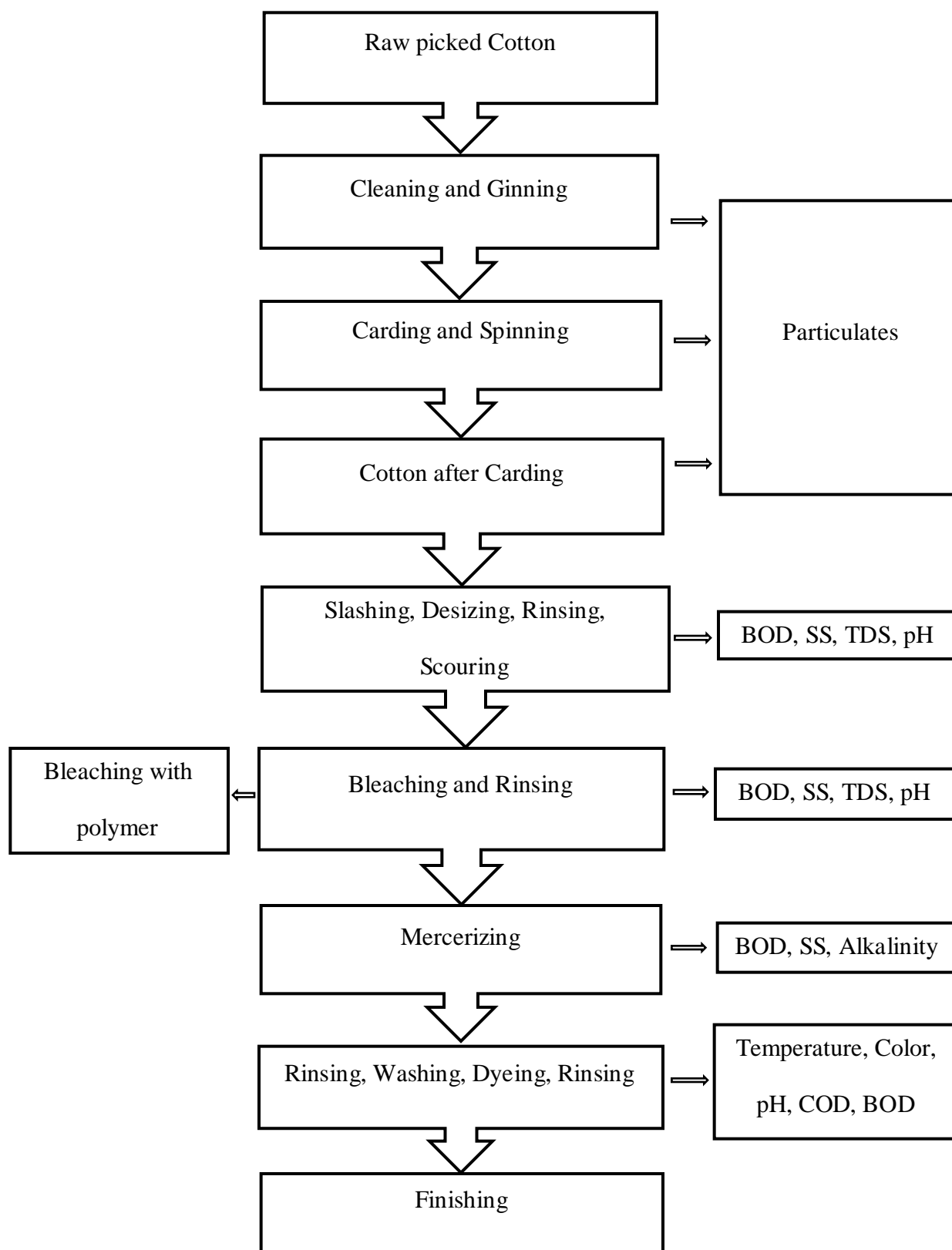


Figure 2.15: Cotton processing steps and associated pollutants

Textile wastewaters are characterized by extreme fluctuations in parameters such as biochemical oxygen demand (BOD), chemical oxygen demand (COD), pH, salinity and color.

The wastewater composition depends on the organic based compounds, dyes and chemicals used in the dry and wet processing steps. Recalcitrant organic, colored, toxicant chlorinated compounds, surfactants, and salts are the main pollutants in the textile effluents.

In addition, other effects caused by textile effluents are reduction in the aesthetic quality and transparency of water bodies such as rivers, lakes and others leading to the destruction of the aquatic environment.

From Table 2.4 about 10 - 50% of colorants are lost to the environment hence contaminating it with about one million tons of the compounds. Notably, some of the dyes in the textile effluents are highly toxic and mutagenic and decrease the penetration of light and photosynthetic activities of aquatic plants leading to oxygen deficiency and limiting beneficial activities such as recreation, irrigation and drinking water.

Table 2.4: Fixation degree of different dye classes

Dye class	Fiber type	Fixation degree (%)	Interaction between dye and fiber
Acid	Wool, silk, nylon	80-95	Hydrogen bonding, ionic bonding, van der Waals forces
Basic	Acrylic, silk	95-100	Hydrogen bonding, ionic bonding
Direct	Cellulose	70-95	Hydrogen bonding, van der Waals forces
Metal complex	Wool	92-98	Hydrogen bonding, ionic bonding, van der Waals forces, hydrophobic bonding
Reactive	Cellulose	50-90	Covalent bonding, hydrogen bonding
Sulphur	Cellulose	60-90	Hydrogen bonding, van der Waals forces
Vat	Cellulose	80-95	Hydrogen bonding, van der Waals forces
Disperse	Polyester, nylon	90-100	Van der Waals forces, hydrophobic bonding
Modified basic	Acrylic	95-98	Ionic bonding, van der Waals, hydrophobic bonding

Source: (Ammayappan, Technology, et al., 2016)

Every year, 200,000 tons of the dyes are lost as effluents during the dyeing and the finishing processes (Ogugbue & Sawidis, 2011). Unfortunately, most of the dyes in the effluents escape the conventional treatment processes and find their way into the environment as a result of their high stability to temperature, light, water, detergents, chemicals, soap and other parameters such as perspiration and bleach.

In addition, anti-microbial agents used in the manufacture of textiles, particularly for natural fibers such as cotton are resistant to biological degradation because of the synthetic origin and complex aromatic structure.

However, environmental legislations oblige industries to eliminate color from their dye-containing effluents, before disposal into water bodies. Appendices 3 and 4 highlight the standards of effluent discharge into both public sewers and environment.

2.9.2 Key parameters for textile dyeing effluent

The main parameters listed in the water quality discharge standards are briefly discussed to give a working knowledge of what they are and why they are important (Dey & Islam, 2015b).

I. Color

Color is an issue in the dye house because it is so visible. It is therefore reduced or removed to enhance public perception of the factory. International buyers are also setting discharge standards for color. However, it is of less concern compared to other parameters in terms of health and environmental issues. One of the difficulties experienced in wastewater treatment of the textile industries is the color removal because dyes and pigments are designed to resist biodegradation hence remain in the environment for a long

period. An example is the hydrolyzed Reactive Blue 19, which takes about 46 years at pH 7 and 25 °C (Dey & Islam, 2015b).

II. Biological oxygen demand (BOD) and Chemical oxygen demand (COD)

Determination of the oxidisable organic matter is achieved by determining the 5-day biological oxygen demand (BOD₅), the chemical oxygen demand (COD) and the total organic carbon (TOC). BOD₅ is a measure of the quantity of dissolved oxygen used by microorganisms in the biochemical oxidation of the organic matter in the wastewater over a 5 - day period at 20 °C (Dey & Islam, 2015b).

The test is important as it determines the approximate quantity of oxygen that will be removed from water by an effluent or how much may be required for treatment. COD is a substitute of BOD and takes only few hours and not five days to determine. It is a measure of the oxygen equivalent of the organic matter chemically oxidized in the reaction. It is determined by adding dichromate in an acid solution of the wastewater.

III. Dissolved oxygen

This is the measure of gaseous oxygen dissolved in an aqueous solution. Oxygen gets into water by diffusion from the surrounding air by rapid movement process of aeration and as a waste product of photosynthesis. In performing the test, only grab samples are used and the analysis performed immediately. This is a field-test that is done on site.

IV. Total dissolved solids (TDS) and total suspended solids (TSS)

Analysis of total dissolved solids (TDS) and total suspended solids (TSS) is done after the removal of coarse solids such as rags and grit. A sample of wastewater is taken then filtered through a standard filter paper and the mass of the residue gotten is used to calculate TSS. Total solids (TS) are found by evaporating water at a specific temperature.

TDS is then calculated by subtracting TS to TSS. Currently TSS and TDS are measured by pocked sized meters.

V. Phosphorus, Total Nitrogen, Nitrate and Ammonia

These parameters measure the nutrients present in the wastewater. A high nutrient content results in excessive plant growth in receiving water bodies, subsequent oxygen removal and the death of aquatic life.

VI. pH

This is the measure of the negative logarithm of hydrogen ions concentration in the wastewater. It gives an indication of the acidity or the alkalinity of the wastewater. pH is important because aquatic life such as fish can survive in a pH of around 6 - 9.

VII. Sulphur and sulphide

The textile dyeing process uses large quantities of sodium sulphate and other sulphur salts. The wastewater will therefore contain sulphur compounds and once in the environment, the sulphate can be converted to sulphide when the BOD process removes oxygen. Hydrogen sulphide can be formed which is very poisonous and has unpleasant smell of rotten eggs. The presence of sulphide in effluent interferes with biological treatment processes.

VIII. Oil and grease

This includes lubricating oils and kerosene, oil, fats and waxes. Oils and grease cause unpleasant films on open water bodies and negatively affect aquatic life by blocking penetration of oxygen into water bodies through aeration process. They can interfere with biological treatment processes and cause maintenance problems as they coat the surface of components.

IX. EC (Electrical conductivity)

The electrical conductivity estimates the total amounts of solids dissolved in water - TDS. TDS is measured in ppm (parts per million) or in mg/l. Electrical conductivity is directly related to the concentration of the salts dissolved in water, and therefore the Total Dissolved Solids (TDS). The electrical conductivity of the water depends on the water temperature i.e. the higher the temperature, the higher the electrical conductivity. For every increase of 1 degree Celsius of water temperature, electrical conductivity increases by 2 - 3% (Dey & Islam, 2015a). The commonly used units for electrical conductivity are $\mu\text{S}/\text{cm}$ (micro Siemens/cm) or mS/cm (milli-Siemens), where: $1 \text{ mS} = 1000 \mu\text{S}$. Table 2.5 therefore summarizes the characteristics of textile-dyeing effluent at different stages of processing.

Table 2.5: Effluent Characteristics of Textile Industry Processes

Process	Effluent Composition	Pollutant Nature
Sizing	Starch, waxes, Carboxymethyl Cellulose (CMC), Polyvinyl Alcohol (PVA), wetting agents.	High in BOD, COD
Desizing	Starch, CMC, PVA, fats, waxes, pectins	High in BOD, COD, SS, dissolved solids (DS)
Bleaching	Sodium Hypochlorite, Cl ₂ , NaOH, H ₂ O ₂ , acids, Surfactants, NaSiO ₃ , Sodium Phosphate, short cotton fibre	High alkalinity, high SS
Mercerizing	Sodium Hydroxide, cotton wax	High pH, low BOD, high DS
Dyeing	Dyestuffs Urea, reducing agents, oxidizing agents, Acetic acid, detergents, wetting agents.	Strongly colored, high BOD, DS, low SS, heavy metals
Printing	Pastes, urea, starches, gums, oils, binders, acids, Thickeners, cross-linkers, reducing agents, alkali	Highly colored, high BOD Oily, appearance, SS, slightly alkaline

Source: (Dey & Islam, 2015b)

X. Toxic metals

Wastewater from textile industries is not free from metal contents. There are two main sources of the metals. Either, they may come as impurities with the chemicals used during processing such as sodium carbonate, caustic soda and salts or could be dyestuffs like metalized mordent dyes.

A number of metals are listed in the national environmental quality standards for industrial wastewater, including zinc, nickel, cadmium, copper, chromium, iron, lead and mercury (Appendix 3). Metal complex dyes are mostly based on chromium. Many metals, which are naturally available in trace elements, can be toxic to humans, fish, plants and other aquatic life (Dey & Islam, 2015b; Okareh, 2015; Profile, 2016b). Lead for example leads to Kidney damage, brain damage in fetals and appetite loss.

Zinc is known to cause depression, increased thirst, complete or partial paralysis and neurological problems. Nickel causes nausea, coughing, dermatitis, chronic asthma and it is carcinogenic. Chromium leads to headache, nausea, vomiting and diarrhoea. Cadmium is carcinogenic besides causing kidney failure and renal disorders. Mercury is associated with rheumatoid arthritis, kidney problems, circulatory and nervous systems disorders (A. Kaur & Sharma, 2017).

2.9.3 Technologies for dye removal

According to Adegoke & Solomon, 2015, there are three main categories of methods for textile wastewater treatment (Appendix 5). These include biological, chemical, and physical methods (Adegoke & Solomon, 2015). However, all the methods have their advantages and disadvantages. The high cost and the disposal problems registered by many of these conventional methods have made it difficult for these methods to be applied at

large scale in both the paper and textile industries. At the present, there is no single process capable of complete wastewater treatment because of the complex nature of the effluents (Janoš & Šmídová, 2005; Zhu & Ma, 2008).

Due to the high concentration of organics in the effluents and the high stability of modern synthetic dyes, discharge of textile effluents into water bodies is harmful to aquatic life. Thus, there is an urgency of finding an advanced treatment process, which is both economical and effective for colored wastewater. Therefore, finding substitutes that are efficient, economical and eco – friendly are important. The process of adsorption is a well-established process for removing both organic and inorganic compounds and metals. The process requires less investment in terms of both land and initial cost, the operation is easy and with a simple design.

Furthermore, there is no threat from toxic substances and removes larger extent of organic waste constituents (complete removal possible) as compared to conventional biological treatment process (Profile, 2016a; Reza & Abedin, 2011).

Adsorption employing commercial activated carbon (CAC) effectively removes dyes from wastewater. The effectiveness is due to structural characteristics and the porous texture leading to larger surface area. The chemical nature is easily modified by chemical treatment.

Application of activated carbon produces quality effluents in the adsorption process (Yang, Kheireddine, Mohd, & Wan, 2008).

In spite of the above, CAC has high cost, ineffective against disperse and vat dyes, regeneration process after exhaustion is expensive and it results in the loss of the adsorbent

efficiency when regenerated (Chandra, Deo, & Mani, 2007). These and other problems led to more research done on the area.

Water hyacinth and bagasse do not require any energy consumption. It can be adopted for water treatment as it is economical, eco – friendly, and requires less space. It does provide a greater scope in future as a beneficial substitute for the conventional processes (Magar, Khan, & Honnutagi, 2018).

Among the methods, adsorption is preferred because it is cheap and produces high-quality effluents especially if the process is well designed (Qadeer, 2007).

2.9.4 Sugarcane Biosorption

Biosorption concept is the passive adsorption of the organic and inorganic substances in soluble or insoluble forms from an aqueous solution using dead biological materials. It is different from bioaccumulation, which is the active, metabolic accumulation of metals and other substances by living organisms.

In comparison with other bio-treatment processes, biosorption is highly effective reducing the concentration of pollutants to very low levels and sometimes removing them completely altogether.

Factors such as initial pollutant concentration, biosorbent dosage, temperature and soil pH, contact time and sorbent particle size have significant influence on sorption processes and their potential. Generally, adsorption increases with an increase in the adsorbent dose. This is because; the increased surface area yields more active sites that bind pollutant ions. Increasing the initial concentration of the pollutant ions decreases the adsorption efficiency indicating the saturation of the available active sites for binding the pollutants. Moreover, exceeding the optimum contact time leads to a decrease in the removal efficiency. The pH

controls the magnitude of the electrostatic charges imparted by the pollutant ions and thus can also affect the adsorption process.

The process of biosorption involves two phases i.e., the solid and the liquid phases. The solid phase is the sorbent phase and the liquid the solvent phase containing a dissolved species to be removed. The pollutant ions having very high sorbent affinities are bound together by complex processes, which must be overcome by the biosorption process.

The principal mechanisms in the adsorption process involving dyes and metals by cellulosic biosorbents are chelation, ion exchange and complexation with the functional groups on the surface of the sorbent, and the subsequent release of the H_3O^+ into the synthetic aqueous solutions. Ion exchange takes place because of the electrostatic interaction between negative and positive charged groups in the biosorbent.

The efficiency of adsorption of sugarcane bagasse depends on initial pollutant concentration, temperature, solution pH, the biosorbent dosage, contact time and the size of the adsorbent particles. Moubarik and Grimi observed Cd (II) maximum removal capacity of 96% using the sugarcane bagasse with the initial Cd (II) concentration of 10 ppm in an aqueous solution of pH 7.0 after 25 minutes of contact time. Karnitz et al. reported that chemically modified sugarcane bagasse showed maximum adsorption capacities of 92.6, 149.0, and 333.0 $mg\ g^{-1}$ for Cu (II), Cd (II), and Pb (II) ions. In another study by Esfandiar et al. of Mn (II) removal using sugarcane bagasse treated with HCl, it was found that the removal efficiency decreased when the initial Mn (II) ion concentration increased, but increased as the adsorbent dosage increased (Sarker, Golam, Azam, El-gawad, et al., 2017).

Recently, sugarcane bagasse and its derivatives have been tested for pollutant removal. The three main forms of the bagasse include (1) raw bagasse, (2) bagasse - based activated carbon, and (3) bagasse fly ash. The raw sugarcane bagasse has been studied in pollutant removal without physical or chemical treatments and therefore environmentally friendly. In a study by Diriba et al. (2014) raw sugarcane bagasse and wheat removed 90% and 63% nitrate ions respectively from aqueous solutions. Modified sugarcane bagasse is very effective and faster in pollutant removal compared to raw bagasse.

Bagasse - based activated carbon and bagasse fly ash are also effective and able to remove pollutants including dyes, metals, herbicides, phenolic compounds and pesticides from aqueous solution. In optimum conditions, bagasse fly ash can remove up to 96% of different heavy metal ions from an aqueous solution. Abdelhafez and Li (2016) used sugarcane bagasse biochar and orange peel biochar for Pb (II) removal and found that the sugarcane-derived biochar was more efficient (86.96 mg g⁻¹) than the orange peel biochar (27.86 mg g⁻¹) in the elimination of these ions (Sarker, Golam, Azam, Abd, et al., 2017).

Contrasting results were found by Adamu and Ahmadu (2015), however, who reported that activated carbon prepared from sugarcane bagasse is less efficient at adsorbing heavy metal ions from wastewater than activated carbon prepared from *Parkia biglobosa* (locust bean) pods. However, biochar is a well-studied biosorbent; its utilization is sometimes restricted because of its higher cost.

Cueva et al. 2017 investigated the potential use of sugarcane bagasse for the treatment of basic red 46 dye and found 86.4 % removal percentage (Cueva-orjuela & Hormaza-anaguano, 2017). Sachin et al. 2011 investigated the removal of acid – orange II dye using sugarcane bagasse ash as an adsorbent (Kanawade & Gaikwad, 2011). In another study,

Ahmad et al. investigated the treatment of reactive red 120 (RR120) using sugarcane bagasse powder. The batch study was carried out under varying parameters such as 60 minutes contact time, pH (1-8), dye concentration (5-25 mg/l), particle size (125-500 μm) and biosorbent dosage (0.01- 0.2 g/l). The maximum adsorption percentage of RR120 was 94.62%. The adsorption of dye was increased with the decreasing of pH, initial dye concentration and particle size (Science, 2018).

2.9.5 Factors affecting the adsorption process

I. Adsorbent dosage

The influence of adsorbent dosage on the removal efficiency increases with an increase in adsorbent dosage. In a study conducted by (Franca et al., 2009) on the removal of methylene blue (MB), the removal percentage varied from 95 to 99% with an increase in adsorbent concentration from 0.5 to 15 gL^{-1} . This is attributed to the increase in surface area resulting from the increase in adsorbent mass, thus increasing the number of active adsorption sites. When the adsorbent dosage is increased, the amount of dye adsorbed per unit mass of the adsorbent decreased, due to the reduction in effective surface area. This may be due to overlapping or aggregation of adsorption sites resulting in a decrease in total adsorbent surface area available to dye and an increase in diffusion path length (Sartape et al., 2014).

II. Particle sizes

(Jain et al., 2004) studied the adsorption of four phenols (Phenol, 2-chlorophenol, 4-chlorophenol, and 2,4-dichlorophenol) at three particle sizes of 100 - 150, 150 - 200, and 200 - 250 British Standard Size (BSS) mesh, respectively. The results showed that the adsorption capacity increases to some extent with a decrease in particle size of the

adsorbent. Accessing all pores is facilitated by particle sizes becoming smaller. The BSS mesh of 200 - 250 showed maximum adsorption capacity.

III. Initial dye concentration

In an experiment to investigate the adsorption of acid green 25 (AG25) dye on durian peel (DP), Hameed et al, found the uptake of AG25 dye increased from 27.31 to 56.57 mg/g with an increase in the initial dye concentration from 50 to 500 mg/L. This is due to the increasing initial dye concentration providing the necessary driving force to overcome the resistances to the mass transfer of dye between the solid and aqueous phases. The increase in initial concentration also enhances the interaction between the dye and the DP sorbent. Therefore, an increase in initial dye concentration enhances the adsorption uptake of the dye. Similar result was reported for biosorption of acid red 88 (AR88), acid green 3 (AG3) and acid orange (Hameed & Hakimi, 2008).

2.10 Research gap

Many researchers have used different agricultural wastes in adsorption of different dyes. However, optimization studies have not been conducted on blended natural adsorbents from the studies of natural adsorbents reviewed.

CHAPTER THREE

3 MATERIALS AND METHODS

3.1 Materials

Water hyacinth samples were collected from Ahero rice canals in Kisumu County then preserved using tap water at normal temperature with no added nutrient. For sugarcane bagasse, the samples were collected from Kibos Sugar Company located in Kisumu East.

The reactive red 198 dye was sourced from Sigma Aldrich Company in Nairobi.

3.1.1 Preparation of Sugarcane Bagasse (SB) adsorbents

Sugarcane bagasse was cut into small pieces (approximately 2 cm) and washed 3 times with tap water followed by deionized water to remove the dust and any dirt. It was then dried under sunlight for about 48 hours. The sugar cane bagasse was soaked in 0.1 M HCl solution for 18 hours then washed with distilled water. Chemical treatment with HCl increases the surface oxygen complexes which enhance the active adsorbent sites that improves the dye removal rate. There was creation of aggregated and rough surface morphology with links between the surface particles creating more pores at the surface than the natural material. This was revealed by scanning electron microscope (SEM) analysis. The observed changes in the material surface is in terms of band shift, band disappearances and new band formations. The changes in the spectra and surface morphology of the materials are attributed to the introduction of activating agents for surface modifications (Abegunde, Idowu, Adejuwon, & Adeyemi-adejolu, 2020).

The bagasse was dried in an oven with a built in time control unit to set the drying time to a desired duration at 105 °C and further crushed using a blender until uniform size particle

were obtained as shown in Figure 3.1. The material obtained were packed in hermetically sealed containers and labeled (Reza & Abedin, 2011).



Figure 3.1: Crushed sugarcane bagasse

Source: Author

3.1.2 Preparation of adsorbent from Water hyacinth

Water hyacinth was allowed to grow in 5 liters of fresh water for 6 to 8 days. The plant was separated into different parts i.e. leaves, stems and roots as shown in Figure 3.2, cut into pieces then soaked in 0.1M sodium hydroxide for 3 hours. The parts were then washed with distilled water and dried in an oven at 150 °C then ground using a mortar to a uniform size (Magar et al., 2018; Reza & Abedin, 2011).

Treatment with an alkali improves the relative content of the alkali groups and improve the non-polar surface hence enhancing the adsorption capacity of the adsorbent for non-polar substances (Liu & Xiao, 2018). Alkali treatment of an adsorbent makes the adsorbent adsorbs a positive charge on the surface thereby enhancing the adsorption of negatively charged species (Rehman, Park, & Park, 2019).

Treatment with NaOH leads to a significant reduction in the surface oxygen-containing functional groups. However, there is an increase in specific surface area and pore volume concentration which results in a higher adsorption capacity (Abegunde et al., 2020).



Figure 3.2: Water hyacinth leaves, stems and roots

3.1.3 Preparation of blended adsorbents from sugarcane bagasse and water hyacinth

The ground sugarcane bagasse and water hyacinth were thoroughly mixed using a centrifuge in different blend ratios i.e. 0%:100%, 25%:75%, 50%:50%, 75%:25% and 100%:0% to form a mixture, which was then stored in, sealed containers.

3.1.4 Preparation of the initial dye solution

The tests were performed using a stock solution of 100 mg of the dye per liter of distilled water. For the calibration curve, different initial dye concentrations in the range of 10 mg/l to 50 mg/l were prepared by diluting 10 ml of the stock solution with distilled water. Other experiments were performed by taking 10 ml volumes of the stock solution then diluted to 5 mg/l, 10 mg/l, 25 mg/l, 40 mg/l and 50 mg/l (Cueva-orjuela & Hormaza-anaguano, 2017).

3.2 Design of experiment

Minitab software was used to design the experiments and the worksheet generated is given in Table Appendix 1. All the actual and coded values were varied on five levels as shown in Table 3.1.

Table 3.1: Experimental factor levels

Variables	Factor levels				
Coded factor values	-1.68179	-1	0	1	1.68179
Initial dye concentration (mg/l)	5	10	25	40	50
Particle sizes (um)	280	400	800	1000	2000
Blend ratio	0:100	25:75	50:50	75:25	100:0

A two level, rotatable central composite design with 6 center points, -1.68179 and 1.68179 as axial points was used because it allows for efficient estimation of quadratic terms in the regression model.

A set of 20 experiments with three replicas were done for the three factors resulting into 60 experimental runs. The experiments were randomized in three blocks to do away with the nuisance variables. Each block represented the replica category in which the particular run was done. The experimental runs were conducted based on the worksheet and the absorbance for each run measured using a UV spectrophotometer and recorded.

3.3 Generation of Regression Equation and Analysis of Variance (ANOVA)

The regression equation, analysis of variance table, coded coefficient table and model summary based on the dye removal percentage for all the experimental runs were generated. The terms in the regression equation generated were checked and their significance determined.

3.4 Optimization of Reaction Conditions

The reaction conditions for the dye removal percentage for reactive red 198 were optimized using Minitab software to maximize the amount of dye removed from the wastewater. Using experimental data from the design of experiments and optimization

plots, the optimum conditions were generated. A confirmatory adsorption experiment using the optimum conditions obtained was done and response recorded.

3.5 Effect of interactive variables

The interactive effect between two variables was investigated keeping the other variable constant. Three-dimensional (3D) surface plot and their contours were generated and analyzed. The three-dimensional surface plots represent the regression equation.

The analysis of the 3D surface plots and their contours was done based on the following interactions:

- Initial dye concentration and particle sizes
- Initial dye concentration and blend ratio

Table 3.2 is a blend ratio representation of the two adsorbents as used in the batch experiments.

Table 3.2: Blend ratio representation

Blend ratio	Sugarcane bagasse	Water hyacinth
0 (0:100)	0	100
0.3 (25:75)	25	75
1.0 (50:50)	50	50
3.0 (75:25)	75	25
>3.5 (100:0)	100	0

3.6 Computation of dye removal

A UV-VIS spectrophotometer, type UVM, ini-1240, 220-240V, 50/60 Hz from Shimadzu was used to get the absorbance of the samples once reaction had occurred.

A standard curve for reactive red 198 showing the maximum wavelength peaks was obtained by first running distilled water as the blank solution then a solution containing reactive red 198. A standard graph for estimating the concentration of the reactive red 198 was obtained by reading the absorbance of the dye against known initial dye concentrations.

At low concentrations, the absorbance is directly proportional to the initial dye concentrations and therefore dye removal percentage (DRP) can be calculated using Equation 3.1.

$$\text{DRP} = \frac{A_0 - A}{A_0} \times 100\% \quad \text{Equation 3.1}$$

Where DRP – dye removal percentage

A_0 – initial dye concentration

A – final dye concentration

3.7 The adsorption process

2g of the adsorbent blend was measured using a weighing scale model HI 2211, power 12V dc from Hanna instruments and added to 50 ml of the dye solution in a batch experiment and the contents were shaken for 30 minutes by a magnetic stirrer at room temperature. The magnetic stirrer model, Heldolph MR200 with a maximum speed of 1500 revolutions per minute was used to agitate the water as reactions were taking place. This was done to make sure that the adsorbent surface was fully available for the reaction with the dye molecules. The mixture was then sieved using a metallic sieve with a pore size of 250 μm .

The experiments were carried out while varying the adsorbent blend ratios and initial dye concentrations. The absorbance was then determined using the spectrophotometer (Srilajan, Janpattanapong, & Piyamongkala, 2014).

3.8 Adsorption capacity

This was done to determine the amount of dye taken up per unit mass of the adsorbent.

Equation 3.2 was used to determine the adsorption capacity.

$$\text{Adsorption capacity} = \frac{\text{Initial} - \text{final dye concentration}}{\text{Mass of the adsorbent}} \times 100\% \quad \text{Equation 3.2}$$

3.9 Measurement of Chemical Oxygen Demand

Chemical oxygen demand was done to determine the degree of degradation of the reactive red 198. The process was done before and after the degradation had been carried out at optimum conditions. The procedure used for COD determination was according to the American Public Health Association (APHA) standard procedure. The closed reflux titrimetric method was used.

Reagents for analysis:

- i) 0.01667M standard potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) digestion solution

Potassium dichromate solution was prepared by adding 4.903g of $\text{K}_2\text{Cr}_2\text{O}_7$ previously dried at 150°C , 167 mL of concentrated Sulphuric (VI) acid (H_2SO_4) and 33.3g mercuric sulphate (HgSO_4) to 500 mL of distilled water. The solution was allowed to cool and diluted to 1000 mL.

ii) Sulphuric acid reagent

The reagent was prepared by adding 5.5g of silver sulphate (Ag_2SO_4) to concentrated sulphuric (VI) acid. It was then left to stand for one day to dissolve and mix.

iii) Ferroin Indicator solution

Ferroin serves as an indicator in the titrimetric redox reaction. It tells the endpoint of the reduction of potassium dichromate. When all the excess dichromate has been reduced, the indicator changes color from blue-green to reddish brown.

iv) 0.10M Standard Ferrous Ammonium Sulfate (FAS) titrant

This titrant was prepared by dissolving 39.2g of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ in distilled water. 20 mL of concentrated H_2SO_4 was then added, cooled and diluted to 1000 mL. The solution was then standardized using standard $\text{K}_2\text{Cr}_2\text{O}_7$ digestion solutions as follows:

- 5.0 mL of digestion solution was pipetted into a beaker
- 10.0 mL reagent water was added as substitute for sample
- 2 drops of the diluted Ferroin indicator added and titrated with the FAS indicator.

The molarity of FAS solution was determined using equation 3.3

$$\text{Molarity of FAS solution} = \frac{\text{Volume of 0.01667M K}_2\text{Cr}_2\text{O}_7}{\text{Volume of FAS solution titrated}} \times 100\% \quad \text{Equation 3.3}$$

The procedure below was used to determine the COD:

- Culture tubes and caps were washed with 20% H_2SO_4
- A sample size of 2.5 mL was placed in the culture tube and 1.5 mL $\text{K}_2\text{Cr}_2\text{O}_7$ digestion solution added
- 3.5 mL sulphuric acid reagent was poured on the inside walls of the vessel to form an acid layer under the sample digestion layer

- The tubes were tightly capped then inverted for proper mixing
- The tubes were then placed in the block digester, preheated to 150 °C and refluxed for 2 hours.
- The tubes were allowed to cool to room temperature and placed in the test tube rack
- 2 drops of the Ferroin indicator was added and stirred with the magnetic stirrer while titrating with standardized 0.10M FAS to the end point.
- A blank containing the reagents and distilled water with a volume equal to that of the sample was also refluxed and titrated.

Equation 3.4 was used to determine the COD

$$\text{COD in mg O}_2/\text{L} = \frac{(A - B) \times M \times 8000}{\text{mL sample}} \quad \text{Equation 3.4}$$

Where,

A = mL FAS used for blank,

B = mL FAS used for sample,

M = molarity of FAS

3.10 Dyeing of Cotton Fiber

2g of cotton fiber was weighed and put in aluminium beaker containing 200 mL of distilled water. 0.04g of reactive red 198 was weighed and put in the aluminium beaker containing the fabric. 10g of sodium chloride was added into the content and heated for about 1 hour at 65 °C.

3.11 Determination of Parametric effects

3.11.1 Initial dye concentration

The effect of initial dye concentration was determined by varying concentration at 5 mg/l, 10 mg/l, 25 mg/l, 40 mg/l and 50 mg/l while keeping particle size and blend ratio constant

at optimal level. Absorbance of the samples was taken after 30 minutes reaction time and percentage dye removal and adsorption capacity calculated using Equation 3.1 and 3.2 respectively.

3.11.2 Particle sizes

The process was carried out while varying particle sizes at 280 μm , 400 μm , 800 μm , 1000 μm and 2000 μm and maintaining initial dye concentration and blend ratios at optimum values. After 30 minutes of reaction time, the samples were taken and the absorbance read off using UV spectrophotometer and adsorption capacity calculated. The results were then plotted on a graph for analysis.

3.11.3 Blend Ratio

At optimum initial dye concentration and particle size, the process was carried out while varying the blend ratio (sugarcane bagasse: water hyacinth) of the adsorbent at 0%:100%, 25%:75%, 50%:50%, 75%:25% and 100%:0%. After 30 minutes, the samples were taken and the absorbance read off using UV spectrophotometer and adsorption capacity calculated. The results were then plotted on a graph to analyze the effect.

CHAPTER FOUR

4 RESULTS AND DISCUSSIONS

4.1 Introduction

This chapter covers the experimental results and the reasons underlying the observations. Included are the regression model, analysis of variance (ANOVA), effects of interactive variables and the optimization conditions.

The UV – Vis spectrophotometer was used to measure the absorbance of Reactive red 198. Figure 4.1 shows an absorbance spectra obtained from a solution of reactive red 198 dye at a concentration of 20 mg/l.

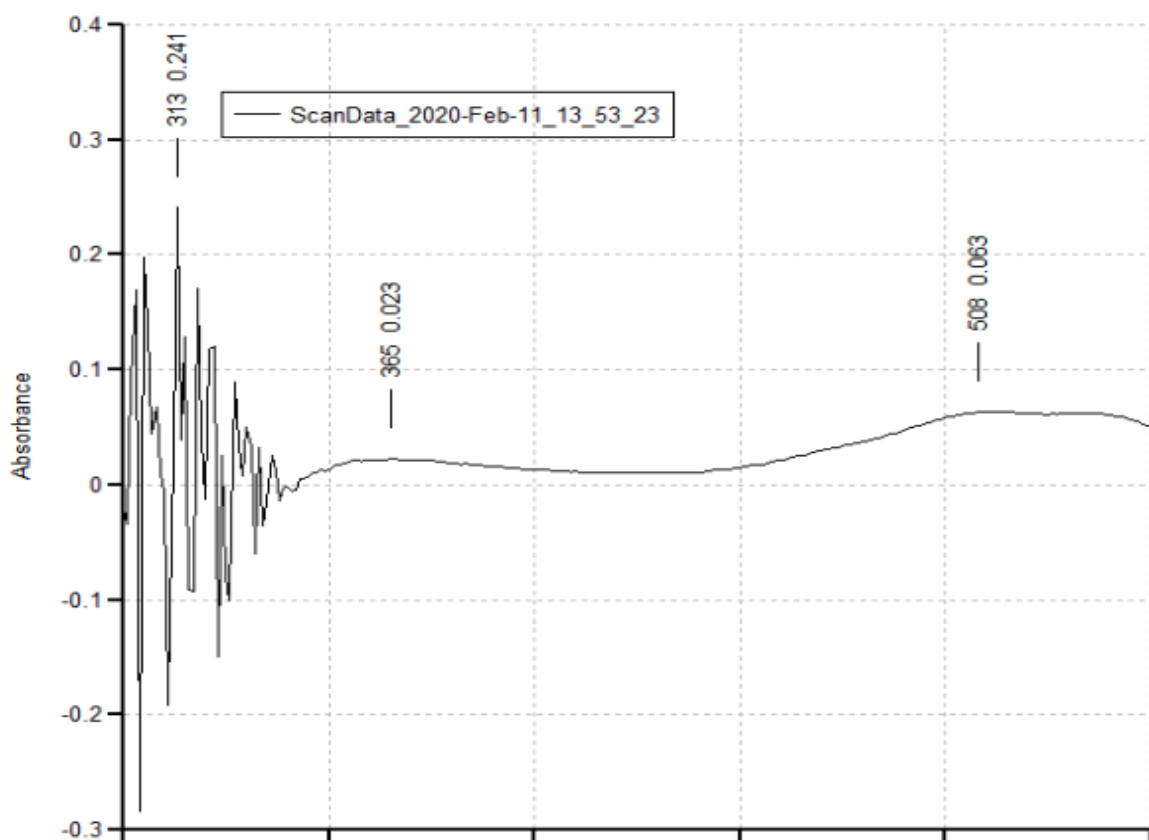


Figure 4.1: Standard calibration spectra for reactive red 198 at 20 mg/l concentration

From the spectra, maximum peak wavelength occurred at 508 nm. Sample absorbance was therefore read from this wavelength. A standard curve relating the Absorbance of Reactive Red 198 at different dye concentrations was developed as shown in Figure 4.2. To capture the concentration of the dye at its known absorbance, interpolation technique is applied.

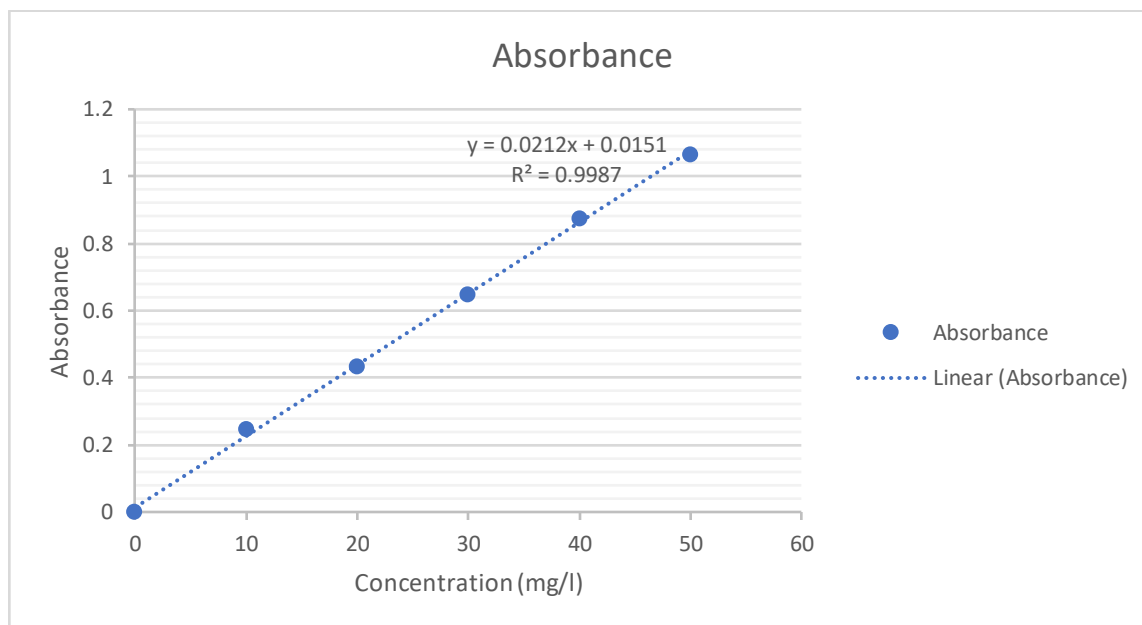


Figure 4.2: Standard absorbance calibration curve.

4.2 Baseline processes

(a) Optimum time and water hyacinth section for the adsorption process

To determine the optimum time and the best part of water hyacinth plant to be used for adsorption process, sugarcane bagasse and different parts of the water hyacinth i.e. the stems, leaves and roots were subjected to a preliminary test under different time intervals at the standard concentration of 20 mg/l and the results recorded. From the results in Table 4.1, it was realized that the roots are the best results out of the three parts for the adsorption process. This is because the roots adsorbed more dyes thus giving the lowest absorbance value.

Table 4.1: Baseline for the adsorption process

Water hyacinth/Time	Absorbance		
	30 minutes	1 hour	4 hours
Roots	0.03	0.022	0.025
Stem	0.211	0.16	0.078
Leaves	0.139	0.106	0.082
Sugarcane Bagasse	0.01	0.015	0.01

Source: Experimental data

(b) Adsorbent dosage

In another experiment to determine the baseline for the adsorbent dosage, several experiments were run and the average results presented in Figure 4.3. The optimum adsorbent dosage obtained was 2g.

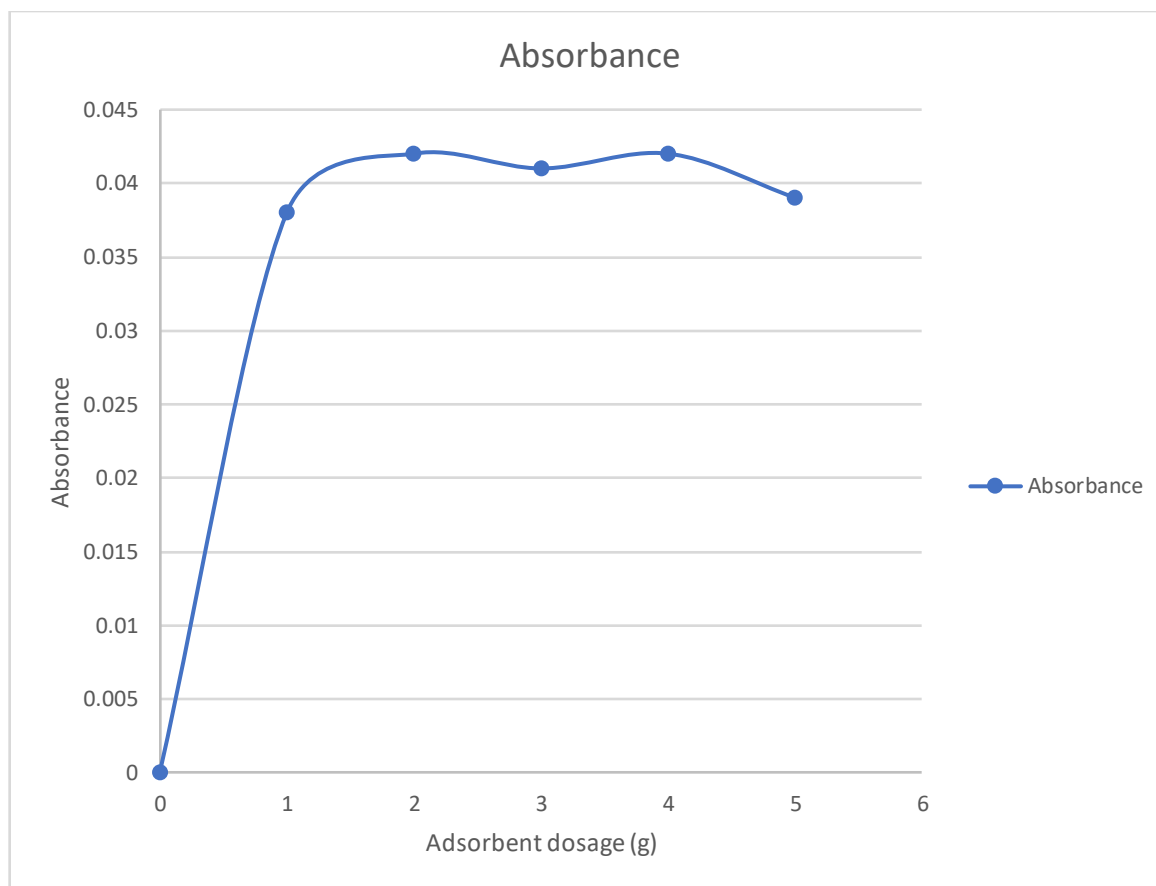


Figure 4.3: Graph of baseline for adsorbent dosage

4.3 Chemical modification of the adsorbents

Chemical modification is done to enhance the porosity of the adsorbent structures. Comparing the adsorbent structures in Figure 2.14 and Figure 4.4 shows a more open structure in Figure 2.14 than Figure 4.4. Modification significantly improved the adsorption capacity. Unmodified sugarcane bagasse have lower adsorption potential than modified sugarcane bagasse (Sarker, Golam, Azam, El-gawad, et al., 2017).

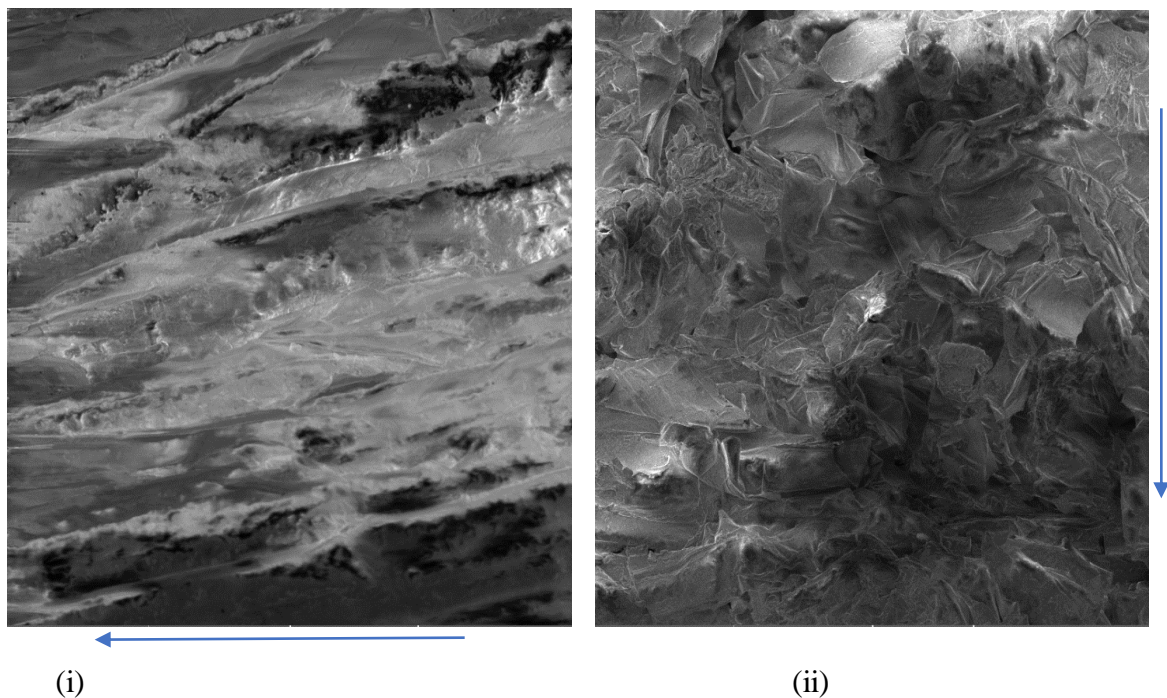


Figure 4.4: Scanning electron micrographs of unmodified sugarcane bagasse fiber surface in i and fiber cross-section in ii

4.4 Remediation regression model

The regression model that predicts the remediation of reactive red 198 using the mixture of sugarcane bagasse and water hyacinth was generated. The full quadratic equation (equation 4.1) was obtained.

$$y = 39.2 - 0.540 X_1 + 0.0774 X_2 - 15.81 X_3 - 0.00410 X_1^2 - 0.000095 X_2^2 + 3.68 X_3^2 + 0.001136 X_1 X_2 + 0.260 X_1 X_3 + 0.00176 X_2 X_3 \quad \text{Equation 4.1}$$

Where; y = Dye removal percentage

X_1 = Initial dye concentration (mg/l)

X_2 = Particle size (um)

X_3 = Blend ratio

Table 4.2: Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value	Effect	VIF	Remarks
Model	11	11875.9	1079.63	16.65	0.000			Significant
Blocks	2	28.4	14.20	0.22	0.804			Not Significant
Linear	3	6801.7	2267.24	34.96	0.000			Significant
A	1	2995.6	2995.63	46.19	0.000	17.10	1.00	Significant
B	1	2001.7	2001.69	30.86	0.000	-13.98	1.00	Significant
C	1	1804.4	1804.40	27.82	0.000	13.27	1.00	Significant
Square	3	4046.9	1348.97	20.80	0.000			Significant
X_1^2	1	36.7	36.71	0.57	0.456	-1.84	1.02	Not Significant
X_2^2	1	3142.6	3142.64	48.46	0.000	-17.05	1.02	Significant
X_3^2	1	584.9	584.94	9.02	0.004	7.36	1.02	Significant
2-Way								Significant
Interaction	3	998.9	332.96	5.13	0.004			
X_1X_2	1	627.2	627.20	9.67	0.003	10.22	1.00	Significant
X_1X_3	1	365.0	364.96	5.63	0.022	7.80	1.00	Significant
X_2X_3	1	6.7	6.71	0.10	0.749	1.06	1.00	Not Significant
Error	48	3112.9	64.85					
Lack-of-Fit								Significant
Fit	33	3085.0	93.49	50.19	0.000			
Pure Error	15	27.9	1.86					
Total	59	14988.9						

From Table 4.2, all the terms are significant in predicting the response (dye removal percentage) except for two terms (X_1^2 and X_2X_3) because their P-values in the table are more than 0.05. Two squared terms in the quadratic model are significant meaning there are two points of curvature in the response surface.

The initial dye concentration has the greatest effect of 17.10 on the remediation process compared to the other variables and therefore must be carefully optimized in the dye removal process.

Variance Inflation Factor, (VIF) is a measure of how much variance of the estimated regression coefficients are inflated compared to when the predictor variables are not linearly related. VIF indicates the extent to which multicollinearity (correlation among predictors) is present in a regression analysis. In the analysis, it can be seen that VIF are all close to 1 meaning the predictors are not correlated and that the variance of regression coefficients is minimal and stable. The coefficients in the regression equation are therefore reliable in predicting the response and can be used to analyze the reaction system.

Table 4.3: Model summary

Parameter	
S	8.05314
R ²	79.23%
R ² Adjusted	74.47%
R ² Predicted	63.51%
Unusual Observations	
17 th	14.76 Residual
33 rd	27.01 Residual
60 th	14.24 Residual

In the model summary, shown in Table 4.3, the S value for the statistics was found to be 8.05314, meaning the average distance of the data points from the fitted line is about 8%.

R² is a statistical measure of how close the data are to the fitted line regression. From the

model summary table, R^2 of 79.23% indicates that the model explains 79.23% of all the variability of the response data.

R^2 adjusted indicates that the terms improved the model fit by 74.47% and R^2 predicted of 63.51% means the mathematical model in the equation (equation 4.1) can accurately predict 63.51% of the new observations. The analysis showed unusual observations in the 17th, 33rd and 60th experimental runs with residual values of 14.76, 27.01 and 14.24 respectively. This could have been as a result of a possible error during the experimental run or an external factor that affected the reaction process. Owing to the fact that there are only 3 unusual behaviours out of 60 experimental runs representing only 5%, it can be concluded that about 95% of the data is a good fit for the prediction response.

From the statistical analysis of the regression model, it was concluded that the full quadratic equation (equation 4.1) is a good representative of the dye removal percentage from the experimental data generated.

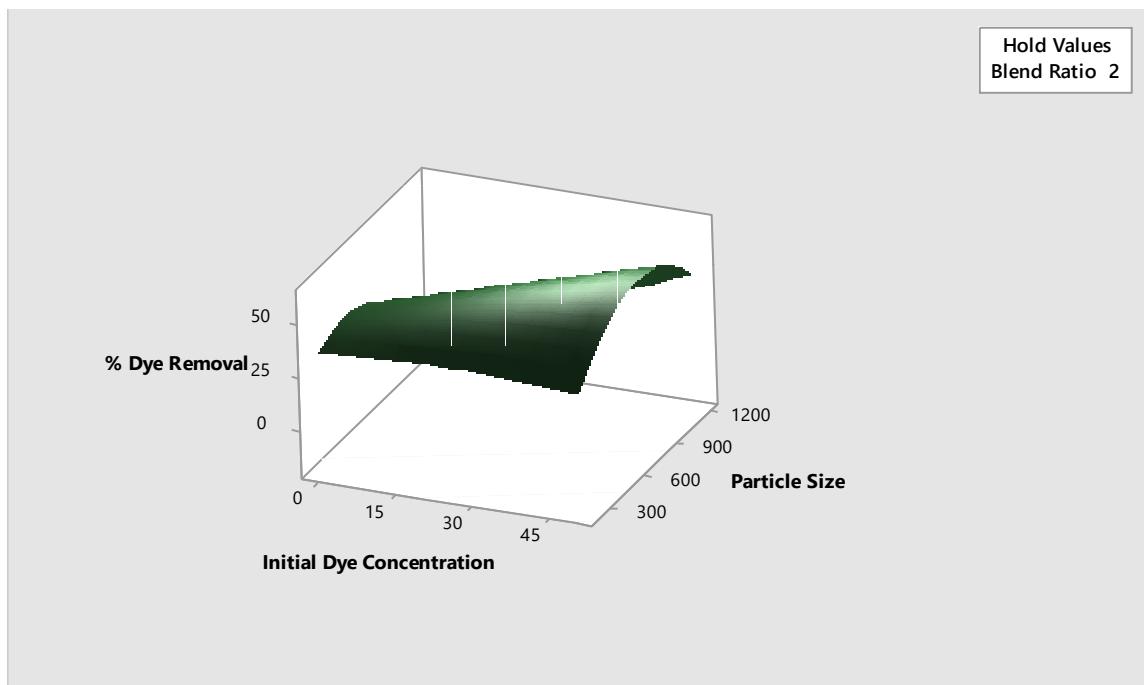
4.5 Effect of interactive variable

The main aim of investigating the interaction effect is to efficiently mark the points that give maximum dye removal percentage. In order to investigate interaction effect between two variables, the other variable is kept at its optimum values and their 3-D surface and contour plots analyzed.

4.5.1 Interaction Effect of initial dye concentration and particle size

From Figure 4.5, percentage dye removal increases with an increase in initial dye concentration. Increase in particle sizes also increases the dye removal percentage up to an optimum particle size of about 700 μm then the dye removal percentage started to decrease. This can be attributed to a decrease in the surface area of the available active

sites of the adsorbent surfaces (Jain et al., 2004). Highest dye removal percentage (>60%) was found at initial dye concentration of 50 mg/l and particle size of 745 μm . The contour lines in the plots are elliptical suggesting that the interaction effects between initial dye concentration and the adsorbent particle size is significant (Rajeshkannan, Rajasimman, & Rajamohan, 2010).



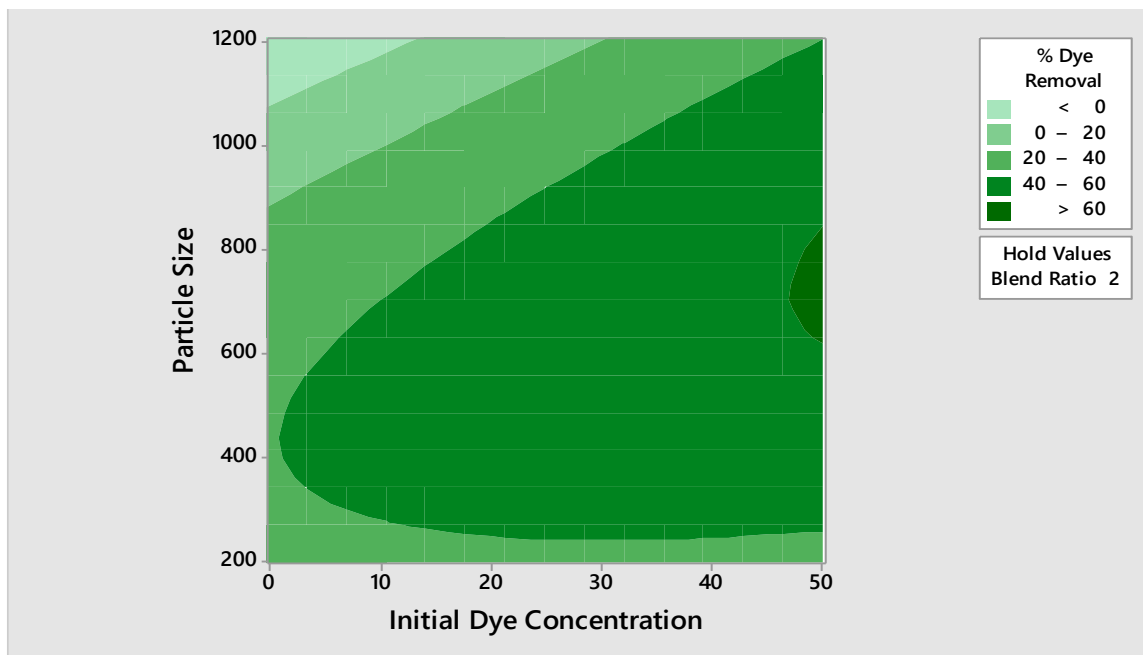


Figure 4.5: Response surface and contour plots for dye concentration and particle size

4.5.2 Interaction Effect of initial dye concentration and blend ratio

From the contour plot graph, shown in Figure 4.6, from a blend ratio of 0:100 to 100:0, the dye removal percentage increases from about <40 to >90%. Highest dye removal percentage was obtained at 50 mg/l initial dye concentration and blend ratio of 100:0. It shows that the optimum initial dye concentration is 50 mg/l and the optimum blend ratio is 100:0.

As the initial dye concentration increases from 10 mg/l to 50 mg/l, the percentage dye removal also increases. This is may be attributed to the presence of the binding sites and high level of silica that make sugarcane bagasse and its derivatives effective in pollutant removal. The biological polymers such as cellulose and lignin also provide additional properties to the developed adsorbent materials (Sarker, Golam, Azam, El-gawad, et al., 2017).

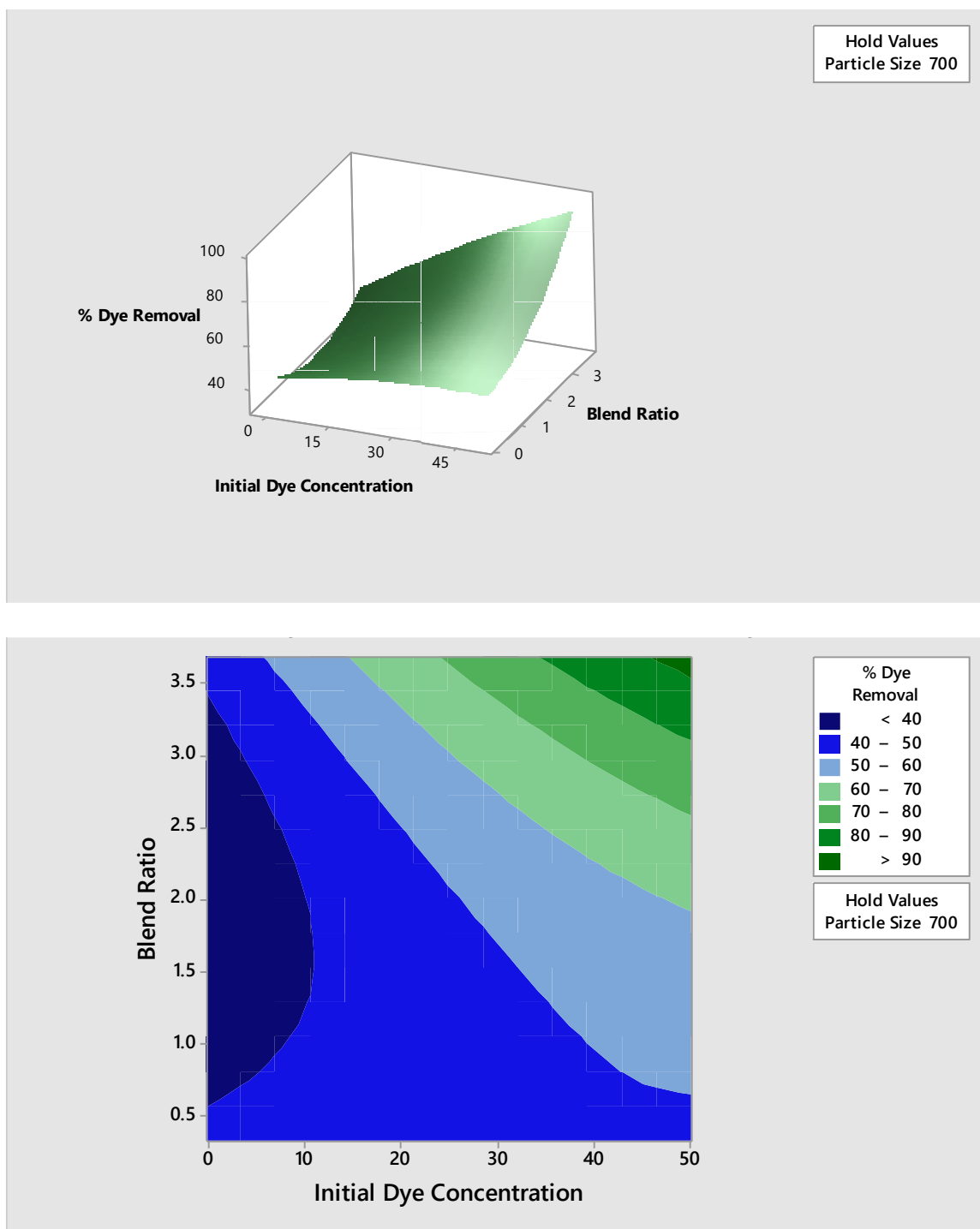


Figure 4.6: Response surface and contour plots for initial dye concentration and blend ratio

4.6 Optimization of reaction conditions

After running the experimental data on the response optimizer on the statistical tool, the results shown in Table 4.4 were generated.

It can be seen that the optimum conditions for the dye removal process is an initial dye concentration of 50.23 mg/l, particle size of 745.87 um and a blend ratio of 100:0. To confirm this result, an experiment was done with the optimum conditions and the dye removal percentage was found to be 89%.

Table 4.4: Optimum conditions for dye removal of Reactive Red 198

Parameter	
Response	Dye Removal Percentage
Goal	Maximize
Weight	1
Importance	1
Multiple Response Prediction	
Variable	Setting
Initial dye concentration	50.2269
Particle size	745.867
Blend Ratio	100:0
Dye removal Percentage Fit	93.90
Composite Fit Desirability	1

A comparison was made to evaluate the treatment effect by using treated and untreated sugarcane bagasse. The initial dye concentration was kept constant at the optimum concentration of 50.23 mg/l, the particle size at 745.87 um, blend ratio of 100:0 and total reaction time of 30 minutes. Two experimental trials were run and the average absorbance of the samples plotted. From the graph in Figure 4.7, the highest dye removal percentage

(89%) occurred when the adsorbent (sugarcane bagasse) was treated with hydrochloric acid (HCl) as shown in graph 2.

There was a percentage removal of 49% when the bagasse was untreated as shown in graph 1. This means that treating the adsorbent with HCl enhanced the adsorption of the adsorbent.

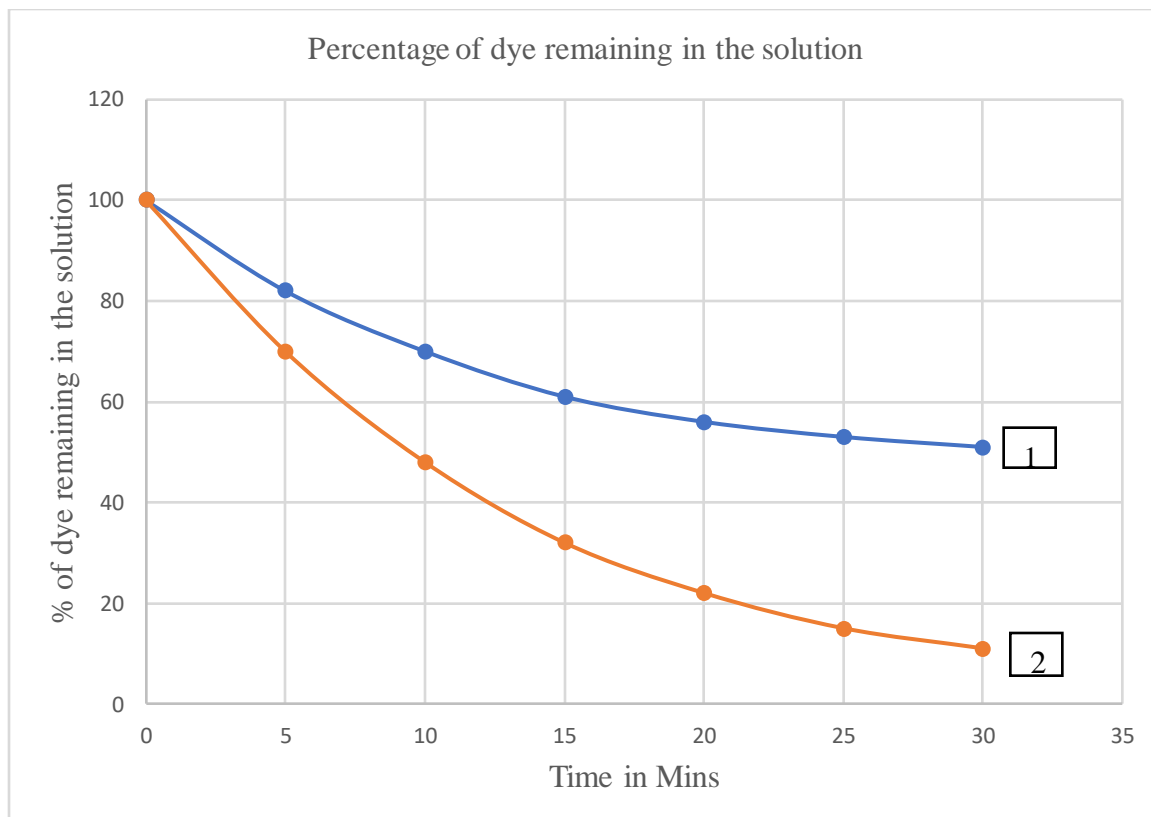


Figure 4.7: Graph for dye removal percentage of treated and untreated sugarcane bagasse

4.7 Determination of Chemical Oxygen Demand (COD)

The chemical Oxygen Demand was determined at optimum conditions, which are 50.23 mg/l, particle size of 745.87 μm , blend ratio of 100:0 and total reaction time of 30 minutes. Before treating the waste, the chemical Oxygen demand found was 1010 mg/l and after treatment, it reduced to 50 mg/l representing 95% COD reduction.

Environmental Management and Coordination Authority (EMCA) on water regulations recommend a COD level not exceeding 50 mg/l for all the effluent discharges into the environment (Monitoring, 2008). A COD of 50 mg/l is therefore within the recommended levels.

The absorbance of the wastewater from the dyeing of the cotton fiber was found to be 0.89 representing a concentration of 45 mg/l as determined from the graph in Figure 4.2. Initial dye concentration in the dye bath before the dyeing process was 200 mg/l. This means that the unfixd dye in the wastewater represents 22.5% of the initial amount of the reactive red dye used.

The wastewater was treated with 745.87 μm adsorbent particle sizes, blend ratio of 100:0. After a reaction time of 30 minutes, the absorbance was measured and found to be 0.22. This represents 78% removal of the dye from the wastewater.

The COD for the actual dye effluent was determined and found to be 48 mg/l from 1015 mg/l representing a 95% reduction.

4.8 Parametric Effects on adsorption capacity of the adsorbent

4.8.1 Effects of initial dye concentration

The adsorption capacity was determined at different initial dye concentrations and the process evaluated. The particle size was kept at optimum of 745.87 μm , blend ratio at 100:0 and reaction time of 30 minutes. It was seen that as the initial dye concentration increased, the adsorption capacity of the adsorbent also increased. This is due to the high initial dye concentration enhancing the interaction between the dye molecules and the adsorbent surface. The high initial dye concentration also overcame resistance to the flow

of the dye molecules hence aiding the transfer process between the solid and the aqueous phases (Hameed & Hakimi, 2008). The results are presented in Figure 4.8.

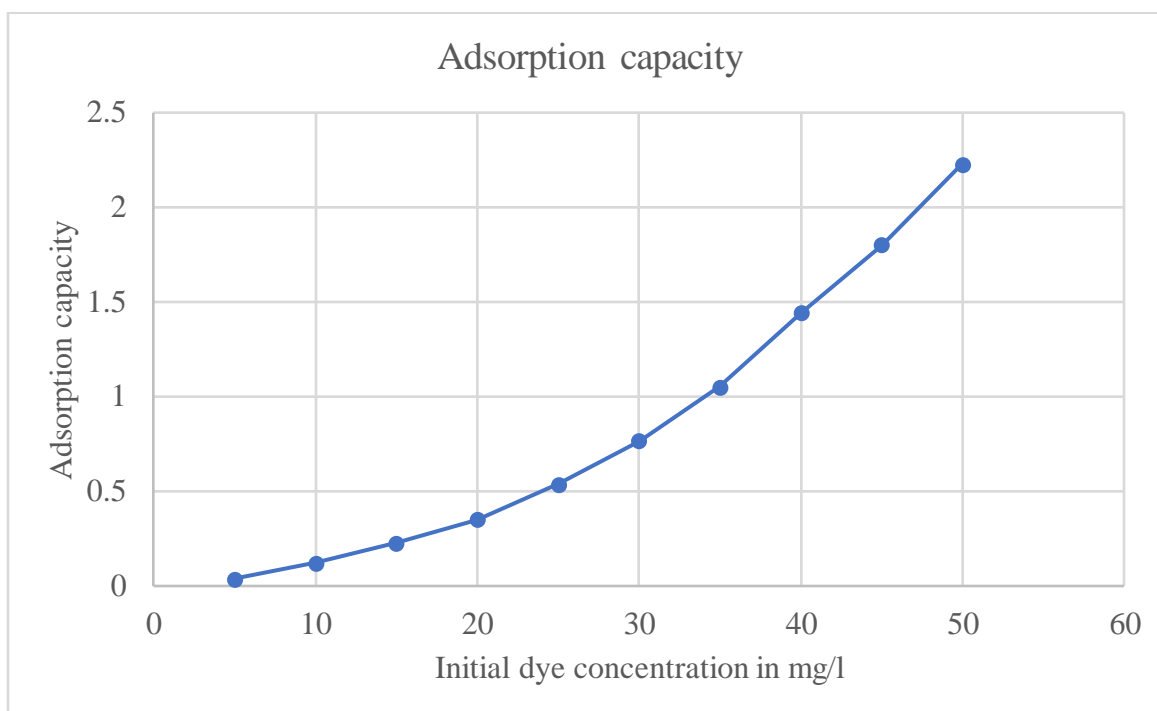


Figure 4.8: Graph showing the effect of initial dye concentration on adsorption capacity

4.8.2 Effect of the size of particles

The size of particles was varied while the initial dye concentration kept at constant value of 50.23 mg/l and blend ratio at 100:0. The adsorption capacity was determined when the dye was subjected to adsorption process after 30 minutes and the results shown in Figure 4.9. From the graph, adsorption capacity increased with an increase in the size of particles up to a point then dropped. Smaller particle sizes offer a large surface area of the available active sites of the adsorbent. As the size of the particles increase, the available surface area of the active sites reduce slowing the adsorption process and hence lowering the dye removal percentage (Jain et al., 2004).

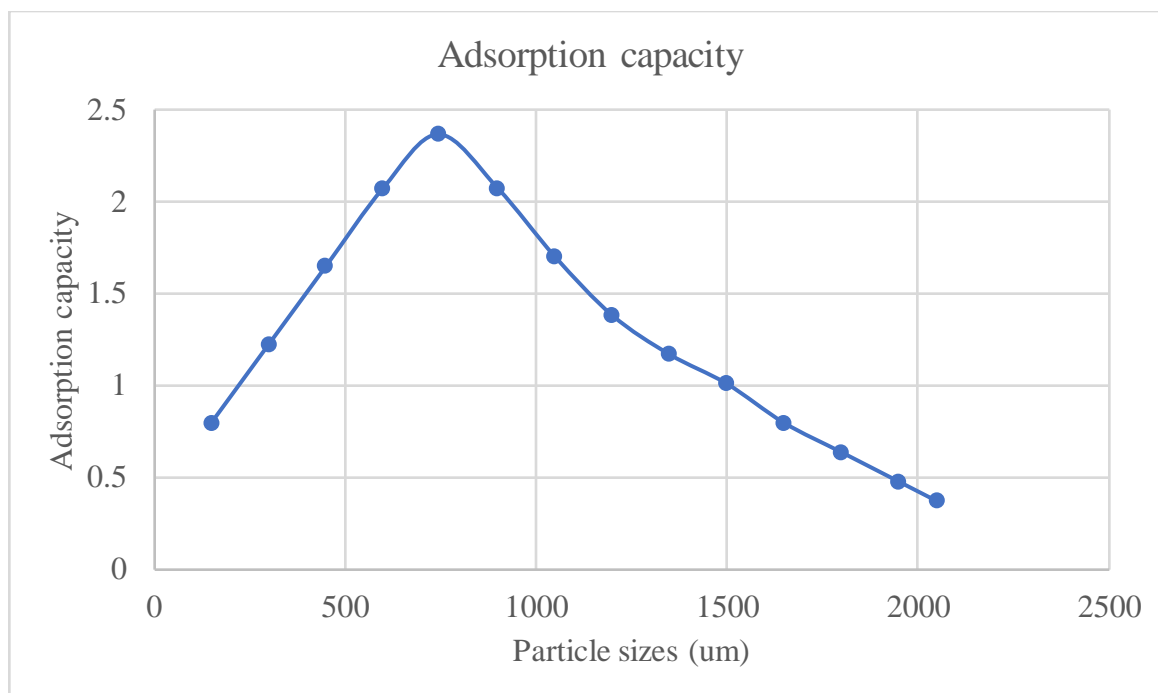


Figure 4.9: Graph showing the effect of the size of particles on adsorption capacity

4.8.3 Effect of blend ratio

The blend ratio was varied as initial dye concentration kept at optimum conditions of 50.23 mg/l and particle sizes at 745.87 um. The adsorption capacity was determined after 30 minutes and the results plotted in Figure 4.10. From the graph, the adsorption capacity increases with the increase in sugarcane content in the adsorbent. This may be attributed to the high level of silica content of sugarcane bagasse and its derivatives making it very effective in dye removal. Moreover, the biological polymers such as cellulose and lignin present in the bagasse also provide additional properties that aid in effective dye removal process (Sarker, Golam, Azam, El-gawad, et al., 2017). Increasing the water hyacinth content in the ratio decreases the adsorption of the adsorbent blend. This may be due to overlapping or masking up of adsorption sites of the sugarcane bagasse resulting in a decrease in the total available sites to adsorb the dye (Franca et al., 2009).

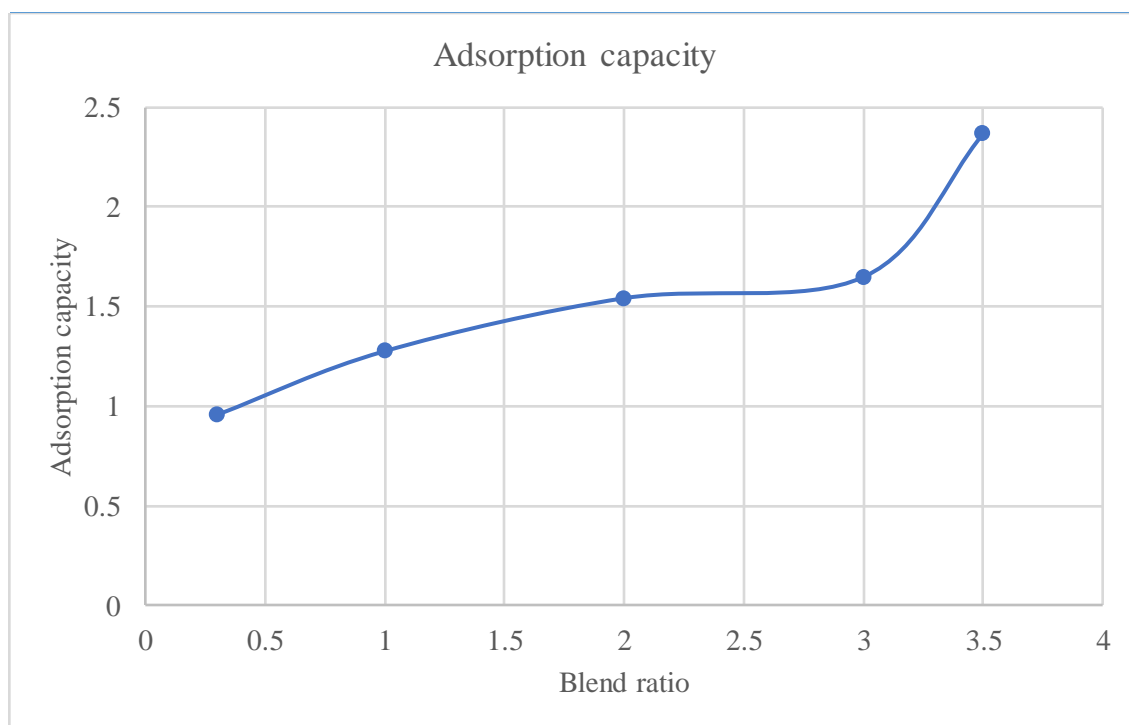


Figure 4.10: Graph showing the effect of Blend ratio on adsorbent adsorption capacity

CHAPTER FIVE

5 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In this study, a mixture of chemically modified sugarcane bagasse and water hyacinth was used in the treatment of reactive red 198 wastewaters. From the study, the following conclusions were drawn:

Treatment of sugarcane bagasse and water hyacinth with 0.1M HCl and 0.1M NaOH respectively enhances their dye adsorption compared to non-modified adsorbents.

Adsorption capacity increases with increase in initial dye concentration while dye removal efficiency increases with increasing particles size up to an optimum size of 745.87 μm before dropping as particle size increases to 2000 μm . Pure sugarcane bagasse exhibits better adsorption of reactive red 198 dye than its blend with water hyacinth.

The optimum working conditions that maximizes percentage dye removal were found to be an adsorbent dosage of 2g, initial dye concentration of 50.23 mg/l, particle size of 745.87 μm , a blend ratio of 100:0 and a reaction time of 30 minutes. At these conditions, the dye removal percentage was found to be 89% with a COD reduction of 95%. The COD after dye removal was found to be 50 mg/l, which is within the recommended standard levels by NEMA.

Adsorption process effectively removed 89% reactive red 198 dye from actual textile wastewater and may therefore be employed as a clean technology in wastewater treatment.

5.2 Recommendation

Adsorption using modified sugarcane bagasse and water hyacinth present clean technology in wastewater treatment. However, the two adsorbents should be used separately to obtain better results unless an optimal blend is established. More research can be done on modified sugarcane bagasse and water hyacinth under varying pH modification conditions. Other variables like temperature need also to be investigated to bring more light into the subject.

5.3 Areas of future studies

More research should be done to determine optimal blend of sugarcane bagasse and water hyacinth under varying chemical treatment methods.

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6 APPENDICES

6.1 Appendix 1: Operation Experimental Worksheet

Standard Order	Run Order	Blocks	Initial dye concentration	Particle Size	Blend Ratio	% dye removal (response)	Adsorption capacity
3	1	1	10	1000	25:75	7.26	0.0363
12	2	1	25	2000	50:50	15.99	0.1999
13	3	1	25	800	0:100	35.99	0.4499
10	4	1	50	800	50:50	58.55	1.464
1	5	1	10	400	25:75	47.06	0.2353
16	6	1	25	800	50:50	49.47	0.6184
20	7	1	25	800	50:50	50.00	0.625
19	8	1	25	800	50:50	49.65	0.6206
7	9	1	10	1000	75:25	18.15	0.09075
8	10	1	40	1000	75:25	56.24	1.125
9	11	1	5	800	50:50	33.33	0.0833
2	12	1	40	400	25:75	50.46	1.009
15	13	1	25	800	50:50	49.29	0.6161
18	14	1	25	800	50:50	48.58	0.6073
14	15	1	25	800	100:0	83.69	1.046
17	16	1	25	800	50:50	48.17	0.6021
11	17	1	25	280	50:50	51.60	0.645
4	18	1	40	1000	25:75	44.89	0.8978

6	19	1	40	400	75:25	61.64	1.233
5	20	1	10	400	75:25	45.16	0.2258
24	21	2	40	1000	25:75	43.95	0.879
21	22	2	10	400	25:75	47.26	0.2363
31	23	2	25	280	50:50	28.72	0.359
28	24	2	40	1000	75:25	56.38	1.128
37	25	2	25	800	50:50	50.89	0.6361
34	26	2	25	800	100:0	84.04	1.051
27	27	2	10	1000	75:25	17.66	0.0883
38	28	2	25	800	50:50	48.76	0.6095
36	29	2	25	800	50:50	49.11	0.6139
39	30	2	25	800	50:50	47.87	0.5984
30	31	2	50	800	50:50	58.64	1.466
22	32	2	40	400	25:75	52.28	1.046
23	33	2	10	1000	25:75	47.58	0.2379
33	34	2	25	800	0:100	39.54	0.4943
25	35	2	10	400	75:25	42.74	0.2137
26	36	2	40	400	75:25	59.36	1.187
32	37	2	25	2000	50:50	16.31	0.2039
35	38	2	25	800	50:50	48.00	0.6
29	39	2	5	800	50:50	37.88	0.0947
40	40	2	25	800	50:50	49.47	0.6184
56	41	3	25	800	50:50	47.52	0.594

58	42	3	25	800	50:50	47.96	0.5995
43	43	3	10	1000	25:75	11.29	0.0565
53	44	3	25	800	0:100	36.52	0.4565
50	45	3	50	800	50:50	58.33	1.458
51	46	3	25	280	50:50	28.00	0.35
46	47	3	40	400	75:25	59.93	1.199
55	48	3	25	800	50:50	50.71	0.6339
41	49	3	10	400	25:75	51.09	0.2555
47	50	3	10	1000	75:25	18.06	0.0903
42	51	3	40	400	25:75	50.00	1
45	52	3	10	400	75:25	41.13	0.2057
60	53	3	25	800	50:50	48.37	0.6046
57	54	3	25	800	50:50	51.42	0.6428
59	55	3	25	800	50:50	52.13	0.6516
52	56	3	25	2000	50:50	16.45	0.205625
49	57	3	5	800	50:50	39.39	0.09848
48	58	3	40	1000	75:25	56.72	1.134
44	59	3	40	1000	25:75	43.74	0.8748
54	60	3	25	800	100:0	84.40	1.055

6.2 Appendix 2: Removal of heavy metals using water hyacinth

Type of waste water	Uptake of heavy metals	Findings/Highlights
Wastewater from simulated wetland	(Cr), (Cu)	Almost 65% removal of heavy metals was achieved using water hyacinth
Synthetic wastewater	(Cu)	Concentration of Cu decreased as mentioned below: $5.5 - 2.1 \text{ mg/L} = (61.6\% \text{ removal})$ $2.5 - 0.11 \text{ mg/L} = (95.6\% \text{ removal})$ $1.5 - 0.04 \text{ mg/L} = (97.3\% \text{ removal})$
Agricultural drain, river and mixed industrial drain	(Zn), (Cu), (Ni)	The order of trace metal accumulation in the root tissue was found to be as $Zi > Cu > Ni$. The bio concentration factor for Cu, Ni and Zi present in the water hyacinth root was found to be 1344.6, 1250.0, and 22758.6 respectively.
Simulated radio contaminated aqueous solution	(Cs), (Co)	Higher removal rate of ^{60}Co (100%) in presence of ^{60}Co of waste solution obtained, where highest ^{137}Cs uptake value from the waste solution, near to 80% was observed with the exposure

		to sunlight along with the presence of ^{60}Co .
Artificial lake water	(Zn), (Cu), (Pb), (Cd)	Initial concentration of Zn, Cu, Pb and Cd in water (500, 250, 250 and 50 mg/L) was found to decrease in the order of $\text{nPb} > \text{Cu} > \text{Cd} > \text{Zn}$ during the first day. After 8 days, the removal efficiency was 8% and 24% (Cu), 11% and 26% (Pb), 24% and 50% (Cd), 18% and 57% (Zn) at pH 8 and pH 6.
Composting Wastewater	(Cd), (Zn), (Fe), (Mn), (Pb), (Ni), (Cr), (Cu)	Total metal concentration was found to increase during the process of composting. Water soluble Cd, Pb, Ni and DTPA extractable Pb and Cd were not detected, but all of the metal concentrations were observed in the TCLP test during composting.
Industrial wastewater	(Zn), (Cu), (Cd), (Cr)	Appreciable amount of heavy metal occurred during a 15-day experiment. Maximum removal efficiency of metal was recorded during the 10 th day and the leaves of water hyacinth was found to be as least accumulator in

		comparison to the roots.
Diluting stock solution in drinking water	As (V), As (III)	A prototype filter made from water hyacinth (20 g) was capable of removing 80% and 84% of arsenic from drinking water with the concentration of 250 and 1000 ug/L.
Hydroponic medium	(Hg)	Accumulation of mercury ion was 1.99, 1.74 and 1.39 mg/g dry weight in the root, leaf, and petiole tissues.
Artificial wastewater (Cd(NO ₃) ₂ .4H ₂ O in deionized water)	(Cd)	Used of biochar pyrolyzed from water hyacinth resulted in the removal of nearly 100% Cd from the aqueous solution within 1 hr at initial Cd less than or equals to 50 mgL ⁻¹
Artificial wastewater (NiCl ₂ .6H ₂ O) was added to obtain concentration of 1, 2, 3 and 4 mgL ⁻¹	(Ni)	Ni adsorption was found to be quick during first 24 hours. Higher Ni accumulation was observed in roots in comparison to aerial parts.

Source: (Rezania et al., 2015)

6.3 Appendix 3: Standards for effluent discharge into public sewers

Parameter	Maximum levels permissible
Suspended solids (mg/L)	250
Total dissolved solids (mg/L)	2000
Temperature °C	20 - 35
pH	6 - 9
Oil and Grease (mg/L) -where conventional treatment shall be used	10
Oil and Grease (mg/L)- where ponds is a final treatment method	5
Ammonia Nitrogen (mg/L)	20
Substances with an obnoxious smell	Shall not be discharged into the sewers
Biological Oxygen Demand BOD ₅ days at 20 °C (mg/L)	500
Chemical Oxygen Demand COD (mg/L)	1000
Arsenic (mg/L)	0.02
Mercury (mg/L)	0.05
Lead (mg/L)	1
Cadmium (mg/L)	0.5
Chromium VI (mg/L)	0.05
Chromium (Total) (mg/L)	2
Copper (mg/L)	1

Zinc (mg/L)	5
Selenium (mg/L)	0.2
Nickel (mg/L)	3
Nitrates (mg/L)	20
Phosphates (mg/L)	30
Cyanide Total (mg/L)	2
Sulphide (mg/L)	2
Phenols (mg/L)	10
Detergents (mg/L)	15
Colour	Less than 40 Hazen units
Alkyl Mercury	Not Detectable (nd)
Free and saline Ammonia as N (mg/L)	4
Calcium Carbide	Nil
Chloroform	Nil
Inflammable solvents	Nil
Radioactive residues	Nil
Degreasing solvents of mono-di-trichloroethylene type	Nil

Source: Environmental management and co-ordination (water quality) regulations, 2006

(Monitoring, 2008)

Arrangement of regulations, *Kenya Gazette supplement No 68, (Legislative supplement No.*

36).

6.4 Appendix 4: Standards for effluent discharge into the environment

Parameter	Max Allowable Limits
1,1,1-trichloroethane (mg/l)	3
1,1,2-trichloroethane (mg/l)	0.06
1,1-dichloroethylene	0.2
1,2-dichloroethane	0.04
1,3-dichloropropene (mg/l)	0.02
Alkyl Mercury compounds	Nd
Ammonia, ammonium compounds, NO ₃ compounds and NO ₂ compounds (Sum total of ammonia-N times 4 plus nitrate-N and Nitrite-N) (mg/l)	100
Arsenic (mg/l)	0.02
Arsenic and its compounds (mg/l)	0.1
Benzene (mg/l)	0.1
Biochemical Oxygen Demand (BOD 5days at 20 °C) (mg/l)	30
Boron (mg/l)	1
Boron and its compounds – non marine (mg/l)	10
Boron and its compounds –marine (mg/l)	30
Cadmium (mg/l)	0.01
Cadmium and its compounds (mg/l)	0.1
Carbon tetrachloride	0.02
Chemical Oxygen Demand (COD (mg/l)	50
Chromium VI (mg/l)	0.05

Chloride (mg/l)	250
Chlorine free residue	0.1
Chromium total	2
cis -1,2- dichloro ethylene	0.4
Copper (mg/l)	1
Dichloromethane (mg/l)	0.2
Dissolved iron (mg/l)	10
Dissolved Manganese(mg/l)	10
E.coli (Counts / 100 ml)	Nil
Fluoride (mg/l)	1.5
Fluoride and its compounds (marine and non-marine) (mg/l)	8
Lead (mg/l)	0.01
Lead and its compounds (mg/l)	0.1
n-Hexane extracts (animal and vegetable fats) (mg/l)	30
n-Hexane extracts (mineral oil) (mg/l)	5
Oil and grease	Nil
Organo-Phosphorus compounds (parathion, methyl parathion, methyl demeton and Ethyl parantrophenyl phenylphosphorothroate, EPN only) (mg/l)	1
Polychlorinated biphenyls, PCBs (mg/l)	0.003
pH (Hydrogen ion activity----marine)	5.0-9.0
pH (Hydrogen ion activity--non marine)	6.5-8.5
Phenols (mg/l)	0.001

Selenium (mg/l)	0.01
Selenium and its compounds (mg/l)	0.1
Hexavalent Chromium VI compounds (mg/l)	0.5
Sulphide (mg/l)	0.1
Simazine (mg/l)	0.03
Total Suspended Solids, (mg/l)	30
Tetrachloroethylene (mg/l)	0.1
Thiobencarb (mg/l)	0.1
Temperature (in degrees Celsius) based on ambient temperature	based on ambient temperature ± 3
Thiram (mg/l)	0.06
Total coliforms (counts /100 ml)	30
Total Cyanogen (mg/l)	Nd
Total Nickel (mg/l)	0.3
Total Dissolved solids (mg/l)	1200
Colour in Hazen Units (H.U)	15
Detergents (mg/l)	Nil
Total mercury (mg/l)	0.005
Trichloroethylene (mg/l)	0.3
Zinc (mg/l)	0.5
Whole effluent	toxicity
Total Phosphorus (mg/l)	2 Guideline value
Total Nitrogen	2 Guideline value

Not detectable (nd) means that the pollution status is below the detectable level by the measurement methods established by the Authority.

Source: Environmental management and co-ordination (water quality) regulations, 2006 (Monitoring, 2008)

Arrangement of regulations, *Kenya Gazette supplement No 68, (Legislative supplement No. 36)*.

6.5 Appendix 5: Technologies for dye removal

Methods	Advantages	Disadvantages
Chemical treatment		
Oxidative process	Simplicity of application	(H ₂ O ₂) agent needs to activate by some means
H ₂ O ₂ and Fe (II) salts (Fenton's reagent)	Fenton's reagent is a suitable chemical means	Sludge generation
Ozonation	Ozone can be applied in its gaseous state and does not increase the volume of waste water and sludge	Short half-life (20min)
Photochemical	No sludge is produced and foul odors are produced	Formation of by-products
Sodium hypochlorite (NaOCl)	Initiate and accelerates azo bond cleavage	Release of aromatic amines
Electrochemical destruction	No consumption of chemicals and no sludge build up	Relatively high flow rates cause a direct decrease in dye removal
Biological treatments		
Decolourization by white rot fungi	White-rot fungi are able to degrade dyes using enzymes	Enzyme production has also been shown to be unreliable

Other microbial cultures (mixed bacterial)	Decolorized in 24–30h	Under aerobic conditions azo dyes are not readily metabolized
Adsorption by living/dead microbial biomass	Certain dyes have a particular affinity for binding with microbial species	Not effective for all dyes
Anaerobic textile – dye bioremediation systems	Allows azo and other water soluble dyes to be decolorized	Anaerobic break down yields methane and hydrogen sulfide
Physical treatments		
Adsorption by activated carbon	Good removal of wide variety of dyes	Very expensive
Membrane filtration	Removes all dye types	Concentrated sludge production
Ion exchange	Regeneration: no adsorbent loss	Not effective for all dyes
Irradiation	Effective oxidation at laboratory scale	Requires a lot of dissolved O ₂
Electro-kinetic coagulation	Economically feasible	High sludge production

Source: (Adegoke & Solomon, 2015)