REMOVAL OF METHYLENE BLUE DYE AND METHYL ORANGE DYE FROM AQUEOUS SOLUTIONS USING *HYPHAENE PETERSIANA* NUTSHELL GRANULAR ACTIVATED CARBON: A CONTINUOUS FLOW STUDY.

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DECLARATION

I, Kanyimo Kudzaiishe C. declare that:

“REMOVAL OF METHYLENE BLUE DYE AND METHYL ORANGE DYE FROM SOLUTION USING *HYPHAENE PETERSIANA* NUTSHELL ACTIVATED CARBON-A CONTINUOUS FLOW STUDY”

is my work and that the sources I have used or quoted have been indicated by means of complete reference.

Signature………………………….                                    Date…………………………..
APPROVAL FORM

The undersigned certify that I have supervised, read and recommend to the Bindura University of Science Education for acceptance a research project entitled:

“REMOVAL OF METHYLENE BLUE DYE AND METHYL ORANGE DYE FROM SOLUTION USING HYPHAENE PETERSIANA NUTSHELL ACTIVATED CARBON”

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ABSTRACT

The adsorption of methylene blue, a cationic dye and methyl orange, an anionic dye from aqueous solution was investigated using fixed bed column adsorption. For methylene blue, the effect of bed depth, particle size, inlet dye concentration and flow rate was studied under room conditions and pH 8. For methyl orange, the effect of bed depth, particle size, inlet dye concentration and flow rate was studied under room conditions and at pH 4. Dye concentrations were determined using UV-Vis spectrophotometry.

The experimental data showed that breakthrough time ($t_b$) and exhaustion time ($t_e$) decreased with increasing flow rate, particle size and inlet dye concentration. For both methylene blue dye and methyl orange time for 50% breakthrough increased as particle size decreased. Breakthrough time and exhaustion time also increased with increase in bed depth. Sorption efficiency and breakpoint time and exhaustion time were lower at lower bed depth and were higher at higher bed depth.

The experimental data was evaluated using the Bed Depth Service Time (BDST) model, the Thomas model as well as the Yoon-Nelson model. The data fitted the BDST model better than the Thomas model or the Yoon-Nelson model. The Yoon-Nelson model showed good agreement with the experimental data. The high correlation coefficients indicate the validity of the Yoon-Nelson model ($R^2 \geq 0.9242$) except for particle size 850 µm which has a lower coefficient of 0.8004.

Evaluation using the Thomas model produced regression coefficients $R^2$ (0.9242-0.9942 except for 0.8004 for 850 micro-meter particle size) which showed that the Thomas model fitted the experimental data well. Evaluation using the BDST model produced $R^2$ values for both MB and MO dyes were greater than 0.99. For MB $R^2=1$ and for MO $R^2=0.9916$.

For both batch desorption studies and continuous flow desorption studies, the adsorption and the removal efficiency for both dyes decreased as the number of regeneration cycles increased. The time taken for $Ct/Co=0.1$ for each dye decreased as the regeneration cycles increased. The adsorption capacity and the efficiency of the adsorbent decreased as the number of adsorption cycles increased. In methylene blue desorption the time to achieve $Ct/Co=0.1$ increased with increase in the concentration of the eluent. In the batch desorption studies the removal efficiency of both dyes decreased as the number of desorption cycles increased.
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DEDICATION

To my parents, my wife Nyaradzai, my two children Unashe and Anopaishe
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ABBREVIATIONS AND SYMBOLS

AC             Activated Carbon
BDST           Bed Depth Service Time
$C_o$          initial dye concentration   mg L$^{-1}$
$C_t$          effluent dye concentration  mg L$^{-1}$
FTIR           fourier transform infrared spectroscopy
GAC            Granular Activated Carbon
HPNS           *Hyphaene petersiana* nut shell
HPNS-GAC       *Hyphaene petersiana* nut shell granular activated carbon
$K_{TH}$       Thomas rate constant ml min$^{-1}$ mg$^{-1}$
$K_{YN}$       Yoon-Nelson rate constant min$^{-1}$
MB             Methylene blue
MO             Methyl orange
$M_{total}$    total adsorbent sent to column mg
$N_o$          adsorption capacity mg g$^{-1}$
Q               volumetric flowrate ml min$^{-1}$
$q_o$          maximum adsorptive capacity mg g$^{-1}$
$q_{total}$    maximum column bed capacity mg g$^{-1}$
t              time min
$t_b$          breakthrough time min
$t_e$          exhaustion time min
UV-Vis         Ultra-Violet/Visible light
\( V_{\text{eff}} \) effluent volume ml

\( X \) mass of adsorbent g

\( X_0 \) critical bed depth cm

\( \tau \) time required for 50 % breakthrough min

\( \mu \) micro
CHAPTER ONE: INTRODUCTION

1.0 Background

The wide-spread and increased use of dyes and pigments has become of paramount concern to environmentalist. Organic substances or compounds are some of the major pollutants from industry. Organic substances such as dyes and pigments have the potential to pollute both groundwater and surface waters. For times immemorial, many chemicals have polluted groundwater supplies. Water bodies have been contaminated via runoff from agricultural land as well as from industrial wastes discharge (Manahan, 2000).

Chemical contamination has been of great concern to humankind and continues to be of great concern even today. In industrialized nations as well as in the developing world chemical contamination is of great concern. Over 2 million tons of waste are discharged into water bodies daily and these wastes include dyes and other chemicals (Sulyman et al., 2017). Over 700 000 tons of dyes are produced every year (Ciardelli, 2001; Sulyman et al., 2017). Between 10 to 15 % of the dyes are released as effluent through various processes. Some are released during the dyeing process due to inefficient binding (Ratna and Padhi, 2012). Hence large amounts of dye remain unbound or unfixed and are lost to the effluent. Dyes are used in the textile industry, paper-printing industry, leather-dyeing industry, photography industry, food industry as well as in the petroleum industry.

The pollution of groundwater and surface water by dyes is certainly of great concern since these chemicals can have negative effects on water quality, aquatic life as well as on other organisms. Dyes are produced as either natural dyes or as synthetic dyes and synthetic dyes pose the greatest problem to the environment because of their stability and resistance to bio-degradation and photo-degradation (Ciardelli and Raneri, 2001; Gupta and Suhas, 2009). Dyes that are released into the environment pose a huge risk of eco-toxicity and bio-accumulation (Naeem et al, 2016). The color from dyes affects the aesthetic value of the water, blocks the passage of sunlight through the water reducing the photosynthetic ability of aquatic plants as well as affecting other
forms of aquatic life. Many of the synthetic dyes and their breakdown products are toxic to several forms of aquatic life (Mogaddasi et al., 2010). Some dyes are mutagenic as well as carcinogenic and hence can be harmful even to humans especially as a result of prolonged exposure (Hameed and El-Khaiary, 2008; Gupta and Suhas, 2009; Pal et al., 2013).

Methylene blue is a basic cationic dye which is used mostly in the textile industry. The dye can cause vomiting, increased heart-rate, cyanosis, jaundice, tissue necrosis and quadriplegia in humans (Kalantry et al., 2015; Naeem, 2016). Methyl orange is also widely used in the textile industry as well as in the printing and paper industry, food and pharmaceutical industries as well as in research laboratories. Methyl orange is carcinogenic and can cause cancer when ingested (Kuar and Datta, 2011; Alzaydien, 2013).

Dyes can be removed from water using a number of ways. A number of methods can be used to remove dyes from water and these include oxidation, ozonation, coagulation and flocculation, filtration, electrochemical treatment as well as adsorption (Gerard et al., 1998). The choice of the type of dye removal technique employed depends on a number of factors. Other treatment techniques have been discovered to have disadvantages such as the incomplete removal of pollutants, low selectivity, high reagent use, high chemical and energy requirements, high costs as well as generation of toxic wastes. Adsorption is becoming the much preferred method because of its reduced initial cost, simplicity of design, versatility, ease of operation and insensitivity to toxic substances (Shah et al., 2012; Chowdhury and Saha, 2012; Mogaddasi et al., 2013). Activated carbon is produced from high carbon materials. The most popular method is adsorption using activated carbon but this method has also proved to be expensive (Hegazi, 2013; Ibrahim et al., 2006; Gupta et al., 2003). Production of activated carbon from coal is expensive and hence researchers are now focusing on alternative precursors or raw-materials. Lignocellulosic materials are now being considered as cheaper raw-materials or precursors for the production of activated carbon (Mahmoudi et al., 2012). The high cost associated with the use of activated carbon has generated a lot of interest among researchers to look for cheaper alternatives as adsorbents (Ferrero et al., 2007; Hesas et al., 2013).
Hyphaene petersiana, also known as Makalani nut or African palm, is a tree that is found in the low-lying regions of Zimbabwe, Botswana, Zambia, Namibia, Mozambique, Angola, Tanzania, DRC, Rwanda and Burundi. The plant has edible fruits and each tree can have up-to 2000 fruits. The pulp of the fruit is edible and can also be used to brew beer or wine. The fruit has a seed with a hard shell when dry. The hard nut inside the shell is used to make ornaments and buttons. To access the nut, the shell is cut or crushed and thrown away.

This research will focus on the removal of Methylene blue dye and Methyl orange dye using granular activated carbon produced from Hyphaene petersiana nutshell using the continuous flow experimental design. In this study Methylene blue and Methyl orange dyes will be adsorbed onto Hyphaene petersiana nutshell activated carbon and the efficacy of adsorption determined.

1.1 Aim

To determine the ability of locally available Hyphaene petersiana nutshell granular activated carbon to remove Methylene blue dye and Methyl orange dye from aqueous solutions by adsorption.

1.2 Objectives

- To prepare granular activated carbon from Hyphaene petersiana nutshell
- To conduct continuous flow experiments to determine the effects of bed depth, flow rate, initial dye concentration and particle size on adsorption of Methylene blue dye and Methyl Orange dye onto Hyphaene petersiana nutshell activated carbon.
- To compare Hyphaene petersiana nutshell activated carbon adsorption capacity on Methylene blue dye and Methyl orange dye.
- To analyze the experimental data using Thomas, Bed Depth Service Time and Yoon-Nelson models.
1.3 Scope of the study

This study investigates the column adsorption ability for the removal of Methylene blue and Methyl orange dyes from aqueous solutions using granular activated carbon produced from *Hyphaene petersiana* nutshell. In the study, the parameters to be investigated are

- Effect of flow-rate
- Effect of inlet dye concentration
- Effect of bed depth
- Effect of particle size

1.4 Justification

Commercial activated carbons are relatively expensive due to the fact that they are produced from non-renewable and relatively expensive material such as coal. There is thus need to consider alternative and cheaper precursor materials for the production of activated carbon. Precursors for the production of activated carbon should be rich in carbon. Lignocellulosic agricultural wastes are relatively less expensive and are rich in carbon. Lignocellulosic structural materials are associated with different functional groups which are responsible for organic molecules adsorption thus have the potential to be converted into activated carbon. This research uses activated carbon as an adsorbent because it is more effective in adsorption. Activated carbon has a high adsorptive capacity as a result of its well-developed internal porosity, pore volume and pore size distribution. *Hyphaene petersiana* nutshell was used to produce granular activated carbon due the abundance of the trees and fruits in the low lying areas of southern and central Africa.

Dyes affect water quality by decreasing its aesthetic value, impeding light penetration thereby affecting aquatic organisms negatively. Dyes also lead to effluent that is toxic, has a high organic content and can cause a variety of negative reactions in humans upon exposure. A number of dyes are toxic or/and produce toxic products when broken down. In humans, dyes can affect the functioning of the reproductive system and kidneys, cause cancer, allergic reactions and skin
irritations. Most dyes do not bio-degrade or photo-degrade easily. It is for these reasons that dyes should be removed before discharging them into water bodies or waste-water treatment plants. Adsorption has been used in removing dyes from aqueous solutions in this study because it has several advantages over other dye removal methods or water treatment methods. Adsorption has reduced initial costs, ease of operation, simplicity of design and low selectivity.

Very few studies have been undertaken under continuous flow conditions (Ong et al., 2009). Continuous flow adsorption studies are more useful for the cycle of adsorption-desorption and it effectively makes use of the sorbent capacity. Continuous flow adsorption is easy to operate and easy to scale up from a laboratory scale study. The column test can be used to quantify the parameters which are required to design an industrial scale continuous flow adsorption column.

1.5 Delimitations

_Hyphaene petersiana_ nutshells for production of granular activated carbon as well as chemicals for adsorption experiments were readily available. The research will only determine the adsorptive capacity of _Hyphaene petersiana_ nut-shell granular activated carbon for Methylene blue dye and Methyl orange dye.

1.6 Limitations

The instrumentation used for characterization of the adsorbent produced and also the instrumentation used in this study depended on the availability and accessibility of appropriate instruments. The lack of readily available adsorbent characterization instruments prevented a more complete and detailed characterization of the adsorbent. More surface characterization could have been done using Scanning Electron Microscopy and surface area determination could have been done using BET.
CHAPTER 2: LITERATURE REVIEW

2.1 Textile effluent

Water is a vital commodity and all forms of life depend on it. Due to a number of factors, the turn of the twenty-first century has seen an increase in the demand for clean water. Of the total water available, only three percent is available as fresh water whereas the rest is salty sea water. Which is not available for human consumption. Only 0.06 % of the 3% fresh water can be accessed easily since the rest is found frozen as ice-cap of as ground water.

Many regions of the world are now facing shortages of fresh clean water due to increased contamination (Pal et al., 2013). Water-borne toxic chemicals pose the greatest risk to the safety of fresh water supplies (Kalantry et al., 2015; Shah et al., 2012). Wastewater from industries and agricultural activities contains a variety of pollutants with the majority of these pollutants being organic pollutants (Kyzas, 2015). The textile industry is also considered as one of the major polluters of water (Gupta and Suhas, 2009). Wastewater from textile industries contains pollutants such as dyes, pigments, salts and auxillaries (Mahmoode et al., 2011). Auxillaries and residual dyes are the major pollutants (Kyzas, 2015). Pretreatment of cotton, fabrics, gum, cellulose and hemi-cellulose produces pollutants in the form of organic matter. Pollutants such as dyes and additives are also discharged during printing and dyeing processes (Ong et al., 2009). About 200 billion litres of textile effluent are produced per year world-wide (Kant, 2012).

Effluent from textile industries have a dark colour due to the presence of dyes and other chemicals and organics and this makes the textile wastewater very turbid (Ratna and Padhi, 2012). The amount of dye in wastewater is determined by the amount of dye that is used per day, the degree of dye fixation on the intended substrate and the dye removal degree (Ciardelli and Raneri, 2001). About 10-25% of dyes are lost during the dyeing and printing process (Ratna and Padhi, 2012). About 2-20% of the dyes are directly discharged as effluent. Water is used in the textile industry for conveying dyes or color to the fabric, cleaning the fabric and equipment and also for removing surplus dye (Kant, 2012). This water is then expelled as wastewater and has a great potential to pollute the environment. Many other industries use dyes to color their products.
There are over 10 000 different dyes and pigments used and over 700 000 dyes and pigments are produced yearly worldwide (Han et al., 2009).

2.2 Dyes

Dyes are colored organic compounds which can be used to color industrial products such as leather, paper, cloths, plastic and other products. When discharged in water, dyes can be viewed as organic pollutants (Putraa et al., 2009). Dyes are soluble in water and can also be soluble in organic solvents.

When in aqueous solution, dyes can be quantified using High Performance Liquid Chromatography-Mass Spectrometry (HPLC-MS), Liquid Chromatography-Mass Spectrometry (LC-MS) and spectroscopy. However, the quantification of dyes in mixtures is difficult due to spectral influence (Ratna, 2012). The detection and quantification of dyes in effluents or in a mixture requires complex procedures which are expensive (Chowdhury, 1996).

Dyes can be classified according to application as shown below;

- Basic dyes-these are water-soluble cationic compounds
- Acidic dyes-these are water-soluble anionic compounds
- Direct dyes-these are anionic compounds that can be applied directly
- Disperse dyes-are water insoluble dyes
- Reactive-are water soluble anionic dyes
- Sulfurous dyes-are organic compounds/dyes containing sulfur
- Vat dyes-are water insoluble and chemically complex dyes.

2.2.1 Methylene blue dye

Methylene blue dye with formula C$_{16}$H$_{18}$N$_{3}$ClS, has the molecular structure;
Figure 2.1 Chemical structure of methylene blue.

Methylene blue dye is an odorless dark green powder which gives a blue solution when dissolved in water. Its solubility in water at 25 °C is 43.6 g/L and it has a molecular weight of 319.85 g/mol. Methylene blue can be used as a dye, a stain in biology laboratories and also as a drug (Oz et al., 2011).

2.2.2 Methyl orange dye

Methyl orange with formula C_{14}H_{14}N_{3}NaO_{3}S, has the molecular structure;

Figure 2.2 Chemical structure of methyl orange

Methyl orange is an orange powder which is red in acid and yellow in alkali hence it is also used as an indicator in acid-base reactions. It has a molecular weight of 327.34 g/mol and its solubility in water at 25 °C is 5 g/L.

2.2 Negative effects of dyes and textile wastewater

The presence of color in wastewater has increased significantly over the past few years and the presence of color is a qualitative indicator that shows the degree of pollution of water (Kyzas, 2015). Textile effluents are dark in color owing to the presence of dyes and auxiliary chemicals and this increases the turbidity of water (Pal et al., 2015). This turbidity due to the presence of dyes blocks the penetration of light in water bodies and this affects the process of photosynthesis.
and hence the entire aquatic food chain is affected negatively (Sulyman et al., 2017; Hameed et al., 2013; Mogaddasi et al., 2010; Zaheria et al., 2009). The reduction in photosynthetic activity affects the growth of some aquatic micro-organisms (Elemen et al., 2012; Han et al., 2009).

High levels of textile organic substances in water greatly reduces the levels of dissolved oxygen which affects the ecological balance significantly and also reduces the population of beneficial biological micro-organisms (Ratna, 2012). The presence of large volumes of organic pollutants may cause an increase in the chemical oxygen demand (COD) and the biological oxygen demand (BOD) which then creates anaerobic conditions which then favors the flourishing of anaerobic bacteria leading to formation of toxic gases (Amin, 2009; Khopka, 2004).

Dyes also have a negative impact on the aesthetic value of the water. Dyes impart color to water and color in water is not pleasing. Many dyes and their breakdown products have negative effects on the environment. Some of these dyes are toxic to aquatic life and to humans (Mahmoodi et al., 2011; Foo and Hameed, 2010; Chen, 2006). Some of these dyes especially synthetic dyes resist biodegradation and photo-degradation due to their chemical and molecular structures and hence can remain in the environment for long periods (Mahmoud et al., 2012; Liu et al., 2011; Gupta, 2009; Ciardelli, 2001). When degraded, some of these dyes yield products that are toxic and carcinogenic (Chen, 2006). Dyes can also be synthesized from carcinogens and they themselves can be carcinogenic, mutagenic and teratogenic (Carmen and Daniela, 2012; Chen, 2006). The cleavage of the azo linkage can lead to formation of carcinogenic products (Foo and Hameed, 2010; Chowdhury, 1996).

The discharge of untreated dye effluent into water bodies can cause pollutants to build up in micro-organisms along the food chain due to bio-accumulation and this can result in the death of micro-organisms as a result of chemical poisoning (Chojnacko, 2010). In humans exposure to dyes can affect the reproductive system, cause allergies, skin irritations, dermatitis, kidney problems as well as cancer (Ratna and Padhi, 2012; Shah et al., 2012; Kant, 2012).

### 2.3 Dye removal methods

Dye removal methods can be classified into chemical, biological and physical methods.
2.3.1 Chemical methods

Chemical methods involve the use of chemicals to remove pollutants. Chemical dye removal methods include techniques such as oxidation, coagulation, flotation, ozonation, flocculation, precipitation, neutralization, reduction, catalysis, ion exchange and electrochemical processes (Zaharia and Suten, 2012). Chemical methods have the disadvantage that they are expensive and they can also lead to the formation of lots of sludge and toxic chemicals (Zaharia and Suten, 2012; Wang et al., 2003). Chemical methods can also cause secondary pollution because of excessive chemical use.

2.3.2 Physical methods

Physical methods used in treating dye wastewater include membrane filtration techniques and adsorption techniques. Membrane processes include nano-filtration, micro-filtration, ultra-filtration, reverse osmosis and electro-dialysis among others (Zewait and Yousef, 2015). Membrane processes are expensive and they are affected by clogging which makes them to require very frequent replacement (Kyzas, 2015).

2.3.3 Biological methods

Biological treatment methods are methods that involve the degradation or decomposition of dyes through the action of micro-organisms such as fungi, bacteria and algae (Aizenchtadt et al., 2008). Methods include stabilization in stabilization ponds, aerated lagoons, trickle filters, activated sludge aerobic and anaerobic digestion (Oliviera et al., 2007). The use of biological treatment methods has the disadvantage that the majority of the dyes are toxic to micro-organisms involved in the decomposition and also that the action of micro-organisms can lead to the production of toxic by-products (Aksu et al., 2005).
2.4 Adsorption

In adsorption, components of a gas or liquid are adsorbed onto the surface of a solid adsorbent leading to separation. It is thus a method of separation where soluble solutes are separated from their solvent. In wastewater treatment, soluble solutes are transferred from wastewater to the surface of solid particles which are porous (Zaharia et al., 2011). Adsorption can be used to remove undesirable color, taste, turbidity, inorganic pollutants as well as organic pollutants (Sulyman et al., 2015). Adsorption is preferred because other dye removal methods have several limitations (Ahmed and Alrozi, 2011).

Adsorption involves three main steps;

1. The diffusion of the adsorbate from the stream to the external surface of the adsorbent particle.
2. The migration of the adsorbate from the external surface to the pores within the adsorbate particle
3. The movement of the adsorbate particle to the pores surface (Han et al., 2009)

When the adsorbent is in contact with the adsorbate, the atoms on the surface of the adsorbent attract the adsorbates. The above phenomenon arises as a result of the fact that the atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and hence are only partially surrounded hence leaving them with the potential to attract the adsorbate (Lui et al., 2012). Atoms on the surface of adsorbents are bond deficient.

The adsorption technique is one of the most efficient wastewater treatment methods because of its low initial cost, flexibility, simple design and operation as well as the non-toxicity of the adsorbents used (Kyzas, 2015; Gupta et al., 2012). Dyes are highly soluble in water and as such are difficult to remove using the conventional water treatment methods. Adsorption also has the advantage that it does not lead to the formation of toxic substances.
2.5 Types of adsorption

Adsorption can be classified into physical adsorption and chemical adsorption.

2.5.1 Physical adsorption
This mode of adsorption is also known as physisorption. In this type of adsorption the adsorbate forms weak intermolecular (van der Waal) forces with the surface of the adsorbent. Physical adsorption is characterized by weak intermolecular forces, low temperature, low enthalpy and multi-layer adsorption (Rahman and Akter, 2015; Putra et al., 2009; Sivakumar and Palanisamy, 2008).

2.5.2 Chemical adsorption
This mode of adsorption is also known as chemisorption. In this type of adsorption the adsorbate forms chemical bonds with the adsorbent. Chemical adsorption is characterized by covalent bonds, high temperatures, high enthalpy and mono-layer adsorption (Rahman and Akter, 2015; Sivakumar and Palanisamy, 2008).

2.6 Factors affecting adsorption

Adsorption can be enhanced by changing certain properties of the liquid or gaseous phase such as temperature, concentration and pH. Adsorption is also affected by the surface area of the adsorbent. Smaller particles tend to have high surface areas and this increases the adsorption capacity. High porosity also leads to high surface area. The more developed the pore system, the greater the internal surface area (Emenike et al., 2016).

The extent of acidity or alkalinity of the adsorbate-adsorbent system has effect on the adsorption capacity. The pH affects the surface charge of the adsorbent and it determines the influence of the surface functional groups (Emenike et al., 2016).
The concentration of the adsorbate also influences the adsorption process. The initial concentration of the adsorbate can lead to either an increase in adsorption capacity or it can lead to a decrease in the adsorption capacity depending on the nature of the adsorbate-adsorbent system (Rout et al., 2014).

2.7 Adsorbents

Adsorbents used in textile wastewater treatment can be of natural origin or it can be as a result of industrial production or chemical engineering (Kyzas, 2015; Sharma, 2015). Natural adsorbents include clay, clay minerals, oxides, zeolites and biopolymers. Engineered adsorbents include carbonaceous adsorbents, oxidic adsorbents and zeolite molecular sieves (Sharma, 2015). Adsorbents differ in their characteristics and hence in their adsorptive capacity (Worch, 2012).

Adsorbents can be produced from natural materials, agricultural waste products, industrial waste products or geological material (Kyzas, 2015). Natural materials include wood, coal, peat, chitosan, clay and natural zeolites. Agricultural waste products include shells, hulls, husks and stones from fruits and nuts (Bark et al., 2013; Chatterjee et al., 2012). Other waste products include saw-dust, corn-cob waste sunflower stalks and other plant or crop residue. Industrial wastes include fly-as, blast-furnace slag, sludge, bagasse and various types of ash. Geological materials include soil and other minerals (Crittenden and Thomes, 1998).

Commercial adsorbents include zeolites, silica gel and activated carbon. Zeolites are materials that contain aluminate and silicon. Some zeolites occur naturally whereas some are synthetically produced (Worch, 2012).

Some biomass can be used as bio-adsorbents in their natural states without any modifications (Mohammadpour et al., 2017; Babel and Kurniawan, 2003). These adsorbents are referred to as biosorbents. Agricultural and industrial wastes can be converted into activated carbon or biochar (Chatterjee et al., 2012). The conversion of material to activated carbon involves carbonization and activation.
2.8 Activated carbon

Activated carbon is the most popularly used adsorbent for dye removal by adsorption. The performance of the activated carbon depends on a number of factors such as large surface area, pore size distribution, surface functional groups and processibility (Al-Qodah and Shawabkah, 2009). In adsorption, activated carbon has proved to have better performance due to its proven capacity to remove pollutants. The availability of low cost agricultural and industrial waste products has the ability to provide good precursors for the preparation of activated carbon (Rahman and Akter, 2016). The costs of preparing activated carbon from agricultural and industrial wastes are lower when comparing with commercial activated carbon which is usually made from coal and charcoal (Sivakumar and Palanisamy, 2008).

Activated carbon can be made from cheap locally available precursor material (Lesmana et al., 2009). Unmodified agricultural and industrial wastes as adsorbents have the disadvantage of having lower mechanical strength, lower densities, lower adsorption capacities, poor structural rigidity and may even cause clogging (Bulgariu and Bulgariu, 2013; Mao et al., 2010; Vijayaraghavan and Yuan, 2008). Activated carbon can be used to remove a number of water pollutants (Belhachemi and Addoun, 2011; Mohammadi et al., 2011; Meshko et al., 2001).

Activated carbon can be manufactured from different precursor materials using different methods. For organic precursor material, a preliminary carbonization process is done. This carbonization process transforms the lignocellulosic material into carbonaceous material (Al-Qodah and Shawabkah, 2009). There are two types of activation which are physical activation and chemical activation.

2.8.1 Physical activation

Carbonization and activation are done in a furnace at very high temperatures. Carbonization is done at temperatures of 400-600 °C so as to remove the volatile matter. The carbonaceous product is then activated at temperatures 600-900 °C. During activation, the pores are opened and existing pores are enlarged (Ghomshes et al., 2011; Tan et al., 2008).
2.8.2 Chemical activation
In chemical activation, the precursor material is impregnated with dehydrating chemicals such as ZnCl$_2$, HCl, H$_2$SO$_4$, HNO$_3$, KOH, ammonium salts, borates and H$_3$PO$_4$. The dehydration leaves a carbon skeleton with fine meso- and micro-porous structure. Chemical activation combines carbonization and activation (Ghomshe et al., 2011; Tan et al, 2008).

2.9 Column adsorption

In an adsorption column the adsorbent is held in position and the adsorbate solution is fed continuously through the adsorbent at a constant flowrate either from the top or from the bottom. Small particles of a solid usually make up the adsorbent. The adsorbate solution is continuously in contact with a given quantity of fresh adsorbent and this enhances the creation and maintenance of a concentration gradient between the adsorbent and the adsorbate (Gupta et al., 2016).

Fixed bed column arrangement is the best arrangement for conducting adsorption studies since experimental data can be scaled up to pilot plants and industrial scale (Ko et al., 2003). In a fixed bed column system, the adsorbent closest to the inlet saturates first because this is where maximum adsorption takes place initially (Chen et al., 2003). This adsorption zone moves with time towards the other end of the adsorption bed. As the adsorption zone moves, the effluent concentration gradually increases until the effluent concentration becomes equal to the feed concentration (Chen and Wang, 2005).

The efficiency of a column can be evaluated by plotting breakthrough curves. A breakthrough curve is obtained by plotting column effluent concentration versus effluent volume or time or by plotting Ct/Co against effluent time or effluent volume, where Ct is effluent concentration at time t and Co is the inlet adsorbate concentration (Vijayaraghavan and Prabu, 2006). The shape of the breakthrough curve describe the operation and the dynamic response of the breakthrough curve (Kumar and Bandyopadhyay, 2006).
2.10 Mathematical analysis of column data

The effluent volume ($V_{eff}$) can be calculated by using the equation (2.1) below;

$$V_{eff} = Q t_{total}$$  \hspace{1cm} \text{(Equation 2.1)}

Where $V_{eff}$ is the effluent volume collected in ml,

$Q$ is the volumetric flowrate in $\text{ml min}^{-1}$,

$t_{total}$ is the total flow time in minutes.

The maximum column bed capacity $q_{total}$ in mg for a given inlet adsorbent concentration and flowrate is calculated using equation (2.2)

$$q_{total} = \frac{Q}{1000} \int_{t=0}^{t=t_{total}} c_{ad} dt$$  \hspace{1cm} \text{(Equation 2.2)}

Where $C_{ad} = C_{o} - C_{t}$,

Where $C_{o}$ is inlet adsorbate concentration in $\text{mg L}^{-1}$

$C_{t}$ is outlet adsorbate concentration in $\text{mg L}^{-1}$.

The total adsorbate sent to the column $M_{total}$ is calculated using equation (2.3),

$$M_{total} = \frac{C_{o} \times Q \times t_{total}}{1000}$$  \hspace{1cm} \text{(Padmesh \textit{et al.}, 2005) \hspace{1cm} \text{(Equation 2.3)}}$$

The maximum adsorption capacity $q_{o(exp)}$ is calculated using equation (2.4)
where $m$ is the mass of the adsorbent packed in the column in g.

Total percentage removal can be calculated using equation 2.5

$$\text{Total Removal } \% = \frac{q_{\text{total}}}{m_{\text{total}}} \times 100$$  \hspace{1cm} \text{(Aksu, 2004)} \hspace{1cm} \text{(Equation 2.5)}$$

2.11 Modelling of breakthrough curves

The performance of the adsorption column and its dynamic behavior can be evaluated and analyzed through various models.

2.11.1 The Thomas model

For evaluation of breakthrough results, the Thomas model can be applied to the experimental data. The Thomas model is based on the mass transfer model and assumes that the adsorbate molecules migrate from the solution to the film around the particle and diffuses through the liquid film to the surface of the adsorbent, followed by intra-particle diffusion and then adsorption on the active site (Rouf and Nogapdma, 2015; Mohamed, 1998). The following is the linearized Thomas model equation;

$$\ln \left( \frac{C_0}{C_t} - 1 \right) = \frac{K_{TH} q_o m}{Q} - K_{YN} C_{ot}$$  \hspace{1cm} \text{(Biswas and Mishra, 2015)} \hspace{1cm} \text{(Equation 2.6)}$$

Where $K_{YN}$ is the Thomas rate constant in $\text{ml min}^{-1} \text{mg}$.

$t$ is the total flow time in $\text{min}$

$Q$ is the volumetric flowrate in $\text{ml min}^{-1}$

$q_o$ is maximum adsorption capacity in $\text{mg g}^{-1}$

$m$ is the mass of the adsorbent in g.
A plot of $\ln(c_o/c_t - 1)$ versus time gives the values of $K_{TH}$ (the Thomas rate constant) and $q_o$ (the maximum adsorption capacity) from the slope and intercept.

### 2.11.2 The Yoon-Nelson model

The Yoon-Nelson model is based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of the adsorbate breakthrough. The model does not require any information on the properties of the adsorbate, adsorbent type and the physical property of the adsorbent bed (Gupta and Suresh, 2010).

The linearized form of the Yoon-Nelson model for a single component system is expressed as

$$\ln\left(\frac{C_t}{C_o - C_t}\right) = K_{YNt} - \tau K_{YN} \quad \text{(Gupta et al., 2016)} \quad \text{(Equation 2.7)}$$

Where $K_{YN}$ is the Yoon-Nelson rate constant (min$^{-1}$)

$\tau$ is the time required for 50 % adsorbate breakthrough.

The values of parameters, $K_{TH}$ and $\tau$ can be calculated from the plot of $\ln \left(\frac{C_t}{C_o - C_t}\right)$ versus time.

### 2.11.3 Bed Depth Service Time (BDST) model

The model states that there is a linear relationship between bed depth and column service time (Ghiribi and Chlendi, 2011). Service time is the time taken by the adsorbent to remove a specific amount of adsorbate from the solution before it is saturated (Rout et al., 2014). The model assumes that the rate of adsorption is determined by the interaction between the adsorbate and the unused adsorbent (Vijayaraghavan and Prabu, 2006). The model only requires three column tests at different bed depths.

The equation (8) below can be used to describe the adsorption process
\[ t = \frac{N_0}{C_0 Q} Z - \frac{1}{k C_0} \ln\left(\frac{C_0}{C_b} - 1\right) \]  

(Equation 2.8)

\( C_0 \) is the inlet adsorbate concentration in mg/L,

\( C_b \) is the solute concentration at a specific breakthrough point in mg/L,

\( k \) is a constant in L/mg h,

\( N_0 \) is adsorption capacity in mg/g,

\( Z \) is the column bed depth in cm.

The quantities \( \frac{N_0}{C_0 Q} \) and \( \frac{1}{k C_0} \ln\left(\frac{C_0}{C_b} - 1\right) \) in equation (2.8) are obtained from the slope and intercept of the linear plot of \( t \) at a specific breakthrough point against bed depth, \( Z \).

The critical bed depth can be calculated using equation (2.9) below and setting the time to \( t=0 \) and then solving for \( X_o \),

\[ X_o = \frac{Q}{k N_0} \ln\left(\frac{C_0}{C_b} - 1\right) \]  

(Equation 2.9)
CHAPTER 3: METHODOLOGY

3.0 Introduction
The chapter focuses on the equipment, chemicals used, sample collection and preparation, methods that were used in characterization of the sample. The chapter also focused on column preparation and how the continuous flow study was done.

3.1 Equipment

A Labotec horizontal shaker was used to agitate suspensions of adsorbents in the synthetic wastewater solutions. An MRC BT300-2J peristaltic pump was used to deliver synthetic wastewater at predetermined flowrates. A Thermo Fisher Scientific GENESYS 10S UV/VIS spectrophotometer was used to measure concentrations of synthetic wastewater solutions before and after adsorption. A Thermo Fisher Scientific nicolet IS5 MIR FTIR spectrophotometer was used to identify key functional groups. A Heraeus laboratory air oven was used to dry samples. A RIOS water purification unit was used to distill water. A muffle furnace was used to carbonize and activate samples and also to conduct ash content and volatile matter content analysis.

3.2 Chemicals

All the chemicals used in the various experiments were of analytical reagent grade and were used without further purification. Double distilled water was used in the preparation of all solutions. Methylene blue dye was used to prepare synthetic wastewater solutions of various concentrations. Methyl orange dye was used to prepare synthetic wastewater solutions of various concentrations. Sulphuric acid (98%) was used to carbonize samples during preparation of the adsorbent. Nitric acid was used to adjust pH of the synthetic wastewater solutions to the required levels and also in desorption studies as an eluent. Sodium hydroxide was used to adjust the pH of the synthetic wastewater solutions to the required levels and also in desorption studies as an eluent. Sodium hydrogen carbonate was used to remove excess acid during the preparation of the adsorbent.
3.3 Preparation of Activated Carbon

3.3.1 Sample collection and pre-treatment

*Hyphaene petersiana* fruits were harvested from *Hyphaene petersiana* trees found around Tongaat Hullet Triangle Estate in Zimbabwe’s South-eastern Lowveld. The edible pulp was removed and the seeds washed with tap water and the seed shell was cut so as to remove the nut and also to reduce the pieces of the shell into small sizes. The *Hyphaene petersiana* nutshell pieces were again washed with water and dried in a hot air oven at 70 °C for 24 hours.

Fig. 3.1 Picture showing a *Hyphaene petersiana* tree and Makalani nut
3.3.2 Preparation of Granular Activated Carbon

The *Hyphaene petersiana* nutshell pieces were dried in a hot air oven at a temperature of 60 °C for 24 hours to remove moisture. The sample was prepared using a method by Theivarasu and Mylsiamy (2010). The shell pieces were then soaked in 98% H₂SO₄ for 48 hours at room temperature. The excess acid was drained and the solid residue was further washed with distilled water to further remove excess acid until neutral pH. After this treatment, the solid product was soaked in 1% NaHCO₃ over-night to remove any left-over excess acid and the product dried in an air oven at 60 °C for 10 hours. The material was then transferred to a muffle furnace kept at 500 °C for seven hours. The dry mass obtained was crushed into granules using mortar-and-pestle and stored in a dessicator before use.

![Fig. 3.3 Picture of the HPNS-GAC produced](image)
3.4 Characterization of Activated Carbon from sugarcane bagasse

3.4.1 FTIR analysis

The surface chemistry of the particles was determined by FT-IR spectroscopy to determine functional groups. The surface chemistry of freshly prepared adsorbent and dye-saturated adsorbent was determined.

3.4.1 pH measurement

For pH determination, 1 g of the prepared sample was added to 100 mL of double distilled water and the mixture was shaken on a laboratory shaker for one hour. The pH was determined using a digital pH meter.

3.4.2 Moisture content

To determine moisture content the method by Malik et al. (2011) was use. 1 g of the prepared sample was weighed and dried in an oven for 24 hours at 105 °C until the weight became constant. The moisture content was calculated using the formula;

\[
\text{Moisture content} = \frac{W_i - W_f}{W_i} \times 100\% \quad \text{(Equation 3.1)}
\]

Where \(W_i\) is the initial weight of the sample in g,

And \(W_f\) is the final weight of the sample in g.

3.4.3 Ash content

To determine the ash content, the method by Malik et al., (2011) was used. 1 g of sample was placed in a porcelain crucible and heated in a muffle furnace at 500°C for 4 hours. The material was allowed to cool in a dessicator and the ash content was calculated using the formula;

\[
\text{Ash content} = \frac{W_b - W_o}{W_a - W_o} \times 100\% \quad \text{(Equation 3.2)}
\]

Where \(W_o\) is the weight of the empty crucible in g,
\( W_a \) is the weight of crucible + sample before heating (g),
\( W_b \) is the weight of the crucible + the ashed sample (g)

### 3.4.4 Volatile matter content

To determine the volatile matter content, the method by Malik et al., (2011) was used. 1 g of sample was put in a crucible, covered with a lid and heated in a furnace at 920 °C for 7 min. The material was then cooled and weighed. The volatile matter content was calculated using the formula:

\[
\text{Volatile matter} = \frac{W_a - W_b}{W_a - W_o} \times 100 \% \quad \text{(Equation 3.3)}
\]

Where \( W_o \) is the weight of the empty crucible (g),
\( W_a \) is the weight of the crucible + sample before heating,
\( W_b \) is the weight of crucible and sample after heating.

### 3.5 Preparation of dye solutions

The single component simulated dye waste water solutions were prepared by dissolving 1.00 g of each dye in a standard 1 L volumetric flask and diluting to 1000 cm\(^3\) using distilled water to make stock solutions of 1000 mg/L. Experimental solutions of desired concentrations were prepared by serial dilutions.

### 3.6 Batch Adsorption Experiments

Batch adsorption experiments were only done to determine the optimum pH for adsorption of methylene blue and methyl orange on HPNS-GAC. The batch mode experiments were carried out using 250 ml conical flasks which were pre-treated with the respective dye solution for 24 hours to avoid adsorption of the dyes on the flask walls.
3.6.1 Effect of initial pH on adsorption
To investigate the effect of initial pH on adsorption, the pH of the dye solutions was adjusted appropriately using 0.1 M solutions of HCl and NaOH to range from 4-10. Exactly 50 cm$^3$ of dye of concentration 12.5 mg/L was measured into each conical flask. 0.2 g of the adsorbent was added and the flasks stoppered and shaken for 90 minutes using a laboratory shaker. The resulting suspension was filtered using Whatman number 1 filter paper and the filtrate analyzed for the corresponding dye residual concentration using a UV/VIS spectrophotometer at the maximum wavelength of absorption of each dye specified above.

3.7 Column studies
Column studies were conducted to determine the effect of flow-rate, inlet dye concentration, particle size and bed depth on adsorption. Column studies were chosen because they can be used to predict the efficacy of an adsorbent in the removal of dyes from flowing natural waste-water. Dye solutions were pumped through the respective columns using a peristaltic pump. The column was operated in a down-flow mode in all the column experiments. Once the column started, samples of the dye effluent were collected at the exit point at different time intervals and the residual dye concentrations determined using a UV/VIS spectrophotometer. The columns were run at room temperature. The inlet dye solution pHs were initially adjusted to 8 and 4 for methylene blue dye and methyl orange dye respectively using 0.1 M HCl and 0.1 M NaOH throughout all the experiments.

3.6.1 Column preparation
A cylindrical glass column of 12 mm diameter was used throughout the investigations. The glass column was packed with a known quantity of HPNS granular activated carbon up to a predetermined depth. The columns were packed with the desired amount of adsorbent to the desired depth. The top and the bottom of the columns was plugged with glass wool for supporting the adsorbent. The columns were conditioned by allowing distilled water to flow through at a flowrate of 1.5 ml min$^{-1}$ until the first few drops of water began to appear
at the exit point. The column was left standing for 4 hours to allow close packing. This method of column preparation was repeated for each set of adsorption experiments.

Fig 3.4 Diagram of column used in adsorption column studies

3.6.2 Effect of bed depth on adsorption
The effect of bed depth is to be investigated by setting column height at 1.5 cm and 2.5 cm and 5 cm respectively. The inlet dye concentration was kept constant at 12.5 mg/L. A flowrate of 2 ml
min\(^{-1}\) was used throughout the experiments. For methylene blue dye, the experiments were conducted at pH 8 which was found to be its optimum adsorption pH. For methyl orange the experiments were conducted at pH 4 which was determined to be its optimum adsorption pH. Effluent dye solutions were collected at the exit points at predetermined time intervals and analyzed for the remaining dye concentration using UV/VIS spectrophotometer.

3.6.3 Effect of flow rate on adsorption
The effect of flowrate was investigated by pumping each of the dye solutions into the respective columns at flowrates of 2 ml min\(^{-1}\) and 4 ml min\(^{-1}\) and 6 ml min\(^{-1}\) respectively using a peristaltic pump. The inlet dye concentration was kept constant at 12 mg/L and the bed depth was kept constant at 2.5 cm throughout this investigation. The pH was 8 and 4 for methylene blue and methyl orange respectively. Dye solutions were collected at the column exit points at regular time intervals and analyzed for residual dye concentration using UV/VIS spectrometry.

3.6.4 Effect of initial dye concentration
The effect of inlet dye concentration was investigated by fixing feed dye concentrations at 6.125 mg/L, 6.25 mg/L and 12.5 mg/L. Bed depth and linear flow rate were kept constant at 2.5 cm and 2 ml/min respectively. The effluent dye solution was collected at regular intervals at the column exit and the effluent analyzed for residual dye concentrations using UV/VIS spectrometry at the maximum wavelength of adsorption of each dye.

3.6.5 Effect of particle size
The effect of particle size was investigated by packing the columns with particles of different sizes. Particles of size 250, 450 and 850 µm were used. Bed depth, linear flow rate and inlet dye concentration were kept constant at 2.5 cm, 2 ml min\(^{-1}\) and 12.5 mg L\(^{-1}\) respectively.
3.7 Treatment of results

The results obtained were used to:

- Construct calibration curves
- Break-through curves
- Construct Bed Depth Service Time graphs for adsorption of dyes onto HPNS-GAC
- Construct Yoon-Nelson model plots for the adsorption of dyes onto HPNS-GAC
- Determine Thomas, BDST and Yoon-Nelson parameters.
- Mathematical treatment of results
CHAPTER FOUR

RESULTS

4.1 PROXIMATE ANALYSIS

Table 4.1 Characteristics of the adsorbent produced

<table>
<thead>
<tr>
<th>Property</th>
<th>Value obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density (g/cm³)</td>
<td>0.801±0.009</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>1.73±0.08</td>
</tr>
<tr>
<td>Ash content (%)</td>
<td>8.44±0.48</td>
</tr>
<tr>
<td>Volatile Matter (%)</td>
<td>0.76±0.09</td>
</tr>
<tr>
<td>pH</td>
<td>8.6±0.02</td>
</tr>
</tbody>
</table>
4.2 Fourier Transform Infra-Red Spectroscopy Analysis

Fig 4.1 FTIR analysis of unused HPNS-GAC, MB-saturated HPNS-GAC and MO saturated HPNS-GAC.
4.3 Effect of flow rate

Fig. 4.2 Graph showing effect of flowrate on methylene blue adsorption onto HPNS-GAC.

Inlet dye concentration=12.5 mg L$^{-1}$; bed depth =2.5 cm; particle size=450 μm ; pH 8.
Fig. 4.3 Graph showing effect of flowrate on sorption of Methyl orange onto HPNS-GAC. 
Inlet dye concentration=12.5 mg L⁻¹; bed depth =2.5 cm; particle size=450 µm; pH 4.
Fig 4.4 Graph showing effect of bed depth on Methylene blue adsorption onto HPNS-GAC. Inlet dye concentration=12.5 mg L\(^{-1}\); flowrate =2 ml min\(^{-1}\); particle size=450 µm; pH 8.
Fig. 4.5 Graph showing effect of bed depth on Methyl orange sorption onto HPNS-GAC.

Inlet dye concentration=12.5 mg L⁻¹; flowrate=2 ml min⁻¹; particle size=450 µm; pH 4.
4.5 Effect of particle size

![Graph showing effect of particle size on Methylene blue adsorption onto HPNS-GAC. Bed depth=2.5 cm; Inlet dye concentration=12.5 mg L$^{-1}$; flowrate=2 ml min$^{-1}$; pH 8.](image)

Fig. 4.6 Graph showing effect of particle size on Methylene blue adsorption onto HPNS-GAC. Bed depth=2.5 cm; Inlet dye concentration=12.5 mg L$^{-1}$; flowrate=2 ml min$^{-1}$; pH 8.
Fig. 4.7 Graph showing effect of particle size on Methyl orange adsorption onto HPNS-GAC. Inlet dye concentration= 12.5 mg L$^{-1}$; Bed depth =2.5 cm; Flowrate= 2 ml min$^{-1}$; pH 4.
4.6 Effect of inlet dye concentration

Fig. 4.8 Graph showing effect of inlet dye concentration on sorption of MB dye onto HPNS-GAC. Flowrate=2 ml min⁻¹; bed depth 2.5 cm; particle size 450 µm; pH 8.
Fig. 4.9 Graph showing effect of inlet dye concentration on MO sorption onto HPNS-GAC.
Flowrate=2 ml min⁻¹; bed depth 2.5 cm; particle size 450 µm; pH 4.
4.7 Mathematical analysis

Table 4.2 Different parameters for the removal of MB dye using HPNS-GAC in a fixed bed adsorption column for different operating conditions

<table>
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<th>Q (ml min(^{-1}))</th>
<th>Z (cm)</th>
<th>(C_o) (mg L(^{-1}))</th>
<th>Particle Size(µm)</th>
<th>(t_e) (min)</th>
<th>(t_{total}) (min)</th>
<th>(q_{total}) (min)</th>
<th>(m_{total}) (min)</th>
<th>(q_e(exp)) mg g(^{-1})</th>
<th>(V_{eff}) (ml)</th>
<th>% Removal</th>
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<td>2</td>
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<td>12.5</td>
<td>450</td>
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<td>280</td>
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<td>316.2</td>
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<td>4.40</td>
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Table 4.3 Different parameters for the removal of MO dye using HPNS-GAC in a fixed bed adsorption column for different operating conditions

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<th>Q (ml min⁻¹)</th>
<th>Z (cm)</th>
<th>C₀ (mg L⁻¹)</th>
<th>Particle size</th>
<th>t₀ (min)</th>
<th>t_total (min)</th>
<th>q_total (mg L⁻¹)</th>
<th>m_total (mg)</th>
<th>qₑ(exp) (mg g⁻¹)</th>
<th>V_eff (ml)</th>
<th>% Removal</th>
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4.7.1 Application of Yoon-Nelson Model

Table 4.4 Yoon-Nelson Model Parameters using Linear Regression Analysis under various operating conditions for MB sorption on HPNS-GAC

<table>
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<tr>
<th>Q ml min⁻¹</th>
<th>Bed depth cm</th>
<th>Dye concentration mg L⁻¹</th>
<th>Particle size µm</th>
<th>τ min</th>
<th>$K_{YN}$</th>
<th>$R^2$</th>
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Table 4.5 Yoon-Nelson Model Parameters using Linear Regression Analysis under various operating conditions for MO sorption on HPNS-GAC

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<th>Q ml min⁻¹</th>
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<th>Dye concentration mg L⁻¹</th>
<th>Particle size µm</th>
<th>τ min</th>
<th>K_{YN}</th>
<th>R²</th>
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4.7.2 Application of Thomas Model

Table 4.6 Thomas Model Parameters using Linear Regression Analysis under various operating conditions for MB dye adsorption onto HPNS-GAC

<table>
<thead>
<tr>
<th>Q (ml/min)</th>
<th>H (cm)</th>
<th>C₀ (mg/L)</th>
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<th>K_{TH}</th>
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<td>0.9562</td>
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Table 4.7 Thomas Model Parameters using Linear Regression Analysis under various operating conditions for MO dye adsorption onto HPNS-GAC

<table>
<thead>
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<th>Q (ml/min)</th>
<th>H (cm)</th>
<th>C₀ (mg/L)</th>
<th>Particle size (μm)</th>
<th>K_{TH}</th>
<th>R²</th>
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4.7.3 Application of BDST Model

Fig. 4.10 Experimental BDST plot for MB sorption onto HPNS-GAC.

Table 4.8 BDST parameters for MB dye adsorption from experimental data

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<th>C&lt;sub&gt;b&lt;/sub&gt; (mg/L)</th>
<th>N&lt;sub&gt;o&lt;/sub&gt; (mg/g)</th>
<th>X&lt;sub&gt;o&lt;/sub&gt; (cm)</th>
<th>K&lt;sub&gt;TH&lt;/sub&gt; (L/mg h)</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
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Fig. 4.11 Experimental BDST plot for MO sorption onto HPNS-GAC.

Table 4.9 Bed Depth Service Time (BDST) parameters for MO dye adsorption from experimental data

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<tr>
<th>C_b (mg/g)</th>
<th>N_o (mg/g)</th>
<th>X_o (cm)</th>
<th>K_{TH} (L/mg h)</th>
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4.8 Desorption studies

Fig. 4.12 1st, 2nd, 3rd methylene blue elution curves using HNO₃ (2ml/min flowrate, 2.5 cm bed depth)

Fig. 4.13 Methylene blue elution curves-showing effect of concentration of eluent (eluent is HNO₃, 2 ml/min flowrate, 2.5 cm bed depth).
Fig. 4.14 Methylene blue elution curve showing effect of flowrate (eluent is 0.1 M HNO₃)
Fig. 4.15 showing consecutive elution curves for methyl orange using 0.1 M NaOH (2 ml/min flowrate, 2.5 cm bed depth)

Fig. 4.16 Removal percentage for 3 desorption cycles for methylene blue and methyl orange
CHAPTER FIVE

DISCUSSION

The continuous flow study was carried out to evaluate the effect of various process parameters namely, column depth, inlet dye concentration, particle size and feed flowrate on the breakthrough time and adsorption capacity of HPNS-GAC in the removal of methyl orange dye and methylene blue dye from simulated dye wastewater.

5.1 CHARACTERISTICS OF HPNS-GAC

The granular activated carbon produced from *Hyphaene petersiana* nutshell had a bulk density of 0.801 g/cm³ which shows that it produces high density carbon. The adsorbent produced also had relatively low moisture as well as ash contents making it a potentially good and potentially effective adsorbent.

In Fig. 4.1 the spectrum of unused HPNS-GAC shows a very broad peak at 3066.77 indicative of –OH stretching vibration or adsorbed water. Peak at 1575.01 could be due to C=C stretching of aromatic rings. Peak at 1113.11 could be due to C-H stretching. In Fig. 4.1 the spectrum of methylene blue saturated HPNS-GAC shows peaks at 1560.17, 1115.73. The peak at 1560.17 could be due to C=C stretching of aromatic rings. The peak at 1115.73 could be due to –S=O or C-H stretching. In Fig. 4.1 the spectrum of methyl orange saturated HPNS-GAC has peaks at 2361.06 and 1115.14. The peak at 2361.06 could be indicative of –N=C=O stretching. The peak at 1115.14 could be due to the stretching vibration of –C-O in carboxylic acids, phenols or alcohol.
5.2 EFFECT OF FLOWRATE

Fig. 4.2 and Fig. 4.3 show the effect flowrate on methylene blue and methyl orange respectively onto HPNS-GAC. From Fig. 4.2 and Fig. 4.3 the breakpoint times ($\frac{C_t}{C_0} = 0.1$) as well as the sorption efficiency of methylene blue and methyl orange respectively onto HPNS-GAC were lower at higher flowrates. The breakpoint times and the adsorption efficiency decreased with increasing flowrate. Breakthrough time and exhaustion time decreased with increase in flowrate. From Fig. 4.2 breakthrough time at $C_t/C_0=0.1$ decreased from 94.72 to 72.83 to 23.64 as flowrate increased from 2 ml/min, 4 ml/min to 6 ml/min respectively for sorption of Methylene blue dye. For Methyl orange dye, breakthrough time also decreased. At a flowrate of 2 ml/min, its breakthrough time was 16.07 and for higher flowrates, breakthrough time was much less. Sorption for Methylene blue dye was much higher than for Methyl orange dye. At first uptake is rapid and then gradually the rate of uptake begins to decrease until saturation is reached. As the flowrate is increased, the breakthrough curves become steeper and breakpoint is reached faster. This can be attributed to the fact that the residence time of the dye in the column is not long enough for adsorption equilibrium to be reached at higher flowrates and the dye solution leaves the column before equilibrium. The contact time between the dye solution and the adsorbent is reduced as flowrate is increased. Results were similar to those of Ghribi and Chlendi (2011).

5.3 EFFECT OF BED DEPTH

Fig. 4.4 and Fig. 4.5 show the effect of bed depth on the sorption of methylene blue and methyl orange respectively onto HPNS-GAC. From the experiments, it was observed that the breakpoint time, exhaustion time as well as the sorption efficiency of the two dyes decreased with decreasing bed depth. Sorption efficiency and breakpoint time and exhaustion time were lower at lower bed depth and were higher at higher bed depth. From Fig. 4.4 breakthrough time at $C_t/C_0=0.1$ increased from 74.23, 96.07 to 172 minutes as bed depth increased from 1.5 cm, 2.5 cm to 5 cm respectively for sorption of Methylene blue dye. From Fig. 4.5 breakthrough time increased from 8.83, 13.66 to 16.07. Sorption for Methylene blue was higher than for Methyl orange. As bed depth increased, the mass of adsorbent also increased and thus the surface area
also increased leading to an increase in the number of available active sites and increased contact time and hence higher adsorptive capacity. Results were similar to those of Gupta et al (2010).

### 5.4 EFFECT OF PARTICLE SIZE

The breakpoint time, the sorption efficiency and the exhaustion time increase with decrease in particle size. The breakthrough curve becomes steeper with increase in particle size. Percentage removal increased with decrease in particle size. For both methylene blue dye and methyl orange time for 50% breakthrough increased as particle size decreased. For methylene blue time for 50% breakthrough increased from 135.6 to 251.3 to 323.1 minutes as particle size decreased from 850 to 450 to 250 micro-meters respectively (Fig 4.6). For methyl orange time for 50% breakthrough increased from 21.7 to 61.3 to 133.8 minutes as particle size decreased from 850 to 450 to 250 micro-meters (Fig 4.7). The use of small particles seem to increase the surface area and this seems to provide increased accessibility of pores to the dye molecules (Satish et al., 2011).

### 5.5 EFFECT OF INLET DYE CONCENTRATION

**Fig. 4.8** and **Fig 4.9** show that as inlet dye concentration increases, breakthrough time and exhaustion time decrease. This could be due to the fact that with high dye concentrations the adsorbent’s active sites saturate more quickly which results in faster breakthrough and exhaustion time. At lower dye concentrations transport is slower this gives the dye molecules more time to bind to the adsorbent active sites. From Fig. 4.8 , 10% breakthrough time for MB dye decreases from 201 min to 139 min to 93 min as dye concentration increases from 3.125 mg/L to 6.25 mg/L to 12.5 mg/L respectively. Results were similar to those of Rout et al., (2014).
5.6 ADSORBENT REGENERATION

The potential for adsorbent regeneration was investigated under both continuous flow mode and batch mode. In pilot studies using batch mode, 0.1 M NaOH and 0.1 M HNO₃ were investigated for their potential to desorb methylene blue and methyl orange dye from HPNS-GAC. 0.2 g of adsorbent was shaken with 50 mls of dye of concentration 12.5 mg/L at the appropriate pH for 90 minutes. The residual dye was determined using UV-Vis spectrophotometry and the dye adsorbed calculated. The dye-saturated adsorbent was then shaken with 50 mls of eluent for 90 minutes at 150 rpm to desorb the dye molecules and the amount of dye desorbed was determined using a UV-Vis spectrophotometer. HNO₃ was found to have a high capacity for desorbing methylene blue dye and NaOH was found to have a high capacity for desorbing methyl orange dye.

For both batch desorption studies and continuous flow desorption studies, the adsorption and the removal efficiency for both dyes decreased as the number of regeneration cycles increased as shown in Fig. 4.12, Fig. 4.14 and Fig. 4.15 and Fig. 4.16. Fig. 4.12 and Fig. 4.16 show first, second and third elution curves for methylene blue and methyl orange. Each elution was done after an adsorption run. The time taken for \( Ct/Co = 0.1 \) for each dye decreased as the regeneration cycles increased. For methylene blue, the time taken to achieve \( Ct/Co = 0.1 \) decreased from 56.8 min to 14.9 min. For methyl orange the time to achieve \( Ct/Co = 0.1 \) also decreased from 35.2 min to 18.6 min which shows that the adsorption capacity and the efficiency of the adsorbent decreased as the number of adsorption cycles increased. In methylene blue desorption the time to achieve \( Ct/Co = 0.1 \) increased with increase in the concentration of the eluent. The time to achieve \( Ct/Co = 0.1 \) increased as the concentration of eluent increased from 0.1 M to 0.2 M from 58 min to 164 min. The time also increased from 9.1 min to 68.7 min as flowrate of the eluent decreased from 4 ml/min to 2 ml/min. In the batch desorption studies the removal efficiency of both dyes decreased as the number of desorption cycles increased. The removal efficiency of methylene blue decreased from 81.1 % to 37.5 % and the removal efficiency of methyl orange decreased from 65 % to 38.7%. The decrease in the removal efficiency could be due to incomplete desorption. Similar results were obtained by Alimohammadi et al., (2016) and by Celekli and Bozkurt (2013).
5.7 ANALYSIS USING KINETIC MODELS

YOON-NELSON MODEL

The values of $\tau$ (the time required for 50% dye breakthrough) and $K_{YN}$ (a rate constant) were obtained from plots of $\ln(C_t/(C_0-C_t))$ versus $t$ at different flowrates (2, 4 and 6 ml/min), different bed depths (1.5, 2.5 and 5 cm), different particle sizes (250, 450, and 850 micrometers) and different dye concentrations (3.125, 6.25 and 12.5 mg/L). The values of $\tau$ and $K_{YN}$ are obtained from the intercept and slope respectively. Table 4.4 and 4.5 show that the rate constant $K_{YN}$ increased with increases in inlet dye concentration, particle size and flowrate, and decreased with increase in bed depth. The time required for 50% dye breakthrough ($\tau$), decreased with decrease in bed depth, with increase in flowrate, increase in dye concentration and increase in particle size. The Yoon-Nelson model showed good agreement with the experimental data. The high correlation coefficients indicate the validity of the Yoon-Nelson model ($R^2 \geq 0.9242$) except for particle size 850 µm which has a lower coefficient of 0.8004.

THOMAS MODEL

The column experimental data for MB dye and MO dye were evaluated using the Thomas model for the different operating conditions. The results are given in Tables 4.6 and 4.7. From these results, it can be seen from the regression coefficients $R^2$ (0.9242-0.9942 except for 0.8004 for 850 micro-meter particle size) that the Thomas model fitted the experimental data well. As shown in Tables 4.6 and 4.7, the value of the Thomas rate constant ($K_{TH}$) decreased as bed depth increased, and the value decreased as flowrate, dye concentration and particle size increased. Hence column performance improved as bed depth and as flowrate, inlet dye concentration and particle size decreased.
**BDST MODEL**

The bed depth service time evaluation of the MB and MO dye sorption experimental data was performed at a constant flowrate of 2 ml/min and inlet dye concentration of 12.5 mg/L. The data obtained from the continuous flow experimental studies for adsorption of MB and MO dyes fitted well with the BDST model. From Table 4.8 and 4.9, $R^2$ values for both MB and MO dyes were greater than 0.99. For MB $R^2=1$ and for MO $R^2=0.9916$. Parameters $N_o$ and $X_o$ were calculated from the plots of service time against bed depth. The higher $N_o$ value (24.138) for MB dye in Table 4.8 indicates higher adsorptive capacity for MB dye. The lower $N_o$ value (3.393) for MO dye indicates a lower adsorptive capacity for MO dye.

**5.8 CONCLUSION**

The ability of HPNS-GAC to remove methylene blue, a basic dye and methyl orange, an acidic dye was evaluated under continuous flow studies. In the study, the effect of feed flowrate, particle size, bed depth and initial dye concentration. From the studies breakthrough and exhaustion times increased with increase in bed depth. Breakthrough and exhaustion times also increased with decreases in inlet dye concentration, particle size and feed flowrate. Results from both the continuous flow and batch studies show that HPNS-GAC can act as an effective adsorbent for the removal of organic pollutants from wastewater. The data from the continuous flow studies was evaluated using the Thomas, Yoon-Nelson, and BDST models. The evaluation showed that the three models can be used to describe the adsorption data and that the results can be used to predict and design adsorption columns at larger scales.

**5.9 RECOMMENDATIONS**

The results of this study show that HPNS-GAC has the potential to remove dyes and other organic pollutants from wastewater. A possible next stage can involve evaluating the efficacy of the adsorbent in a small scale pilot plant or in a large scale water treatment plant.
The efficacy of the adsorbent to remove heavy metals and inorganic pollutants can also be investigated. The *Hyphaene petersiana* nutshell can be evaluated as a bio-sorbent for the remediation of wastewater.
REFERENCES


