



**COLLEGE OF SCIENCE AND TECHNOLOGY  
SCHOOL OF SCIENCE**

**Textile effluent treatment using avocado seeds based activated carbon**

**A dissertation submitted in partial fulfilment of the requirements for the degree of Master  
of Science (MSc) in Environmental Chemistry.**

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**Kigali, February 2022**

**DECLARATION**

I declare that this Dissertation contains my own work except where specifically acknowledged, and it has been passed through the anti-plagiarism system and found to be compliant and this is the approved final version of the Dissertation:

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Date .....

## **DEDICATION**

I dedicate this work to

My wife,

NYESIGIRE Roidah,

My sons,

GAJU Colin Ivan and RUREMESH A Alden Teddy,

And my mother

BAJE Jeanine.

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**MUNYEGAJU JACQUES**

## ABSTRACT

Textile industries consume a lot of water through their various textile production processes. Increased demand for textile products, ultimately increases the formation of wastewater, which labels the textile industry a main source of severe pollution problems worldwide. The agricultural wastes used for adsorbing pollutants were revealed to be efficient and economical adsorbents with high potential for removing dyes from polluted water. In this study, the synthetic textile effluent was simulated using Orange 2 sodium salt (OSS) dye mixed with tap water. The treatment of OSS dye solution by adsorption process was conducted in a batch reactor employing the avocado seeds activated carbon (ASAC). The impacts of temperature, adsorption contact time, OSS dye initial concentration, ASAC biosorbent dosage, and OSS solution pH on the adsorption efficiency were explored and optimized by the Box Behnken design (BBD) of Response surface methodology (RSM). The optimum conditions for the dye removal were: temperature 40°C, adsorbent dosage 0.1g and initial dye concentration 10 mg/L. The yield of the OSS dye removal resulted to 96.5%. The OSS dye adsorption has best fitted with the Freundlich isotherm of adsorption ( $R^2 = 0.9922$ ), suggesting the occurrence of a multilayer adsorption on the non-homogeneous surfaces of the ASAC. The kinetic study fitted with the kinetic model of Pseudo-second order. Also, the dye adsorption thermodynamics manifested that the adsorption of OSS dye was feasible and spontaneous with negative Gibbs free energy changes ( $-\Delta G^0$ ) such as -2.18KJ/mol at 303K, -3.18KJ/mol at 308K, -3.58KJ/mol at 313K and -7.32KJ/mol at 323K. The adsorption was endothermic with positive enthalpy change (+74.73KJ/mol). The entropy study resulted in 0.25KJ/mol K, revealing the augmenting chaos at the interface of the sorbent and dye solution during adsorption process. The use of avocado seeds as biosorbent enables the valorization of this agro-waste and waste management alongside efficient textile effluent treatment.

**Keywords:** Textile effluent, Avocado seeds activated carbon, Orange 2 sodium salt dye, Optimization, Response surface methodology

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## **LIST OF ACRONYMS AND ABBREVIATIONS**

ANOVA: Analysis of variance

AS: Avocado seeds

ASAC: Avocado seeds activated carbon

EAC: East African Community

COD: Chemical oxygen demand

OSS: Orange 2 sodium salt

RSM: Response Surface Methodology

SDGs: Sustainable Development Goals

UR-CST: University of Rwanda, College of Science and Technology

UV: Ultraviolet

## CHAPTER ONE: GENERAL INTRODUCTION

### 1.1 Background of the study

The Water pollution is an undesirable change of water that can harmfully affect the health, survival, or activities of human or other living organisms [1]. The major sources of water pollution can be regarded as municipal, industrial and agricultural [2]. The commonest water pollutants are nutrients, organic matter, heavy metals, microbial contaminants, toxic organic compounds (oil, dyes, pesticides, some plastics, and other industrial chemicals), salts, acids, sediments and suspended solids, and high temperature [3]. These pollutants can bioaccumulate, persist and synergy to affect the ecosystem health and function, food production, human health and wellbeing [4]. Among industrial wastewater, dye wastewater from textile is one of the most difficult to treat because dyes usually have a synthetic origin and complex aromatic molecular structures which make them stable and more difficult to be biodegraded [5]. Technologies for treating wastewaters include sedimentation, flotation, filtering, stripping, ion exchange, adsorption, and other processes that accomplish removal of dissolved and undissolved substances [6]. Biosorption emerges as an attractive alternative to conventional methods for treatment of wastewater. It provides with many advantages over conventional treatment methods such as cost effectiveness, efficiency, and minimization of chemical or biological sludge and possible regeneration of biosorbent [7]. The numerous low cost biosorbents that have been proposed include pine sawdust, sugarcane bagasse, rice husk, oil palm shell, coconut shell, and coconut husk in eliminating pollutants from waste water [8]. Biosorbents prepared from natural materials and wasted agricultural products are found to be effective in removing water soluble dyes [9]. The main objective of this research is the optimisation of the textile effluent treatment by biosorbent using the response surface methodology model. This first consists of adsorption of Orange 2 sodium salt on the activated carbon prepared from Avocado seeds biomass.

## 1.2 Problem statement

Water is a natural and fundamental resource for life and health. Water accumulates different type of compounds during its use and become wastewater and unsuitable for reuse. Water pollution by toxic compounds is one of the major concerns for human health as well as for the environmental quality [10]. The industrial effluents containing dyes are one of the major threats to environment. Even in very low concentrations, the dyes are highly visible and affect the aquatic life and food chain [11]. There are several categories of dyes such as direct, reactive, vat, azo and sulphide dyes which are regularly used in the textile industries [9]. It was estimated that about 10–15 % of dyes are released out during dyeing process and mixed with water bodies and produce serious impact on environment. The colored textile wastewater is considered to be highly toxic with presence of organic contaminants and chemicals, that are responsible for odor, bad taste, foaming etc. In addition, they are toxic to aquatic life, reduce photosynthesis, carcinogenic, mutagenic and some of them make allergy, dermatitis and skin irritation to human [12].

Some of the conventional wastewater treatment techniques like filtration, membrane technology, and ion exchange, Sedimentation, chemical precipitation and electrochemical treatment prove to be very expensive and ineffective. It also results in large sludge production. However, many biological materials have high eradication rate in decreasing the concentration of the contaminants from ppm to ppb level [13] [14]. Biosorption emerges as an attractive alternative to conventional methods for treatment of wastewater. It provides with many advantages over conventional treatment methods such as cost effectiveness, efficiency, and minimization of chemical or biological sludge and possible regeneration of biosorbent. The biosorbent materials include algae, fungi, bacteria, agricultural waste and waste from industries. Recently, the research work has been focused on treatment of wastewater by the use of agricultural bio-waste as adsorbent [7]. The biosorbents prepared from natural materials and wasted agricultural biomass are found to be effective in removing water soluble synthetic dyes such as Alcian Blue, Methylene Blue, Malachite Green, Violet 6, Basic Red 18, etc. [9]. Activated carbons having high specific porosity and high surface areas are extremely versatile adsorbents of major industrial significance [8]. Thus, this study has used the avocado seeds activated carbon as an agricultural by-product to adsorb the Orange 2 sodium salt dye from the synthetic textile effluent rendering the effluent free from the dye.

### **1.3 Significance of the Research**

The EAC in its 16<sup>th</sup> ordinary summit of Heads of State of 20<sup>th</sup> February, 2015, agreed to promote the textile, apparel and leather industries in the region and stopping the importation of the used clothes, shoes and other leather products from outside the region [15]. Textile industry is a large industrial consumer of water used for various steps in the textile production process, as well as producer of wastewater [16] [17]. Increased demand for textile products, ultimately increase in the generation of wastewater, which makes the textile industry a main source of severe pollution problems worldwide [17].

The textile wastewater is considered to be highly toxic due to organic contaminants and chemicals content that are toxic to aquatic life and reduce photosynthesis [12]. As one of the solution, textile effluents treatment by bio-sorbents will efficiently improve the quality of water. Textile wastewater treatment and reuse is a promising solution to conserve and increase available water resources. They reduce harmful pollution discharge into the environment. Textile industries should move toward meeting environmental sustainability goals (SDGs) to reduce operational costs and comply with stricter regulations.

### **1.4 Objectives of the study**

#### **1.4.1 The general objective**

The present study will be carried out to optimize the textile effluent treatment by bio-sorbents using the surface response methodology. This will find the optimal conditions for textile effluent treatment by bio-sorption.

#### **1.4.2 The specific objectives**

- (a) Develop a cost effective and environmental friendly biosorbent that significantly removes the pollutants from the textile effluents.
- (b) Study the effects the adsorption parameters on the dye removal efficiency.
- (c) Optimize the synthetic textile effluent treatment by the developed biosorbent with RSM.

### **1.5 Research questions**

The following questions should be answered for better accomplishment of this research.

- (a) Can the selected biosorbent remove significantly the dye from the synthetic textile effluent?

- (b) Can the adsorption factors influence significantly the adsorption of the Orange 2 sodium salt on the developed biosorbent?
- (c) Can the dye removal the optimal conditions be revealed using the RSM?

### **1.6 Choice of the study**

Rwanda to advance its economic development embraced SDGs in national development frameworks. To enhance the environmental sustainability, the three SDGs are of particular importance. These are: Clean water and sanitation; Good health and well-being; and Life below water. To meet these goals, the industrial effluents must be treated before being drained to water bodies. There are various methods designed to treat wastewater effluents but some have been cost ineffective, requiring high operating cost and high skilled labor, not enough efficient in pollutant removal in ppm and ppb levels, etc. Consequently, economical, efficient, and environmental friendly methods need to be designed, among which bio-adsorption belongs. Bio-sorbents will be assessed for removal of pollutants from textile effluent.

### **1.7 Interest of the study**

This research provides with an option for the environmentalists to explore bio-sorption as an efficient, economical and environment friendly wastewater treatment method. This is important for the developing countries that have little means to allocate for their environment management. Rwanda, being thirsty for textile industries, needs adequate facilities to cope with environmental pollution and appropriate detailed mitigation plan. As one of the solutions, widely available agricultural by-products would be used for improving the quality of water.

Personally, this research has sharpened my knowledge and skills in wastewater treatment and environmental data analysis, as well as gaining skills in research report writing.

### **1.8 Scope of the study**

The research project has been conducted in UR-CST chemistry laboratory based in Nyarugenge campus. It took place from July, 2021 to December, 2021. It has been limited to development of the biosorbent, assess its pollutant removal efficiency and optimization of treatment parameters. This research is subdivided into four chapters: the first chapter is devoted to General introduction and the second is for Literature review. Chapter three is devoted to Materials and methods that are used throughout the research and then the fourth chapter entails the Results and discussion. Then, the Conclusion and recommendations come lastly.

## **1.9 Research methodology**

The bio-adsorbents are agricultural by-products obtained after harvesting the crops. After being designed, the bio-adsorbents are mixed with the textile effluent so that the present pollutants are adsorbed on the surface of the bio-adsorbent material as well as rendering the effluent free from pollutants. This research uses Avocado seeds as a bio-adsorbent material. The effects of the parameters that influence the adsorption have been studied. Then, the optimum effluent treatment parameters were revealed. Observation is important because the dye removal from the textile effluent can be easily visible. In addition, library essentially provides written information about the sample description, handling, treatment and analysis.

## **CHAPTER TWO: LITERATURE REVIEW**

### **2.1 Textile wastewater characteristics and environmental impact**

There are different categories of dyes such as direct, reactive, vat, azo and sulphide dyes which are regularly used in the textile industries [9]. During synthesis and dyeing processes about 10–15% of the whole manufactured colorants are vanished [17]. The industrial effluents containing dyes are one of the major threats to environment. Even in very low concentrations, the dyes are highly visible and affect the aquatic life and food chain [11]. The discharge of effluents contaminated with dyes without treatment affects the health of water bodies because it reduces the photosynthetic capacity of sub-aquatic plants, increases COD and causes eutrophication of surface waters. Likewise, the toxic properties of some dyes have been confirmed, including carcinogenic, mutagenic, allergic and dermatological effects. Even at trace levels (<1 mg/L), these compounds have adverse health effects. It is necessary to treat wastewater containing dyes before it is discharged into the environment [18].

### **2.2 Textile effluent treatment**

Among industrial wastewater, dye wastewater from textile and dyestuff industries is one of the most difficult to treat because dyes usually have a synthetic origin and complex aromatic molecular structures which make them stable and difficult to be biodegraded [5]. Various chemical and physical processes such as flocculation, chemical coagulation, ion exchange, reverse osmosis, ultrafiltration, electrodialysis, precipitation, and adsorption have been widely used to treat the wastewater containing dyes. However, the adsorption has been one of the most efficient methods [18] [19]. The major advantages of bio-sorption over conventional treatment methods include low cost, high efficiency, minimal chemical and biological sludge, no additional nutrient requirement; and possible bio-sorbent regeneration [19]. Agricultural wastes are an excellent source of biosorbents for dye adsorption. They are cheap and abundantly available, mainly consisting of cellulose, hemicellulose and lignin that bind a wide range of contaminants [18]. The inexpensive adsorbents from agricultural wastes were studied such as sugarcane bagasse, rice husk, oil palm shell, coconut shell, coconut husk, etc. [13]

### **2.3 Activated carbon biosorbent**

The activated carbon is an amorphous structure that consists of mostly free carbon that has deep surface layer which allows a higher adsorption rate than most adsorbent [20]. Nowadays, the



sources of activated carbon are extensive and ever expanding. Any low cost material with a high carbon content and low in inorganic content can be used as precursor to produce activated carbon. Most of the activated carbon are produced from coal, petroleum coke, saw dust, bamboo and agricultural by-products [21]. Activated carbon derived from organic substances is considered to be a bio-sorbent that has a high adsorption rate which is produced through carbonization and either chemical or physical activation [20]. The Activated carbon which possesses highly developed pore structure is extensively used as adsorbents for adsorption processes [22]. Organic matters containing lignin, hemicellulose, and cellulose can be used as raw material for the production of activated carbon because they are highly effective for adsorption [20]. The precursor is activated by exposure to high temperature treatments, which remove solid mass, and at the same time creating the pores where the removed mass was previously located. The common properties of activated carbons and other kinds of carbon adsorbents is their well-developed pore network [23]. The two methods are common for production of activated carbon:

### **2.3.1 Physical activation (Thermal activation)**

It involves two consecutive steps. The first step is the carbonization stage followed by an activation stage. The step of carbonization is carried out by pyrolysis in an inert atmosphere for 5-6 hours at a temperature ranging from 400 to 850 °C and can sometimes reaches 1000 °C. This step aims at removing organic compounds such as CO, H<sub>2</sub>, CH<sub>4</sub> and other hydrocarbons to produce a solid residue with high carbon content. Finally, for further development of the pores, an activation step at 800-1000 °C is performed in the presence of steam, carbon dioxide, air or their mixtures for 24 to 72 hours [24].

### **2.3.2 Chemical activation**

It carried out in a single carbonization step. The raw material is first impregnated with appreciable amounts of chemical agent, and then heated up. The product obtained must be washed to eliminate any excess chemical agent after carbonization. The thermal treatment temperature depends on what chemical agent is used. The most common chemical activation agents are: phosphoric acid, zinc chloride and alkaline hydroxides [23]. Chemical activation offers several advantages because it is performed in a single step, combining carbonization and activation, performed at lower temperatures as well as the development of a better porous structure [25].

## **2.4 Adsorption Process**

The basic purpose of biosorption is to encourage the direct attachment of dissolved organic or metallic compounds onto the surface of the biosorbent, where they can passively concentrate and be separated out from the solution at a later time. The physical force of attraction holds the molecules on the adsorbent surface. The pore filling process primarily depends on the size, shape and surface affinity of the compounds and the reduction in adsorption energy [9]. The materials of biological origin (biosorbents) can be used as effective material for removing different substances, such as, heavy metals, nutrients, drugs and dyes from aqueous solutions [26]. Adsorption can be conducted as batch, semi-batch, and continuous processes. When little quantities are to be treated, batch processes are generally carried out and the equilibrium distribution depends on the contact time in batch process [18]. According to the nature of forces involved in adsorption processes, adsorption can conveniently be divided into two types:

### **2.4.1 Physical Adsorption (Physisorption)**

It occurs when the attractive forces present between adsorbate and adsorbent are weak like Van der Waals forces and hydrogen binding. There is no observation of exchange of electrons between the adsorbent and the adsorbate. The heat of adsorption for physisorption is at most a few  $\text{KJ mol}^{-1}$ . It has low enthalpy of adsorption and occurs with development of multilayer of adsorbate on adsorbent. Physical adsorption is a non-specific and a reversible process [10] [13].

### **2.4.2 Chemical Adsorption (Chemisorption)**

It occurs when the attractive forces between the adsorbate and adsorbent are chemical forces of attraction (chemical bond). It involves the reaction of transfer and sharing of electrons between the adsorbate species and the adsorbent. Here only a single layer formation of the adsorbate on adsorbent takes place and it has a high enthalpy of adsorption [10] [13].

### **2.4.3 Equilibriums of Adsorption Process**

The adsorption equilibrium has been studied using isotherms, in order to identify how the adsorbate molecules are distributed between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The data used to obtain isotherms can be fitted by different models to study the nature of the process and can be used to compare the efficiency [18].

The two most frequently used equations applied for describing sorption isotherms are the Langmuir and the Freundlich models [27].

**(i) The Freundlich isotherm**

The Freundlich isotherm is an empirical model applies to heterogeneous surfaces and involves a multilayer adsorption, with clear interaction forces between the adsorbed molecules. This model supposes that when the adsorbate concentration increases, the adsorption process also increases, and accordingly, the sorption energy dramatically decreases due to completion of the sorption sites of the adsorbent. The general linear form of the Freundlich model can be described by the following equation.

$$\log q_e = \log K_F + 1/n \log C_e \quad (1)$$

Where  $q_e$  is the amount of adsorbate at equilibrium (mg/g),  $C_e$  is the equilibrium concentration of adsorbate (mg/L),  $K_F$  is the Freundlich constant and  $n$  is a constant. The constants associated with the Freundlich isotherm model are sorption capacity ( $K_F$ ) and sorption intensity ( $1/n$ ). The exponent ( $1/n$ ) provides an indication of favorability and capacity of the adsorbent-adsorbate system. Plotting  $\ln q_e$  versus  $\ln C_e$  results in a straight line of slope  $1/n$  and intercept  $\ln K_F$ .

If value of  $1/n < 1$  it denotes a natural adsorption. If  $n = 1$  indicates that the distribution between the two phases are not dependent on the concentration. While if  $1/n > 1$  denote cooperative adsorption [27] [28].

**(ii) The Langmuir isotherm**

The Langmuir theory assumes that adsorption occurs at specific homogeneous sites inside of the adsorbent and, once a dye molecule occupies a site, no additional adsorption can occur there. The Langmuir adsorption is valid for monolayer adsorption. The Langmuir isotherms model is described by the following equation.

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (2)$$

Where  $q_e$  is the amount of adsorbate at equilibrium (mg/g),  $C_e$  is the equilibrium concentration of adsorbate (mg/L).  $K_L$  (L/ mg) and  $q_m$  (mg/g) are the Langmuir constants related to energy of adsorption and maximum adsorption capacity respectively. Plotting  $1/q_e$  versus  $1/C_e$  results in a straight line of slope  $1/q_m$  and intercept  $1/K_L q_m$ .

The basic features of the Langmuir isotherm can be described by a constant named the separation factor  $R_L$  which is defined as

$$R_L = \frac{1}{1 + K_L C_o} \quad (3)$$

Where  $K_L$  is the Langmuir constant (L/mg) and  $C_o$  is initial concentration of adsorbate (mg/L).  $R_L$  values refer to the nature of adsorption. The adsorption is assumed to be unfavorable when  $R_L > 1$ , linear when  $R_L = 1$ , favorable when  $0 < R_L < 1$ , and irreversible when  $R_L = 0$  [28][29].

#### **2.4.4 Factors affecting the adsorption process**

##### **(a) Temperature**

Textile industries discharge their wastes at high and different temperatures. Therefore, temperature can be a significant parameter in dye removal process. As the temperature increases, the adsorption efficiency is found to decrease for an exothermic process while it increases for an endothermic one [13].

##### **(b) PH**

pH affects the retention capacity of the adsorbing surface [13]. Controlling the degree of electrostatic charges transmitted by ionized dye molecules result in varying rate of adsorption when pH is changed. Adsorption rate depends on the nature of adsorbate. Anionic dye is highly adsorbed at low pH [30].

##### **(c) Adsorbent Activation**

It provides with higher number of vacant sites on surface of adsorbent by breaking the solid crystal in small pieces, heating the biosorbent at high temperatures, breaking lump of the solid into the powder, or other methods suitable for particular adsorbent [13].

##### **(d) Surface Area of Adsorbent**

As adsorption is a surface phenomenon it increases with increase in surface area. Thus for any big molecule with a higher surface area, the adsorption efficiency will increase [13].

##### **(e) Adsorbent dose**

It is a measure of the amount of adsorbent used to adsorb dye particle. This depends on the number of sorption available on the surface of the adsorbent. The experiment can be done by preparing

solutions with fixed dye concentration and pH varying adsorbent dosage. The higher the rate of adsorption, the higher the adsorbent dosage and vice versa [30].

#### **(f) Initial Concentration**

It is a measure of the amount of dye dissolved in water. The dye particle adsorption depends on the vacant binding sites on the surface of the adsorbent. The experiment can be done by preparing solutions with fixed adsorbent dosage and pH with varying dye concentrations.

The adsorption rate is higher when the dye concentration is low and vice versa [30].

#### **(g) Contact time**

It is a measure of the amount of time the adsorbent and adsorbate are placed in contact with each other. The experiment can be done by preparing the solution with fixed adsorbent dosage, dye concentration and pH but allowing differing contact between the adsorbent and adsorbate [30].

### **4.4 Adsorption kinetics studies**

In order understand the behavior of the adsorbent and to investigate the controlling mechanism of the adsorption procedure, the pseudo first-order, pseudo second order and intraparticle diffusion models are useful to check the kinetic information [31]. A comparison of the adsorption rate is essential to differentiate the performance of samples with varying concentrations and their chemical constituents. To analyze the adsorption kinetics of the adsorbate on the biosorbent, the kinetic models were applied, including Pseudo First Order, and Pseudo Second Order models.

#### **(a) Pseudo-First-order Kinetic model**

The linearized integral form of the Pseudo First Order equation is generally expressed as follows,

$$\log (q_e - q_t) = \log q_e - \frac{k_l}{2.303}t \quad (4)$$

Where  $q_t$  is the adsorption capacity at time  $t$  (mg/g),  $q_e$  the adsorption capacity at equilibrium (mg/g),  $k_l$  is the Lagergren's rate constant of adsorption ( $\text{min}^{-1}$ ) of pseudo-first-order adsorption,  $t$  is the contact time (min). The value of  $k$  and  $q_e$  were given by a linear plot of  $\log (q_e - q_t)$  versus  $t$  [9] [28].

### (b) Pseudo-Second-order Kinetic

The linearized integral form of Lagergren Pseudo Second Order model for adsorption kinetics is as follows.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} - \frac{1}{q_e} t \quad (5)$$

Where  $q_t$  is the adsorption capacity at time  $t$  (mg/g),  $q_e$  the adsorption capacity at equilibrium (mg/g),  $k_2$  (g/mg min) is the rate constant of pseudo second order adsorption and  $t$  is the contact time (min). A plot between  $t/q_t$  against  $t$  gives the value of rate constant  $k_2$  (g/mg min). The value of  $k$  and  $q_e$  were given by a linear plot of  $\log(q_e - q_t)$  against  $t$  [9] [28].

### 4.5 Adsorption thermodynamics

Adsorption thermodynamics are determined using the thermodynamic equilibrium coefficients at different temperatures and concentrations in order to verify possible adsorption mechanisms. The adsorption thermodynamic study of the adsorption process is helpfully in establishing the nature and possibility of reaction. Different thermodynamic parameters which comprise standard enthalpy change ( $\Delta H^\circ$ ), standard entropy change ( $\Delta S^\circ$ ), and standard Gibbs free energy change ( $\Delta G^\circ$ ) can be calculated from temperature and adsorption procedure.

The changes in standard free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) of adsorption process were determined using the following equations:

$$\Delta G^\circ = -RT \ln K_D \quad (6)$$

$$K_D = \frac{q_e}{C_e} \quad (7)$$

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (8)$$

Where  $R$  is the universal gas constant (8.314 J/mol K),  $T$  is the temperature (K) and  $K_D$  is the thermodynamic equilibrium constant (L/g).  $K_D$  can be obtained by plotting  $q_e/C_e$  against  $q_e$  and extrapolating  $q_e$  to zero. A Van't Hoff plot of  $\ln K_D$  as a function of  $1/T$  yields to a straight line. The  $\Delta H^\circ$  and  $\Delta S^\circ$  parameters were calculated from the slope and intercept of the plot, respectively [27] [31].

## 4.6 Statistical analysis

The Response Surface Methodology (RSM) is a collection of mathematical and statistical techniques for the design of experiments, building models, evaluating the effects of several factors, and obtaining the optimum conditions for responses with a limited number of planned experiments. The mathematical models generated by using data on experimental design, define the relationships between the independent variables (factors) and the dependent variables (responses). These models are used in analyzing the effects of independent variables and their interactions on the responses, and also for optimizing the process [32]. A large number of independent variables (factors) can affect the response of a system. Since it is not possible to include all the variables in the experimental design due to economic reasons, the screening experiments are necessary to identify the variables with major effects. Some of the popularly used experimental designs are the following:

- (i) Full three-level factorial design (FFD)
- (ii) Box–Behnken design (BBD)
- (iii) Central composite design (CCD)

The BBD is usually very efficient due to reduced number of runs. The Box–Behnken design does not contain any experimental points at the vertices of the cubic region. This could be advantageous because testing at these points is expensive or impossible due to practical reasons [12]. The relationship between independent variables and response is to be found. The full quadratic second-order equation with interaction terms is generally used in RSM because a simple linear equation cannot describe the interaction effect between different parameters and cannot determine the critical point.

$$y = \beta_0 + \sum_{i=1}^k \beta_{iX_i} + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^k \beta_{ij} X_i X_j + \varepsilon \quad (9)$$

where  $\beta_0$ ,  $\beta_i$ ,  $\beta_{ii}$  and  $\beta_{ij}$  are regression coefficients for intercept, linear, quadratic and interaction coefficients respectively,  $x_i$  and  $x_j$  are coded independent variables and  $\varepsilon$  is the residuals associated to the experiments [12]. This model can evaluate the interactive effects between different independent variables and the critical point (maximum, minimum or saddle points). The overall efficiency of a model prediction is generally explained by coefficient of determination ( $R^2$ ).  $R^2$  is the ratio of regression sum of squares to total sum of squares, and it measures the total variation

of predicted or model values from the mean. For a model with good prediction efficiency, the value of  $R^2$  should be close to 1.0 [33].

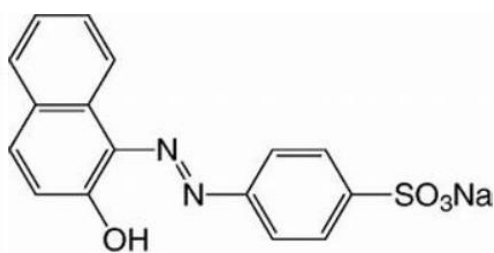


## CHAPTER THREE: MATERIALS AND METHODS

### 3.1 INTRODUCTION

The Avocado seeds (AS) were collected from UR-CST campus restaurant as food waste. In this research AS were used as a Bio-adsorbent material that was intended to remove the dye from the synthetic textile effluent. The AS were selected as a bio-sorbent material because they are a hard to manage agricultural waste. The AS cannot be consumed by animals; not easily biodegradable in environment, but mostly dry and they are not profitable in making manure. The Orange II Sodium salt dye ( $C_{16}H_{11}N_2NaO_4S$ ) also known as Acid Orange 7 and Acid Orange A, was used as an adsorbate. The dye is a main component of the textile effluent.

The Orange II sodium salt dye (OSS) is one of the azo dyes. Its structure is the following;



**Figure 1:** Orange 2 sodium salt molecular structure.

OSS is a water soluble dye with molecular weight of 350.33 g/mol.

### 3.2 Preparation of the biosorbent

#### 3.2.1 Reduction of the Biosorbent size

The Avocado seeds (AS) after being collected were washed with tap water, sliced into small pieces, and dried in an oven at  $80^{\circ}C$  for 15 h. The dry matter was ground in a mortar with a pestle. Then, the powder was sieved through a  $180\ \mu m$  mesh.



**Figure 2:** Avocado seeds



**Figure 3:** Dried sliced AS



**Figure 4:** Powdered AS

### 3.2.2 Biosorbent activation and generation of Avocado Seeds Activated carbon

The obtained powder was activated by mixing it with  $H_3PO_4$  (1:1) and heated in the oven at  $80^{\circ}C$  for 15 h. Then, the product was dried at  $100^{\circ}C$  for 18h. Also, the product obtained was powdered and carbonized  $480^{\circ}C$  for 60 min in a muffle furnace. After cooling in free air, the obtained carbon was washed 3 times with distilled water. The product was dried at  $70^{\circ}C$  for 2h, powdered, and then soaked into 1M NaOH 200 ml solution for 24h to remove the acid. Then, it was washed in distilled water till the neutral pH. The obtained product was dried at  $70^{\circ}C$  for 4 hours and finally powdered and sieved through a 180  $\mu m$  mesh. The Activated carbon produced was keep in an air tight container.



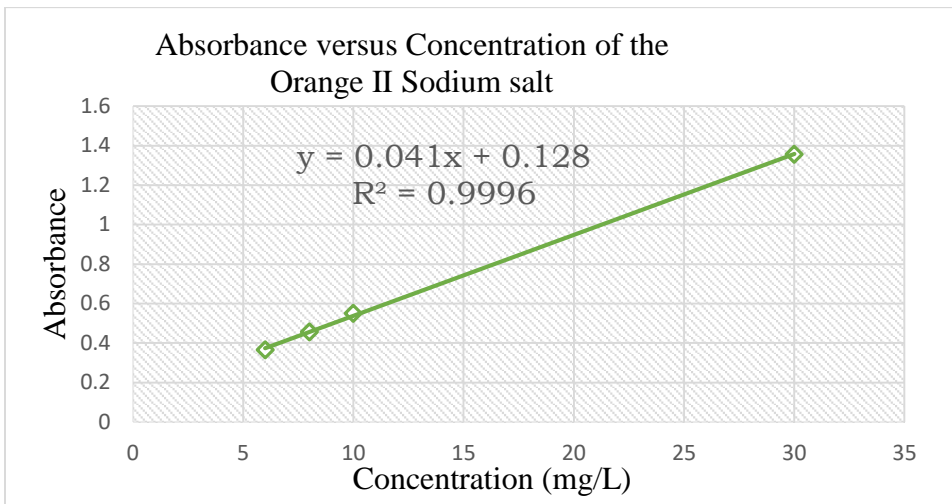
**Figure 5:** Avocado seeds Activated carbon (ASAC)

### 3.3 Preparation of the adsorbate solution

As the main component of textile effluent is the dye, the synthetic textile effluent was prepared by mixing the dye with tap water. So, the Orange sodium salt dye was used. The OSS concentration prepared as the stock solution was  $1gL^{-1}$ . Then, the analytical solutions of 2 mg/L, 4 mg/L, 6 mg/L, 8 mg/L, 10 mg/L, 15 mg/L, 20 mg/L and 30 mg/L were prepared from the stock solution. The other chemicals prepared in the experiment were 1M HCl and 1M NaOH that were used to adjust pH of the OSS solutions.

### 3.4 The OSS dye standard curve

The concentration of OSS in the standard solution before adsorption was determined using a double beam UV spectrophotometer at 483 nm. It was found that the standard solutions (2 to 100mg/l) give some absorbance values and which is important for preparing standard curve.



**Figure 6:** Plot of the Standard Calibration curve for Orange 2 Sodium salt dye.

In the figure 6, the absorbance of standard solution is determined and plotted in the Y-axis and concentration of standard solution is plotted in X-axis. The value of absorbance and concentration gives a straight line equation which has a slope  $m$ . The value of  $m$  is important for determining unknown concentration and absorbance.

### 3.5 Batch adsorption experiment

The biosorbent dosage of 0.05g, 0.075g, 0.1g, 0.5g, 1g, and 2g were mixed with 200 ml of the OSS dye of 2 mg/L, 4 mg/L, 6 mg/L, 8 mg/L, 10 mg/L, 15 mg/L, 20 mg/L and 30 mg/L and shaken at 300 rpm for 60 min. The effects of adsorption parameters such as Contact time, Temperature, Initial dye concentrations, Initial biosorbent dosage and pH were studied. A UV-Visible Spectrophotometer has been used to read the absorbance of the prepared solutions before and after treatment. The absorbance of the OSS was read at the  $\lambda_{max} = 483$  nm. The concentration of each solution can be obtained from the standard calibration curve of the standard solutions. Before reading the absorbance with a UV-Visible Spectrophotometer of the treated solutions, the filter papers were used to remove the ASAC from the solution. The samples were tested in triplicates. The kinetic study on batch adsorption experiment were carried out to understand the adsorption processes. The adsorption capacity of the bioadsorbent,  $Q_e$  (mg/g) and the dye removal efficiency,  $R$  (%) were determined using the following equations:

$$Q_e = ((C_0 - C_e) V) / W \quad (10)$$

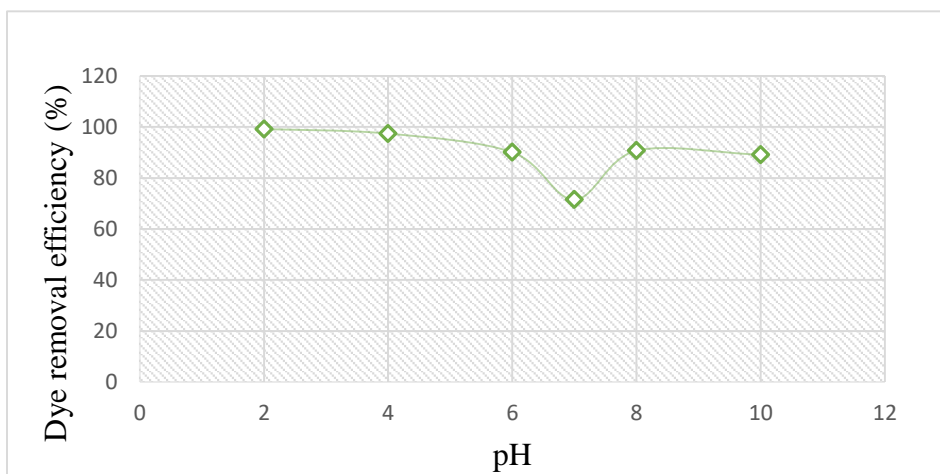
$$R\% = ((C_0 - C_e) / C_0) \times 100 \quad (11)$$

where  $C_0$  (mg/L) is the initial dye concentration of the solution,  $C_e$  (mg/l) is the equilibrium concentration of dye in the solution,  $V$  (L) is the volume of dye solution and  $W$  (g) is the mass of bioadsorbent used for adsorption [10].

## CHAPTER FOUR: RESULTS AND DISCUSSION

### 4.1 Effects of adsorption parameters on dye removal efficiency

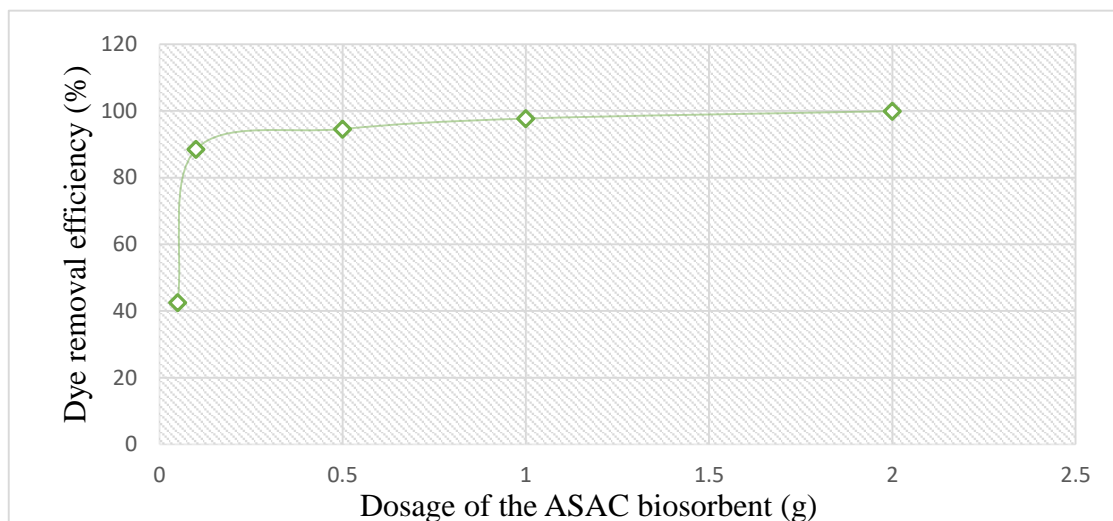
#### 4.1.1 Effect of pH



**Figure 7:** Effect of pH on OSS dye removal efficiency

In the figure 7, the pH of the OSS dye solutions was adjusted from 2 to 10 in 200 ml of the 10 mg/L OSS dye solution mixed with 0.1 g of the ASAC biosorbent by shaking at 300 rpm for 60 min. The dye solution was adjusted using 1M NaOH and 1M HCl solutions with a pHmeter to obtain the required pH. The ASAC Biosorbent was found to have a strong adsorptive surface for the OSS dye in the acidic environment as observed in the figure 7. The OSS dye removal by the ASAC biosorbent was found to be at maximum when the pH of solution was 2. The results in Figure 7 show that there was a decrease in the dye removal efficiency as the pH solution increases until the neutral pH. This behavior may result from the OSS dye becoming an anionic form when dissolve in aqueous solution. Therefore, adsorption of the OSS dye was affected by the surface of the ASAC Biosorbent, which was influenced by pH solution [9]. The pH of the solution influenced not only the surface charge of the ASAC biosorbent, the degree of ionization of the biosorbent material present in the solution and the dissociation of functional groups on the active sites of the adsorbent, but also the solution dye chemistry [34].

#### 4.1.2 Effect of biosorbent dosage



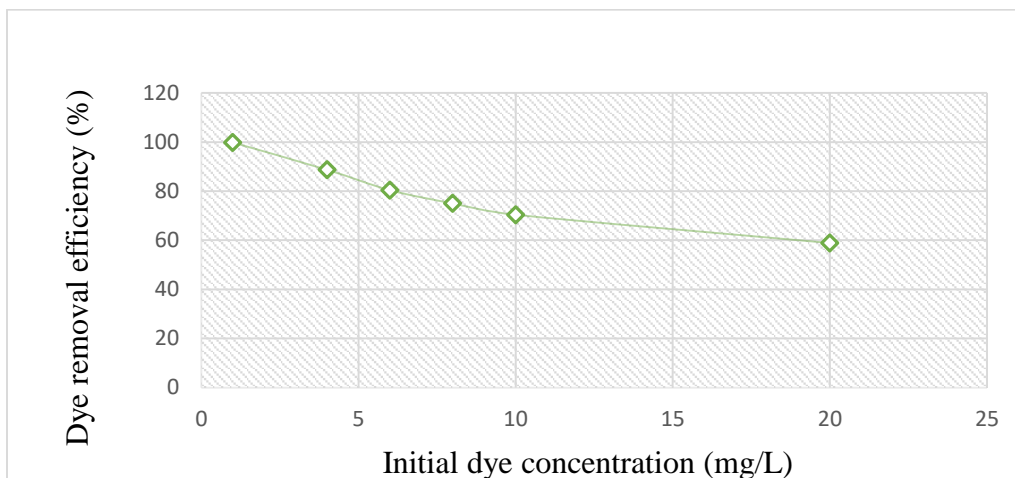
**Figure 8:** Effect of ASAC biosorbent dosage on dye removal efficiency

In the figure 8, the adsorbent dosage was varied from 0.05 to 2g in 200 ml of the 10 mg/L OSS dye solution with shaking at 300 rpm for 60 min. The increase in ASAC biosorbent mass leads to a rise in the percentage removal of the dye. This is due to the increase in active sites on the adsorbent surface by the amount of adsorbent available. The increase in dye removal has stopped as the adsorption equilibrium was attained [18] [28]. The steep escalation in the dye removal efficiency during the initial increase in the dosage can be attributed to presence of a significant number of active sites allowing a large surface area on the ASAC biosorbent [9]. However, the OSS dye removal does not increase with the increase of dosage at higher amount of the biosorbent due to the saturation of the active sites on the adsorbent surface in solution [35]. The optimum ASAC Biosorbent dosage was found to be 0.1 g/200 ml for the experiment.

#### 4.1.3 Effect of initial dye concentration

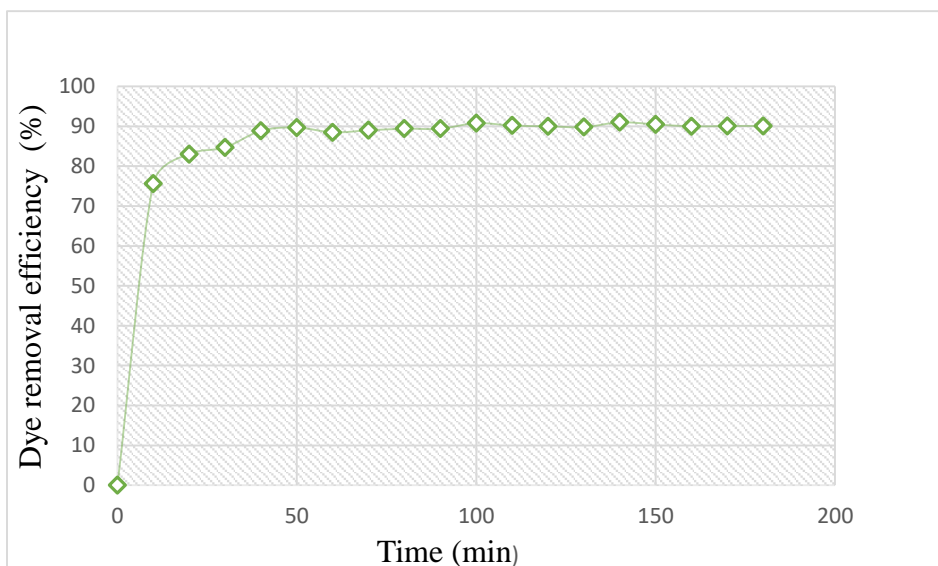
The initial OSS dye concentrations used were varied from 1 mg/L to 20 mg/L. The volume of 200 ml of the OSS dye solutions were mixed with 0.1g of the ASAC biosorbent and shaken at 300 rpm for 60 min. The figure 9 shows that the dye removal decreased with increasing initial dye concentrations. This effect of the initial dye concentrations depends on the relationship between the effective sites available on a surface of the ASAC Biosorbent and the OSS dye concentration. At low concentration there were several unoccupied effective sites on the biosorbent surface and when the initial dye concentration increased, the effective sites required for adsorption of the OSS

dye molecules lacked [28]. So, the lack of sufficient surface area of the biosorbent to accommodate much more OSS dye available in the solution resulted in the dye removal decrease [36].



**Figure 9:** Effect of Initial dye concentration of OSS dye on Dye removal efficiency

#### 4.1.4 Effect of contact time

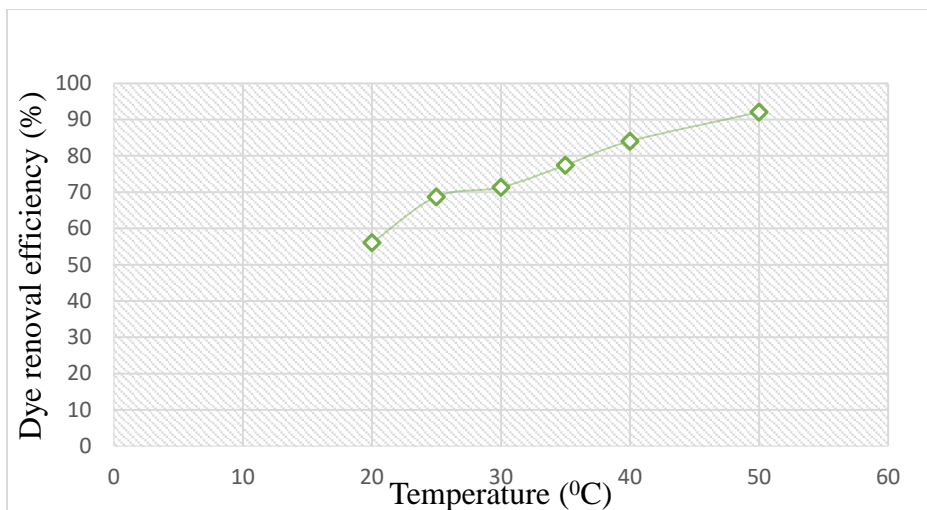


**Figure 10:** Effect of Contact time on OSS dye removal efficiency

In the figure 10, the contact time was varied from 10 to 180 min for studying a solution of 200 ml of the 10 mg/L OSS dye mixed with 0.1 g of the ASAC biosorbent by shaking at 300 rpm for 60 min. Initially, the OSS dye removal increased rapidly with an increase in contact time. The rapid the removal of dye is observed at the beginning of the contact time due to the percentage of large number of binding sites available to accommodate the OSS dye molecules [28]. The results in the figure 10 show that a rapid removal of OSS dye occurred at 10 min and reaches 75.6%. At 40 min, the dye removal has reached a maximum of 89.7% and remains constant. The longer the contact

time of the dye solution and the biosorbent, the more the collisions between the particles of ASAC biosorbent and the OSS dye molecules until the establishment of the equilibrium [37]. Therefore, 40 min is determined as the optimum contact time.

#### 4.1.5 Effect of temperature



**Figure 11:** Effect of Temperature on OSS dye removal efficiency.

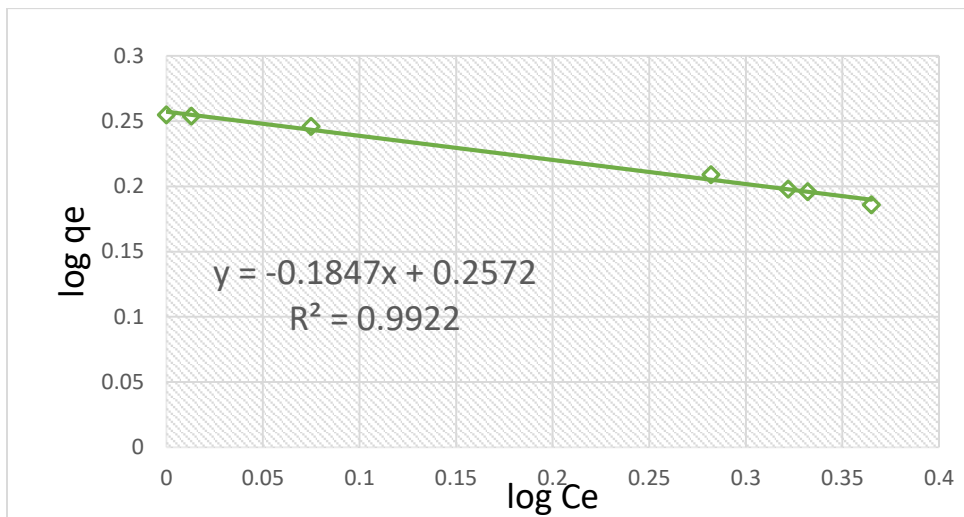
In the figure 11, the temperature was varied from 20 to 40<sup>0</sup>C for studying a solution of 200 ml of the 10 mg/L OSS dye mixed with 0.1 g of the ASAC biosorbent by shaking at 300 rpm for 60 min. The figure 11 shows that the dye removal increased as the temperature increased. An increase in temperature was expected to increase the bio-sorption by decreasing the viscosity of the dye solution and increasing the mobility of the ASAC biosorbent particles. The results indicate that the removal of the OSS dye was higher at high temperatures. This suggested the occurrence of endothermic adsorption processes [28]. The OSS dye adsorption on the ASAC biosorbent were favored at higher temperature within the appropriate temperature range. The increased mobility of the dye molecules increased with the interaction with the active sites of the ASAC biosorbent [38].

#### 4.2 Adsorption isotherm study

Adsorption isotherms are useful for the characterization of how the dye concentrations interact with the surface of adsorbent. This can help to improve the sorbent surface for the removable dyes. They are one of the basic requirements to understand adsorption systems [28]. Moreover, the isotherm constant values are helpful to predict the maximum adsorption capacity and describe the affinity and surface properties of the adsorbent [39].

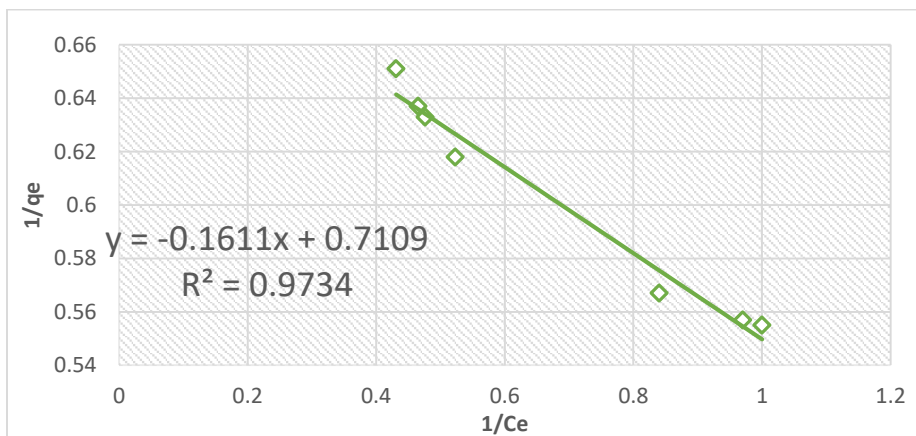
To characterize the adsorption of the OSS dye on ASAC biosorbent, the experimental equilibrium data were analyzed using Freundlich and Langmuir isothermal models.

The Langmuir model assumes that there is monolayer coverage of adsorbate on a homogeneous adsorbent surface while the Freundlich isothermal model assumes the heterogeneity of the adsorbent material and multi-layer coverage of the adsorbate [40] [41]. From the general linear form of the Freundlich model stated in equation 1, the figure 12 was generated.



**Figure 12:** Freundlich adsorption isotherm for adsorption of OSS dye onto ASAC biosorbent.

From the general linear form of the Langmuir model stated in equation 2, the figure 13 was generated.



**Figure 13:** Langmuir adsorption isotherm for adsorption of the OSS dye onto the ASAC biosorbent.



**Table 1:** Langmuir and Freundlich isotherm parameters for OSS dye adsorption onto ASAC biosorbent. (OSS dye concentration = 10 mg/L)

Langmuir model			Freundlich model		
$k_L$ (L/mg)	$q_m$ (mg/g)	$R^2$	$k_F$ (mg/g)(L/mg) <sup>1/2</sup>	1/n	$R^2$
-4.4	1.4	0.9734	1.81	-0.184	0.9922

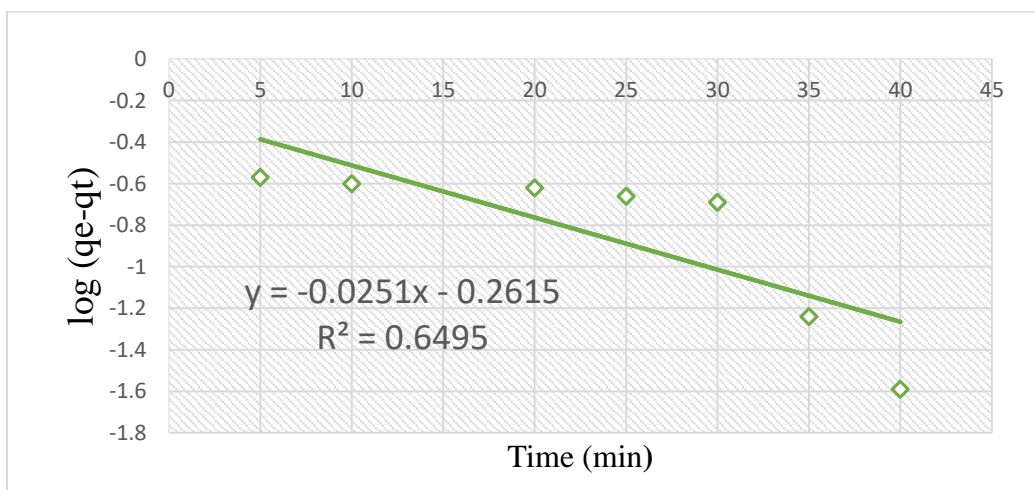
From the data computed in table 1, it is deduced that the Freundlich isotherm ( $R^2 = 0.9922$  and  $K_F = 1.81$ ) was a more fit to the adsorption of the OSS dye. It was assumed that the removal process of the OSS dye occurred in multilayers inside the pores of the bioadsorbent, achieving a maximum removal capacity of 1.81 mg/g [9]. The value of  $R_L$  was found to be  $0 < 0.4 < 1$  indicating the favorable uptake of the dye from the solution.

### 4.3 Adsorption kinetics study

To analyze the adsorption kinetics of OSS dye onto ASAC biosorbent, the kinetic models were applied, including Pseudo First Order, and Pseudo Second Order models.

#### (a) Pseudo-First-order Kinetic model

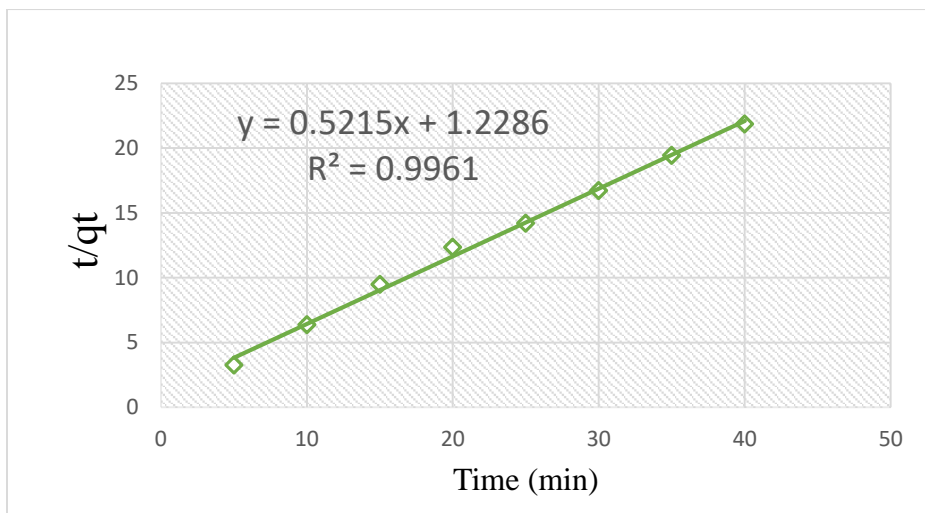
The linearized integral form of the Pseudo First Order equation is generally expressed in the equation 4, has produced the figure 14.



**Figure 14:** Pseudo first order kinetic for adsorption of OSS dye onto ASAC biosorbent.

### (b) Pseudo-Second-order Kinetic model

The linearized integral form of Lagergren Pseudo Second Order model for adsorption kinetics in equation 5 has produced the figure 15.



**Figure 15:** Pseudo second order kinetic for adsorption of OSS dye onto ASAC biosorbent.

**Table 2:** Adsorption parameters obtained from kinetic studies

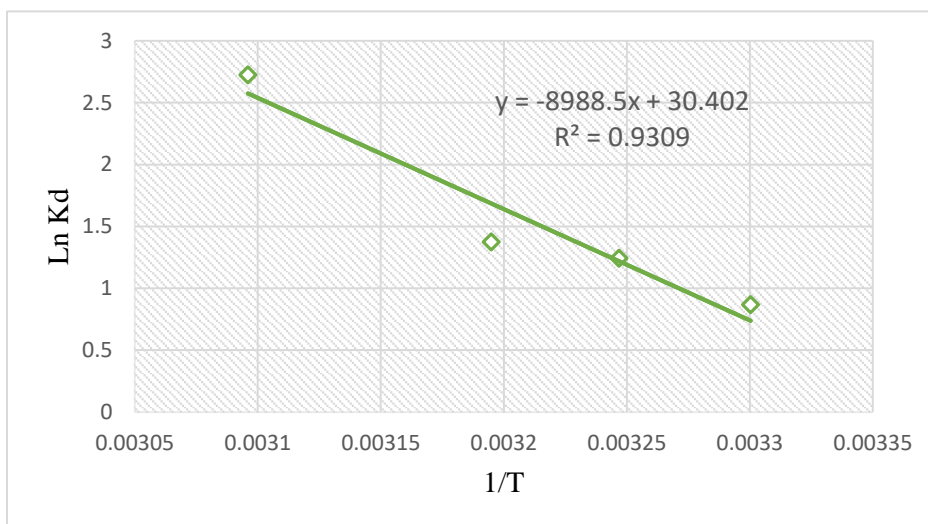
Pseudo First Order model			Pseudo Second Order model		
$k_1$ ( $\text{min}^{-1}$ )	$q_e$ (mg/g)	$R^2$	$k_2$	$q_e$ (mg/g)	$R^2$
0.314	1.82	0.6495	0.986	1.82	0.9961

The lower determination coefficients ( $R^2 = 0.6495$ ) in the table 2 suggest that adsorption of OSS dye onto ASAC biosorbent does not follow the pseudo first order model. However, the higher determination coefficients ( $R^2 = 0.9961$ ) in the table 2 suggest that the pseudo second order model is more likely to predict the behavior over the whole experimental range of adsorption. Therefore, the overall rate of OSS dye adsorption process seems to be controlled by the chemical process through adsorbent and adsorbate [28].

#### 4.4 Adsorption thermodynamic study

The thermodynamic study of the adsorption process is more useful in establishing the nature and possibility of the adsorption reaction. The thermodynamic parameters which such as the adsorption standard free energy changes ( $\Delta G^\circ$ ), the standard enthalpy change ( $\Delta H^\circ$ ), and the standard

entropy change ( $\Delta S^\circ$ ) were calculated from the experiments at different temperatures [31]. The equations 6, 7 and 8 were used in the experiment. The values of  $\Delta G^\circ$  were calculated in table 3 showing the values of  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  at different initial dye concentration and temperatures. The adsorption of OSS dye onto ASAC biosorbent at different temperatures (30, 35, 40 and 50°C) and the initial dye concentrations of 10 mg/l and the 0.1g of the ASAC biosorbent in 200ml of the dye solution shaken at 300 rpm for 60 min were studied.



**Figure 16:** Plot of  $\ln K_d$  versus  $1/T$  for adsorption of OSS dye.

**Table 3:** Thermodynamic parameters for the adsorption of the OSS dye onto ASAC biosorbent.

$\Delta S^\circ$ (KJ mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H^\circ$ (KJ mol <sup>-1</sup> )	$\Delta G^\circ$ (KJ mol <sup>-1</sup> )			
		303 K	308K	313K	323K
0.25	74.73	-2.18	-3.18	-3.58	-7.32

The positive standard enthalpy change ( $+\Delta H^\circ$ ) implies that the interaction of the OSS dye adsorbed onto the ASAC biosorbent was the endothermic process which is in accordance with the influence of temperature. The positive standard entropy change ( $+\Delta S^\circ$ ) has revealed the increased randomness at the dye solution interface during the adsorption progress. The negative value of standard free energy change ( $-\Delta G^\circ$ ) indicates the fact that the adsorption of the OSS dye is a spontaneous reaction. The increase in standard free energy changing with the rise in temperature shows an increase in feasibility of adsorption at higher temperatures. This verifies the correctness of the experimental results in theory [28] [38].

#### 4.5 RSM results analysis

The statistical experiment design methods are nowadays more applied because of the decrease in the number of experiments and time and the cost saving [42].

By the use of the Minitab 17 software, the RSM was used to design the OSS dye removal experiment and optimization of the effects of the parameters on the adsorption of the dye onto the ASAC biosorbent. The adsorption parameters studied are the biosorbent dosage, initial concentration of the dye and the temperature. In the data collection design experiment, the BBD is usually very efficient due to reduced number of runs [32].

**Table 4:** Level of different process variables in Coded and Uncoded form for the OSS dye removal.

Variables	Code	Levels		
		-1	0	+1
ASAC dosage (g/200ml)	X <sub>1</sub>	0.05	0.075	0.1
Initial dye Concentration (mg/L)	X <sub>2</sub>	10	15	20
Temperature (°C)	X <sub>3</sub>	20	30	40

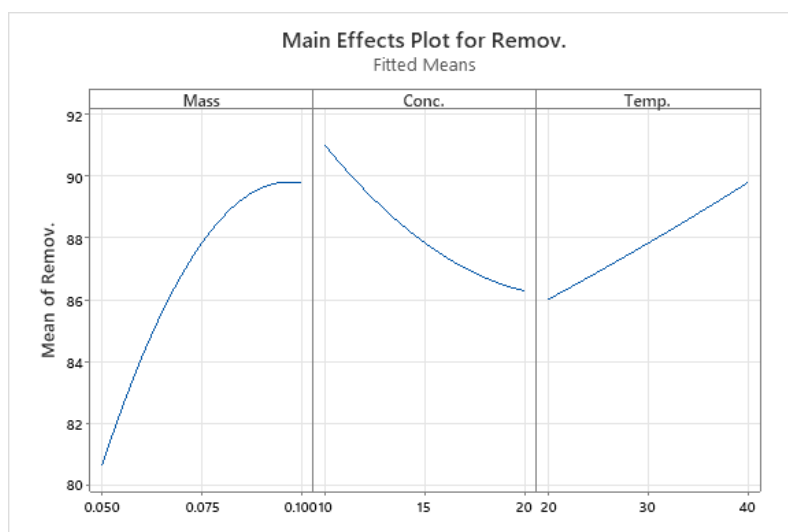
The difference between the predicted and the experimental values plays an important role in judging model adequacy. The calculated Prediction Error of the BBD experiment in Table 5 is 0.659 %. The percentage error between the experimental and predicted values is very small. This confirms the results of the response surface optimization and indicates that the suggested model is adequate for getting the optimum values for the investigated parameters. The results in table 7 and table 8 show that the model is significant with p value = 0.001 ( $p < 0.05$ ) and  $R^2 = 98.24\%$ .

**Table 5:** Experimental design created by Minitab 17 Program and experimental OSS dye removal values.

No	X <sub>1</sub> (g)	X <sub>2</sub> (mg/L)	X <sub>3</sub> (°C)	Removal (%)	
				Exp	Pred
1	0.050	10	30	83.0	82.9
2	0.100	10	30	93.1	92.4
3	0.050	20	30	81.3	80.3
4	0.100	20	30	86.6	85.2
5	0.050	15	20	78.0	76.9
6	0.100	15	20	88.6	88
7	0.050	15	40	82.0	81.4
8	0.100	15	40	92.5	93
9	0.075	10	20	89.1	87.9
10	0.075	20	20	84.7	83.3
11	0.075	10	40	93.6	93.1
12	0.075	20	40	87.4	86.8
13	0.075	15	30	87.9	87.5
14	0.075	15	30	88.0	87.8
15	0.075	15	30	87.6	87.8

The results in Table 6 allow to conclude that the coefficients for the linear effect of all factors: Biosorbent dosage (X<sub>1</sub>), Initial dye concentration (X<sub>2</sub>) and temperature (X<sub>3</sub>), ( $P < 0.05$  for all), are highly significant. However, the only biosorbent dosage coefficient of the quadratic effect (X<sub>1</sub><sup>2</sup>) ( $P < 0.05$ ) is considered as significant.

To obtain a successful experimental design, the parameters with major effects on the treatment were selected. The figure 17 shows the parameters with main effects on the dye removal efficiency. They are mass of the biosorbent, dye concentration and treatment temperature.



**Figure 17:** Factorial Plots for Dye Removal Efficiency

When the surface area increases, the adsorption efficiency increases. In addition, at low concentration there were several unoccupied effective sites on the biosorbent surface. Moreover, an increase in temperature increases the biosorption by decreasing the viscosity of the dye solution and increasing the mobility of the ASAC biosorbent particles [13] [28].

#### 4.5.1 Response surface regression: Dye removal efficiency (%) versus mass, concentration and temperature

**Table 6:** Coded Coefficients

<b>Term</b>	<b>Coef</b>	<b>SE Coef</b>	<b>T-Value</b>	<b>P-Value</b>	<b>VIF</b>
Constant	87.833	0.573	153.22	0.000	
X <sub>1</sub>	4.562	0.351	13.00	0.000	1.00
X <sub>2</sub>	-2.350	0.351	-6.69	0.001	1.00
X <sub>3</sub>	1.888	0.351	5.38	0.003	1.00
X <sub>1</sub> <sup>2</sup>	-2.629	0.517	-5.09	0.004	1.01
X <sub>2</sub> <sup>2</sup>	0.796	0.517	1.54	0.184	1.01
X <sub>3</sub> <sup>2</sup>	0.071	0.517	0.14	0.896	1.01
X <sub>1</sub> X <sub>2</sub>	-1.200	0.496	-2.42	0.060	1.00
X <sub>1</sub> X <sub>3</sub>	-0.025	0.496	-0.05	0.962	1.00
X <sub>2</sub> X <sub>3</sub>	-0.450	0.496	-0.91	0.406	1.00

#### Regression Equation in Coded Units

Dye removal efficiency (%) =

$$87.833 + 4.562 X_1 - 2.35 X_2 + 1.888 X_3 - 2.629 X_1^2 + 0.796 X_2^2 + 0.071 X_3^2 - 1.2 X_1X_2 - 0.025 X_1X_3 - 0.45 X_2X_3$$

A positive sign in the regression equation represents a synergistic effect of the variables, while a negative sign indicates an antagonistic effect. The fit of models is evaluated by the correlation coefficient  $R^2$  and adjusted coefficient  $R^2$  ( $R^2_{adj}$ ) [33]. The high values of  $R^2$  (= 0.9824) and  $R^2_{adj}$  (= 0.9507) indicate that the response surface quadratic model is appropriate for predicting the performance of OSS dye adsorption onto ASAC as shown in Table 7. Moreover, both  $F$  (= 31.01) and  $p$  (< 0.001) prove statistically the significance of the used model.

**Table 7: Model Summary**

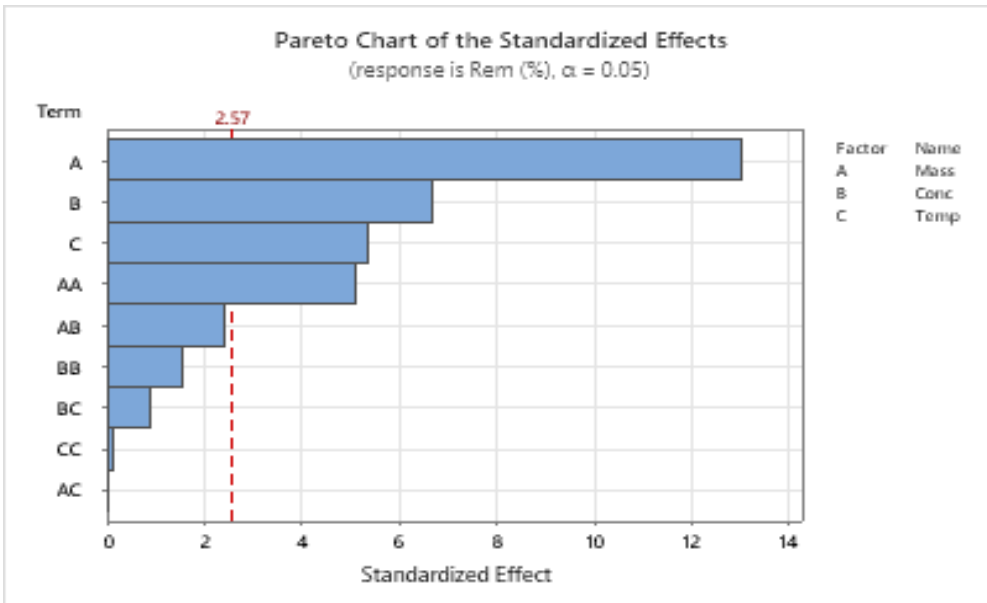
<b>S</b>	<b>R-sq</b>	<b>R-sq(adj)</b>	<b>R-sq(pred)</b>
0.992891	98.24%	95.07%	72.27%

The overall efficiency of a model prediction is generally explained by its determination coefficient of determination ( $R^2$ ) [32]. The value of  $R^2$  should be close to 1.0 for a model with a good prediction efficiency. The table 7 shows that the  $R^2$  (98.24%) is in a reasonable agreement with the Adjusted  $R^2$  (95.07%).

The designed model can also be evaluated by the lack of fit test. The lack of fit test is a measure of the model failure. It represents the data points in the experimental domain by comparing the residual error to the pure error from the replicated experimental design points. The lack of fit should be insignificant. This statement confirms the results in table 8 showing that the Lack of fit for generated model is insignificant with p value = 0.6 ( $p > 0.05$ ). Since this ratio is less than the tabulated F value ( $p < F$ ), it is concluded that there is no evidence of a lack of fit and the model works well [32].

**Table 8: ANOVA table**

<b>Source</b>	<b>DF</b>	<b>Adj SS</b>	<b>Adj MS</b>	<b>F-Value</b>	<b>P-Value</b>
Model	9	275.160	30.573	31.01	0.001
Linear	3	239.212	79.737	80.88	0.000
$X_1$	1	166.531	166.531	168.92	0.000
$X_2$	1	44.180	44.180	44.81	0.001
$X_3$	1	28.501	28.501	28.91	0.003
Square	3	29.375	9.792	9.93	0.015
$X_1^2$	1	25.523	25.523	25.89	0.004
$X_2^2$	1	2.339	2.339	2.37	0.184
$X_3^2$	1	0.019	0.019	0.02	0.896
2-Way	3	6.572	2.191	2.22	0.204
Interaction					
$X_1X_2$	1	5.760	5.760	5.84	0.060
$X_1X_3$	1	0.002	0.002	0.00	0.962
$X_2X_3$	1	0.810	0.810	0.82	0.406
Error	5	4.929	0.986		
Lack-of-Fit	3	4.842	1.614	37.25	0.06
Pure Error	2	0.087	0.043		
Total	14	280.089			



**Figure 18:** Pareto Chart of the standardized effects

The figure 18 shows the effects of the designed parameters: Mass of the biosorbent (A), the dye concentration (B) and Temperature (C). The results in figure 18 confirms the results in table 6 concluding that the coefficients for the linear effect of all factors ( $P < 0.05$  for all), are highly significant. However, the coefficients of the quadratic effects and those of the interaction terms (BB, CC, AB, AC, BC) are insignificant ( $p > 0.05$ ), with exception of AA ( $P < 0.05$ ) which is considered as significant.

#### 4.5.2 Response optimization of dye removal efficiency

The optimum OSS dye removal conditions obtained are biosorbent dosage of 0.1 g/200 ml, initial dye concentration of 10 mg/L and the temperature of 40<sup>0</sup>C shaking the solution at 300 rpm for 60 min as shown in table 9 and figure 25 with the dye removal efficiency of 96.5%.

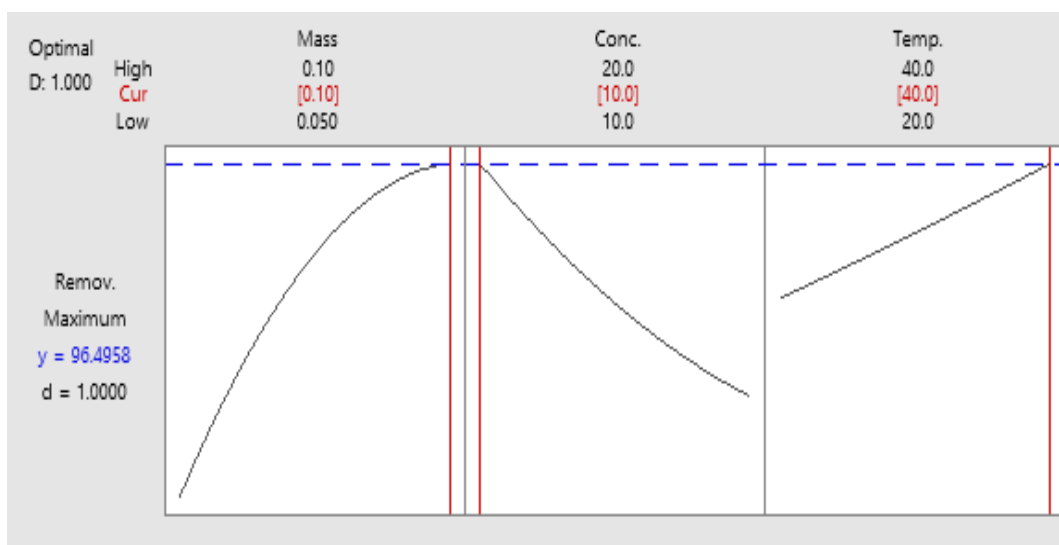


**Table 9:** Multiple Response Prediction

Variable	Setting
Mass	0.1
Conc.	10
Temp.	40

Response	Fit	SE		
		Fit	95% CI	95% PI
Remov.	96.50	1.17	(93.48,99.51)	(92.55,100.45)



**Figure 19:** Optimum conditions for obtaining the maximum OSS dye removal.

## CONCLUSIONS AND RECOMMENDATIONS

### i) Conclusion

The selected avocado seed biomaterial allowed the production of a cheap and effective biosorbent. It was found that acidic medium affects greatly the adsorption of the OSS dye onto the ASAC. The study of adsorption isotherms, kinetic and thermodynamics revealed the nature and behavior of the OSS dye adsorption onto the ASAC. The adsorption isotherms study revealed that dye adsorption followed the Freundlich model. This implies the occurrence of a multilayer adsorption on the heterogeneous surfaces of the biosorbent. Also, the dye adsorption kinetic study assumed the Pseudo second order rate. Moreover, the dye adsorption thermodynamics showed that the OSS dye adsorption process was feasible and spontaneous ( $-\Delta G^\circ$ ) and endothermic ( $+\Delta H^\circ$ ). The RSM enabled the experiment design and optimization of the effects of the major adsorption parameters. The selected parameters were biosorbent dosage, initial dye concentration and temperature. It was revealed that the treatment optimal conditions were 0.1 g/200 ml; 10 mg/L and 40°C by shaking at 300 rpm for 60 min and the predicted dye removal efficiency was 96.5%. According to the experimental data, the production of the activated carbon from avocado seeds seems interesting to waste management and valorization of this agro-waste that is produced abundantly in Rwanda.

### ii) Recommendations

For further study, we recommend the researcher to carry out the structural characterization of the ASAC biosorbent by the BET method, Fourier transform infrared spectroscopy, and Scanning electron microscopy. In addition, Design Expert software may be used to study the optimum conditions by graphically superimposing the contours of the response surfaces of the regression models in an overlay plot. Furthermore, in the future work the dye removal by activated carbon may be scaled up from laboratory to pilot plant by using continuous fixed bed reactor. It will be interesting to do the technico-economic analysis of preparation of activated carbon from avocado seeds and adsorption process in order to assess the viability of the avocado seeds to treat the textile effluent through the cost-effectiveness of the whole process.

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