# ADSORPTION OF DYE-EXTRACT FROM *PERISTOPHE ROXBURGHIANA* ONTO COTTON FABRIC: KINETIC, THERMODYNAMIC AND ISOTHERMIC EVALUATION

**BY**

**OGUZIE, CHIMA KENNETH (**B.Eng)

**(20134873498)**

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**SUPERVISORS: ENGR. PROF. M. U. OBIDIEGWU**

**ENGR. DR. H.C OBASI**

**ENGR. DR. O.O. NNOROM**

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# CERTIFICATION

This is to certify that this project "**ADSORPTION OF DYE-EXTRACT FROM *PERISTOPHE ROXBURGHIANA* ONTO COTTON FABRIC: KINETIC, THERMODYNAMIC AND ISOTHERMIC EVALUATION**" was carried out by **Oguzie, Chima Kenneth** with Registration Number: **20134873498** in partial fulfillment of the requirements for the award of Masters (M.Sc) degree in Textile Science and Engineering in the Department of Polymer and Textile Engineering, Federal University of Technology, Owerri.

……………………………… 13/11/23 ……………………
**Engr. Prof. M.U. Obidiegwu** **Date**
(Principal Supervisor)

……………………………… 13/11/2023 ……………………
**Engr. Dr. H.C Obasi** **Date**
(Co-Supervisor)

……………………………… 13/11/2023 ……………………
**Engr. Dr. O. O. Nnorom** **Date**
(Co-Supervisor)

……………………………… 13/11/2023 ……………………
**Engr. Dr. I. O. Eze** **Date**
(Head of Department)

……………………………… 24/01/24 ……………………
**Engr. Prof. Remy Uche** **Date**
(Dean, SEET)

……………………………… ……………………
**Prof. B.O. Esonu** **Date**
(Dean, School of Post Graduate Studies)

……………………………… ……………………
**Engr. Prof M.C Menkiti** **Date**
**External Examiner**

# DEDICATION

The work is dedicated to my late mother Mrs. Peace Okwuiri Oguzie who saw me start this program but now watches from above as it ends and to my father Mr. C.I Oguzie.

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# ABSTRACT

Adsorption of dye-extract from *Peristophe roxburghiana* onto cotton fabric: Kinetic, thermodynamics and Isothermic evaluation was studied at different temperatures (50°C, 60°C, and 70°C) and concentration (2, 2.5, 3, 3.5, 4, 4.5, 5g/l). Peristophe roxburghiana (PR) plant leaf sample was extracted using aqueous extraction method for 40mins at 70°C. The plant extract was characterized using UV-VIS spectrophotometer and FTIR. The wavelength of maximum adsorption was at 580nm and the functional group identified at 1200.2 $cm^{-1}$, 1.323.3 $cm^{-}$ , and 3272.6 $cm^{-1}$ in the plant extract showed that the dye is an Anthocyanin dye as it contains hydroxyl ($OH^{+}$), ketone ($CO^{-}$), hydroxylated aromatic ring**.** The adsorption mechanism was affected by temperature and concentration while its kinetic pattern obeyed pseudo second order model and type 1 Langmuir isotherm model perfectly. Thermodynamic parameters values 3438.4J/Mol for (ΔH°) and -9.991 J/Mol/K(ΔS°) respectively revealed the reaction was endothermic in nature. This study also showed that the reaction of the dye is chemisorption with a definable adsorption mechanism. In conclusion, a design for colour control and colour optimization can be achieved with proper understands of the adsorption behavior of the dye extract from this plant leaf.



Keyword: Adsorption, Peristophe Roxburghiana, Cotton, Kinetic, Thermodynamic, Isothermic, Evaluation.

# CHAPTER ONE

# INTRODUCTION

## 1.1 BACKGROUND OF STUDY

*Peristophe roxburghiana* is a plant domiciled in our biodiversity. Regarded as weed with some scientific report as a medicinal remedy as orthodox blood supplement. This plant produces colour from its leaves. With the environmental challenges synthetic dyes pose with generation of textile waste water, which scientist are trying to solve with treatment of these waste water and possible substituting synthetic dyes with natural occurring ones give this plant an edge for exploration for dyeing operation and then the need to standardize and control the colour yield and dyeing process using it. The plant is sustainable as it can be cultivated local at low cost and can be extracted using several means with aqueous extraction method less cumbersome to apply. The need to understand its behavior for effective design of the colour control to ensure colour consistency, sustainability and use when applied to textile substrate gave rise to the study of its adsorption behaviours; with respect to its kinetics, thermodynamic and isotherm behavior.

This study if successfully will help mitigate the use of second hand cloth of which more than 50% of them end up as waste in our landfill clogging water ways and posing risk to aquatic body. Secondly, it will value to our local content as dyeing is an art in Africa and Nigeria respectively. Thirdly, it will help our local industries who produce textile fabric have option to less expensive yet effective dye for dyeing operation in contrast to the synthetic dyes shipped into the country from Europe, India and China.

## 1.2 STATEMENT OF PROBLEM

There have been huge efforts to restore the pride of place of natural dyes to the center stage in dyeing operation in order to help promote healthier and safer environment by reducing dye effluents which are hazardous to aquatic lives which synthetic dyes notably used industrially bring with it.

Nigerian textile industry is faced with the problem of growth and stability due to insufficient raw materials (dyes and fibers), smuggling of foreign textiles which causes waste, and shortage of electric power and spare parts for industrial machines (Diogu et al 2014).

Textile industries involve diverse operations including fiber synthesis, weaving, manufacturing, dyeing and finishing. These operations come with numerous health and safety issues. These ranges from chemical exposure from the processing and dyeing of materials, exposure to cotton and other organic dusts, musculoskeletal stresses, and noise exposure. All of which a different approach with the use of more environmentally friend dyes that need less chemical auxiliaries will help mitigate some of this health and safety issues.

While natural dyes have gained popularity due to their eco-friendly and sustainable nature, there are some challenges and problems associated with their use. Here are some common issues:

Color Inconsistency: Natural dyes often result in less vibrant and consistent colors compared to synthetic dyes. The color outcome can be affected by factors such as the type of plant or source used, variations in climate, and the method of extraction.

Limited Color Range: The range of colors achievable with natural dyes is more limited compared to synthetic dyes. Getting certain shades may be challenging, and achieving bright or deep colors can be particularly difficult.

Fading and Wash Fastness: Natural dyes tend to have lower wash fastness and light fastness compared to synthetic dyes. Colors may fade over time with washing and exposure to sunlight, making them less suitable for items that require frequent cleaning.

Mordanting Process: Most natural dyes require mordants (substances that fix the dye to the fabric) to improve color fastness. The mordanting process can be complex, and the use of some mordants may pose environmental and health concerns.

Limited Availability and Cost: Sourcing natural dye materials can be challenging and may be influenced by factors like seasonal availability, geographical location, and climate conditions. This can make natural dyes more expensive and less reliable for large-scale production.

Time-Consuming Process: The dyeing process with natural dyes is often more time-consuming compared to synthetic dyes. It may involve longer dyeing times and additional steps, which can increase production costs.

Environmental Impact: While natural dyes are generally considered more environmentally friendly than their synthetic counterparts, the environmental impact is not completely negligible. Issues can arise in terms of land use, water consumption, and energy required for extraction and dyeing processes.

Allergenic Potential: Some individuals may be allergic to certain natural dye sources. This can pose a problem for people who have sensitivities or allergies, especially when these dyes are used in textiles that come into direct contact with the skin.

Regulatory Compliance: Meeting regulatory standards for colorfastness, toxicity, and other factors can be more challenging with natural dyes. This can be a barrier for manufacturers aiming to comply with industry regulations.

Despite these challenges, the understanding of the adsorption behaviours and and best conditions of extraction and use will eliminate problems of a) Colour consistency b) colour control c) widen the colour range of which this study is aimed at achieving

This study will aim at widening the knowledge of handling natural dyes with respect to dye extracted from *Peristrophe roxburghiana* plant by trying to explain it's kinetic, thermodynamic and adsorption behaviours and best dyeing time and temperature which will enhance the design of coour control and optimization of the colour consistency and handle.

## 1.3 OBJECTIVES OF STUDY

The main objective of this work is to determine the kinetics, thermodynamic and adsorption Isotherm behaviours of dye extract from *Peristophe roxburghiana* on cotton fabric sample.

Other specific objectives are:

i. To extract natural dye from *Peristophe roxburghiana* plant leaves.

ii. To dye cotton fabric with extracted dye at different temperatures achieved through adsorption.

iii. To characterize the natural dye extract using UV-VIS Spectrophotometer and Fourier-transform infrared spectroscopy (FTIR).

**iv.** To investigate process kinetic, thermodynamics and isotherms

## 1.4 JUSTIFICATION OF STUDY

Gaudani et al (2010) peristophe plant have been explored in details for its pharmacognostical study of stem and leaf as well as physicochemical parameters, phytochemical screening and leaf constant. While Mansurah et al (2022)investigated its cytotoxic principles that could be potential leads for developing novel anti-cancer and anti-tumor agents. They found chemical constituents, including diterpenes and flavonoids in it which could qualify it as a colourant.

Njan et al (2020) investigated the effect of methanolic leaf extract of Peristrophe Bicalyculata (MEPb) on type 2 diabetes mellitus (T2DM) associated cognitive decline in Wistar rats.They conclude that Methanolic leaf extract of Peristrophe enhanced antioxidant capacity and prevented neuroinflammation, consequently improving brain neuronal cholinergic function in experimental animals and chemical constituents of flavoids was present in it validating its use as a colourant.

Anti-lipidemic effects of combined extracts of Moringa oleifera and Peristrophe bicalyculata in allxoan-induced diabetic rats have been investigated.And to be effective in the treatment of hypertension and presence of flavonoid was seen in the plant (iwara et al., 2014).

Effect of Foaming Conditions on Foam Properties and Drying Behavior of Powder from Magenta (Peristropheroxburghiana) Leaves Extracts was worked on by (Thuy et al., 2022) and the discovered the presence of anthocyanin chemical constituent in the plant.

Rachma et al., (2019) successfully dyed cotton fabric with natural dye from peristrophe plant extract,They discovered that major component of the extract of its leaf was phenoxazine.The dyed cotton showed sunlight, washing, and rubbing fastness indicating the the dye from the plant is good as a natural textile dye.No documented reports have been seen on public domain on this area of scientific inquiry as such justifying the work as novel as wide literature consultations have proved no scientific report(s) has been published on kinetics, thermodynamic and adsorption isotherm behavior of natural dye extract from *Peristophe roxburghiana* plant onto cotton. At the end of this study it will better give response to the understanding of the chemistry of handling natural dye in dyeing textile fabrics especially cotton.

## 1.5 SCOPE OF STUDY

The scope of this research includes the following:

i. Raw material sourcing,
ii. Extraction of natural dye extract from *peristrophe roxburghiana* plant
iii. Characterization using Ultraviolet-visible spectroscopy (UV-VIS)

iv. Characterization using Fourier-transform infrared spectroscopy (FTIR) techniques

v. Dyeing of cotton fabric

vi. Determination of its adsorption kinetics and thermodynamic behaviors

vii. Evaluation of its adsorption behaviour using pseudo first and second order models of adsorption, and isotherm models (Langmuir and Freundlich). Results obtained will be represented in tables and graphs and discussed.

# CHAPTER TWO

# LITERATURE REVIEW

Researchers have documented several works on natural dyes for dyeing and for other application. With reports of its use as in vat dye for dyeing synthetic fibres (Adeel, et al. 2012). Apart from their use in textiles dyeing, they find their use in the colouration of food, medicines, handicraft articles, and in leather (Yusuf, M., Shahid, M., Khan, MI., Khan, MA., Mohammad, F., 2015; Yusuf, M., Mohammad, F., 2017).

Despite their not excellent colour fastness abilities, many of these natural dyes are used in orthodox medicine as antibacterial (Yusuf et al. 2015, Aggarwal, BB., Kumar, A., Bharti, AC., 2003), antifungal (Mansour, R., Haouas, N., Ben Kahla-Nakbi, A., Hammami, S., Mighri, Z., Mhenni, F., Babba, H., 2013), antioxidant (Khan, SA., Ahmad, A., Khan, MI., Yusuf, M., Shahid, M., Manzoor, N., Mohammad, F., 2012), anticancer (Al-Sehaibani, H., 2000; Dweck, 2002), dye-sensitized solar cells (Hao, S., Wu, J., Huang, Y., Lin, J., 2006), histological staining (Tousson, E., Al-Behbehani, B., 2011), pH indicator (Mishra, PK., Singh, P., Gupta, KK., Tiwari, H., Srivastava, P., 2012) and in several other application disciplines.

Current renaissance in research show development, innovation on natural dye production. Science and handlers of dyes have witnessed increasing awareness and need on protecting the natural environment and ensuring environment sustainability to reclaim and safeguard of environs which hazardous materials such as plastics, chemicals including synthetic dye effluents, have done. This thereby makes this area a dynamic field (Khan**.** SA**,** Ahmad, A., Khan, MI., Yusuf, M., Shahid, M., Manzoor, N., Mohammad, F., 2012; Hao **S.,** Wu, J., Huang, Y., Lin, J., 2006).

## 2.1. NATURAL DYE EXTRACTION

The main aim of extracting dyes from natural sources is to prevent and eliminate potency of environmental pollution.

### 2.1.1. METHODS IN DYE EXTRACTION

Extraction method is the act, technique or process involved in bringing out, isolating or extracting the dye from natural dye bearing material or natural sources (plant). This technique also isolate components that are not dye components referred to as phytochemicals (Dawson, TL, 2009). Gulrajani, ML, Gupta, DB, Agarwal, V., Jain, M., (1992) listed some of this compounds such as water-insoluble fibres, carbohydrates, protein, chlorophyll, and tannins.

Isolation of natural dyes from their natural source is simply a solid-liquid extraction process. The principle is to bring the solid material (the absorbate or dye containing source) in contact with a solvent, soluble component in the solid material dissolves in the solvent. Isolation is the main step for the preparation of natural dyes. Extraction is also needed by users of crude dye-bearing materials.

This process of isolation give rise to mass transfer of active soluble compounds from solute into the solvent in a concentrated gradation (Sinha, K., Saha, P.D., Datta, S., 2012). Mass transfer decreases as concentration of active compounds dissolved in the solvent increases, till equilibrium is reached. Natural colouring materials, are not single chemical entity in the plant matrix other varieties of non-dye plant constituents are available this makes isolation of natural dyes through extraction a bit complex or cumbersome in processing. This complexity necessitates the need to determine the nature and solubility attributes of the colouring materials before using an extraction method for isolation. Else a trial and error is best applied to get best extraction scheme based on what the intent for the dye extraction is. Some methods for extraction of colouring materials are:

i. Aqueous extraction

ii. Alkali or acid extraction method

iii. Microwave and ultrasonic assisted extraction

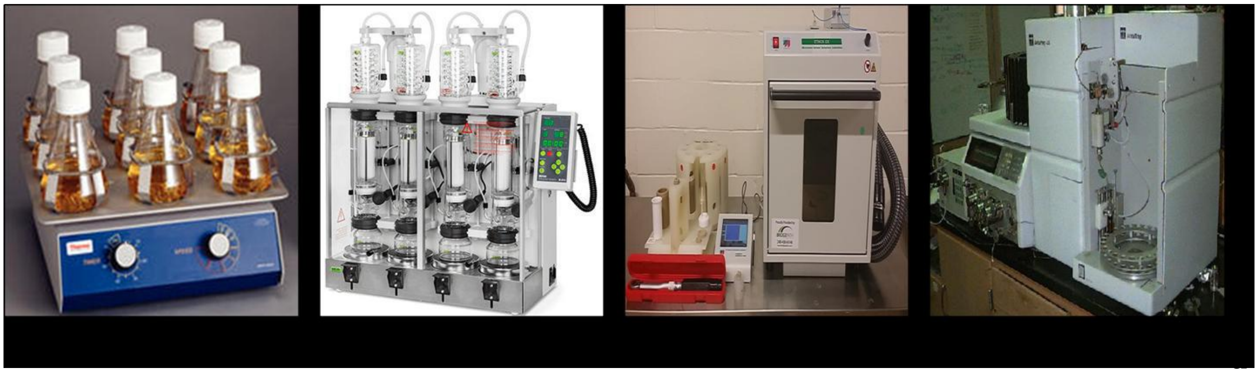
iv. Fermentation Extraction method

v. Enzymatic extraction

vi. Solvent extraction

vii. Super critical fluid extraction.

These aforementioned methods can be used in the isolation of colour bearing materials from natural sources once the nature and structure of the natural source is known. Some apparatus employed in the extraction of natural dyes are represented below in Figure 2.1.



**a** **b** **c** **d**

Plate 2.1: Different extraction methods: **(**a) cold percolation, (b) solvent extraction, (c) Supercritical fluid extraction, (d) Microwave assisted extraction

**Aqueous Extraction**

Aqueous extraction is customary and conventional method of extracting dyes from plants and other natural sources of dye or colouring materials as it needs little or no technical know-how especially when using water as the solvent. The material or natural source bearing the colouring material or dye is first reduced into small pieces, or powdered by grinding, after which sieved this sieving process is aimed at improving extraction efficiency by having even particle sizes. The sieved fine, small piece or powdered dye sourcing material is then soaked with a solvent conventionally used solvent is water in earthen pot/vessel, wooden, or metal vessels (for best choice) for a long time or a chosen duration this is to loosen the cell structure of the plant, followed by then boiling to get the dye solution, which is filtered to remove non-dye plant particles. The process of boiling and filtering is repeated to remove as much dye as possible. Rony Mia, Md. Minhajul Islam, Taosif Ahmed, Md. Azhar Waqar, Nusrath Jahan Khanam, Suraiya Sultana, Md. Sajjadul Karim Bhuiyan, Md. Nizam Uddin,(2022) employed this method to extract dye from Triadica Sebifera plant. Dye extract from Uri plant was extracted using this method (Nnorom et al. 2018). Onuegbu et al (2020) extracted dyes from *Rosella Calyces* (Hibiscus Sabdariffa) using this method.

Sasidharan, et al., (2011) reported that for large scale extraction process for purified dye, it is better to use steel vessel because it offers reduced time for soaking the materials in water which is further reduced by boiling the solution. Generally, in this approach centrifuge is employed for separating residual matter from the dye extract solution. Also using of trickling filters can help in ensuring removal of finer plant material particles enhancing better solubility of the purified natural dye. This is because most of the dyeing operations are carried out in aqueous media, the dye extract obtained by this scheme or method can be easily and readily applied to the textile materials to impact the colouring effect or properties on it (Prabhavathi et al., 2014). In their study (Okonkwo et al. 2019) used a soxhlex extractor to eliminates the stress associated with using the conventional earthen, metal vessel approach for extraction.

Despite the merits of this methods, it is face with demerits of extended extraction time, high volume of water, and high temperature need which can damage plant cell structure, and lower dye yield as not only water-soluble dye components get extracted or isolated.

In the isolation of dyes from plants, water-soluble substances such as sugars are extracted or isolated alongside the dye extraction. As such this constituents that accompany the dye is needed to be removed if the extract is to be concentrated and converted into a powder form (Prabhavathi et al., 2014; Wangatia et al., 2015; Lekshmi., 2015). High boiling temperature affects the yield of heat-sensitive dye substances according to report therefore, a lower temperature should be used for extraction in such instances where the material is heat sensitive (Sasidharan et al., 2011)

**Acid and Alkali Extraction Methods**

This extraction method is carried out using a dilute acidic or alkaline condition. Most dyes are in the form of glycosides (Dweck, 2002), addition of the acid or alkali helps speed up hydrolysis of glycosides giving rise to a better extraction and yield of colouring materials from the natural dye source. In preventing oxidative preparation of some flavones dyes, acidified water is also used for its extraction. (Dweck, 2002). Alkaline extraction is preferred for dyes containing phenolic groups as they are soluble in alkali; this method improves the dye yield. These dyes can be later precipitated by the use of acids (Carle, 2004). Uddin, M.G. (2015) employed this method in the extracting of dye from mango leaves. This method was employed for the extraction of natural dye from the mesocarp and exocarp of *Cocos nucifera* (Rodiah,M.H., Noor Hafizah,S., Noor Asiah, H., Nurhafizah,I.,Norakma, M.N., Norazlina,I., 2022). Divya Lekshmi R. B & Ravi D, (2013) reported using this method to extract dyes from *Aloe vera,Azadirachta indica*, *Bixa orellana*, *Curcuma longa*, *Punica granatum*, *Quercus infectoria*, and *Thymus Vulgaris* for dyeing scoured cotton fabrics.

Using this method offers alongside its merits a risk of destruction of some colouring materials under alkaline conditions considering the fact that some of the natural dyes are pH sensitive (Onuegbu, et al., 2020).

Onuegbu, et al., (2020) according to their report on a hibiscus plant show that this method may result to different hues by variance in pH of the extraction medium by addition of acid or alkali, because many natural dyes contains a mixture of different chemical constituents. This during dyeing gives rise to differing colourfastness properties on the applied textile materials.

**Ultrasonic and Microwave Extraction**

The use of microwave and ultrasound extraction technique is used in the extraction processes for natural dye. There more recent and novel methods of extracting, here extraction efficiency is improved or enhanced when ultrasound or microwaves are used. They method offer reduced quantity of required solvent, time, and temperature of extraction.

This procedure involves using ultrasound with frequencies ranges of 20 kHz to 2000 kHz, leading to increased permeability of cell walls to produce cavitations (Patil G., M.C. Madhusudhan, B.R. Babu, K.S.M.S Raghavarao, 2009). In the extraction of plant-based natural dye treated with water or other solvent using ultrasound method, tiny bubbles known as cavitations are created in the liquid. These expansion continues until a certain size is reached and the bubbles becomes unable to maintain their shape, which causes the cavity to collapse or the bubbles to burst, creating high pressure and temperature.( Selfina Gala, Sumarno Sumarno, and Mahfud Mahfud 2018). Literature reports like the once of (Jassim, Nawras. 2020) optimization the extraction of Chlorophyll dye from *Conocarpus Lancifolius* Leaves, this extraction technique was reported to be employed in the production and characterisation of natural dyes powder from *Brachiaria mutica* for textile application: (Kusumastuti, Adhi, Fardhyanti, Dewi, Anis, Samsudin, Kamis, A. 2021). Natural dyes such as dye from *Coleus atropurpureus* Leaves and Anthocyanin dye from butterfly pea flowers (*Clitoria ternatea*) were obtained using this method (Selfina Gala et al, 2018; Syafa'atullah, Achmad, Amira, Arie, Hidayati, Sonya, Mahfud, Mahfud. 2020).

The generation of extremely high temperatures and pressures during ultrasonic extraction increases extraction efficiency quickly. Heat-sensitive dye molecules are best extracted using this method because it can be carried out at lowered temperatures. (Syafa'atullah et al, 2020; Patil, et al 2009). Minimum amount of solvent is used to treat the natural source for the colouring material in this method (Kusumastuti, et al 2021).

Microwave energy on the other hand has been subject of study in the last two decades on its efficacy in extraction. Microwave energy causes molecular motion by migration of ions and rotation of dipoles with no change in the molecular structures at temperature that is not too high. Microwave energy is a non-ionizing radiation. Non-polar solvents like hexane and toluene have been reported not to be affected by microwave energy (Patil, et al 2009; Selfina Gala et al 2018).

Microwave enhances the rate of reaction of the extraction causing a shortened extraction cycle with better yield. Microwave energy and ultrasound extractions methods can be considered to be a green processes due to reduction in extraction temperature, solvent usage, and time with reduced energy consumption and multiple samples can be analyzed at the same time (Patil, et al 2009; Selfina Gala et al 2018).

**Fermentation Extraction Method**

The extraction mechanism here involves the action of enzymes produced by microorganisms present in the atmosphere or those present in the natural sources from which colouring material is to be obtained to catalyze the extraction process. Indigo extraction process is a notably fermentation extraction process. Indigo extraction process involves the soaking in warm water at about 32 °C freshly harvested indigo leaves (Uri) and twig (Nnorom et al. 2018). Nnorom et al. (2018) fermentation causes the reduction of glucosideindican present in the leaves of Uri into glucose and indoxyl by indimulsin which is an enzyme present in the leaves. Salauddin Sk M, Mia R, Haque MA, Shamim AM. (2021) reported using this technique to extract bioactive compound from plants. Lizamoni Chungkrang, Smita Bhuyan and Ava Rani Phukan. 2021 used this method in their work to obtain dye from natural plants. Lisna Hidayati, Diana Cahya Ningrum, Hendriawan Nugroho and Tri Rini Nuringtyas (2018) applied this method in the characterization and optimization of of Nila Leaves (*IndigoferatinctoriaLinn.)* extract. Fermentation method looks similar to aqueous extraction but here high temperatures are not used. The microorganisms which act as catalyst disintegrate the colouring matter binding substances in natural way. Long extraction time, foul smell due to microbial action occurs; this posses a challenge and demerit using this extraction method (Lisna Hidayati, et al, 2018).

**Enzymatic Extraction**

Enzymatic extraction method employs the use of enzymes. These enzymes are vase biological molecules capable of initiating thousands of metabolic processes that sustain life (Dawson, TL. 2009). They are highly selective biological catalysts, greatly accelerating both the rate and specificity of metabolic reactions, from the digestion of food to the synthesis of DNA. Enzymes adopt a specific three dimensional structure, and may employ organic and inorganic co-factors to assist or aid in catalysis (Dawson, TL. 2009; Patil et al, 2009)

The recent quest is to employ enzymes for assistance in extractions operations. Because of its inert abilities to break down the cells structure of solid material, thereby making the contact of solid with the solvent liquid easier. Plant tissues contain cellulose, starches, and pectins as binding materials these binding materials are broken down by enzymes leading to ease of isolation of colouring matter from them. Sharmila S., Kowsalya E., Kamalambigeswari R., Preetha S., Dinesh M., Shrivatsan B., Shaik Sadik and Jeyanthi Rebecca L. (2017) used this method to obtain natural dyes, Laccase-catalyzed dye synthesis have been reported by (Rıza Atav, Bürhan Buğdaycı & İsmail Yakın 2022), anthocyanin dyes from sweet potatoes have been reported using this technique (Nicole Bridgers E. , Mari S. Chinn, Van-Den Truong,2010), peroxidase lignin immobilized on carbon nanotubes have been obtained using this method (Oliveira, S. F., da Luz, J. M. R., Kasuya, M. C. M., Ladeira, L. O., & Junior, A. C. 2018). Derksen, G. C., Naayer, M., van Beek, T. A., Capelle, A., Haaksman, I. K., van Doren, H. A., & de Groot, Æ. (2003) reporte that anthraquinone glycosides from madder roots was obtained with this method. Chiong, T., Lau, S. Y., Lek, Z. H., Koh, B. Y., & Danquah, M. K. (2016). Reported the use of enzymatic treatment to obtain methyl orange dye from synthetic from wastewater using a plant-based peroxidase enzymes. Commercially available enzymes including cellulase, amylase, and pectinase these have been used by some researchers to loose the surrounding material leading to the extraction and isolation of dye molecules under milder conditions (Vankar, Padma S & Shanker, Rakhi & Verma, Avani. 2007). This process may be suitable in the extraction of dye from hard plant materials such as bark, roots, and the like (Archana, K., Singh, P., Mishra, P. K., Srivastava, P., & Mondal, M. K. 2009; Hany M. Helmy 2020).

## Solvent Extraction

Solvent extraction technique can be employed, depending on the nature of the plant to extract by using organic solvents such as acetone, petroleum ether, chloroform, ethanol, methanol, or a mixture of solvents such as mixture of ethanol and methanol, mixture of water with alcohol, and so on. The water- alcohol extraction method is a solvent extraction method able to extract both water-soluble and water-insoluble substances from the plant sources (Oluwaseun Adedokun, Yekinni K. Sanusi, Ayodeji O. Awodugba, 2018). The extraction yield is higher as compared to the aqueous method as larger number of chemicals and colouring materials can be extracted. Acid or alkali can also be added to alcoholic solvents to facilitate hydrolysis of glycosides and to facilitate a release of colouring matter (Oluwaseun et al, 2018). Purification of extracted colour is easier in this method as solvents can be easily removed by distillation and reused. Norhisamudin N. A. , Sabani N. , Shamimin M.M. , Juhari N. ,  Shaari S., Ahmad M.F.,  Zakaria N., (2021) reported using different solvents in extracting natural dyes from Roselle(Hibiscus Sabdariffa) and Green Tea Leaves This extraction method is performed at lower temperature thus chances of degradation are fewer. Sabarikirishwaran, P., Unpaprom, Y. & Ramaraj, R. (2023) obtained natural dye from Leaf Biomass of *Sandoricum koetjape* and *Syzygium samarangense* was obtained using solvent extraction on the. The disadvantages of the method are the presence of toxic residual solvents and their greenhouse effect (Sabarikirishwaran, et al 2023). Also the extracted material is not readily soluble in water and the subsequent dyeing process has to be carried out in an aqueous medium (Norhisamudin et al, 2021; Oluwaseun et al, 2018)

## Supercritical Fluid Extraction

This recent extraction technique requires carbon dioxide to make it possible to extract non polar compounds from solid matrices. This extraction method is a new innovation in the isolation and purification of natural product.  In this method, $CO_2$ gas helps supercritical fluid function above its critical values of temperature and pressure. With physical attributes that looks like liquid and gas. They spread out along a surface more easily than a true liquid as they have much lower surface tension, and their viscosity is lower than liquid (Vankar, Padma S & Tiwari, V.&Ghorpade, B.. (2001). Vankar et al., (2001) used this technique to extract dye from eucalyptus bark. They reported that the fluids have better interaction with the substrate due to their very good diffusivity. This method has shown to be able to dissolve many substances like a liquid, as solubility of any substance in a solvent is higher at higher pressure and temperature and such conditions are needed to maintain a gas in the supercritical state (Talib, Nabila & Ahmad, Mohd & Ab Kadir, Muhammad & Ismail, Khudzir & Rahim, Ahmad. 2018). Talib et al., (2018), use this technique to optimsie the extraction of dye extract from brown seaweed (*Sargassum Sp*). Supercritical fluid extraction using carbon dioxide ($CO_2$) is a good alternative to solvent extraction as it is nontoxic, cheap, easily available, and does not leave residues. The advantage of the process is that the extract is free from residual solvent traces and heavy metals and is light coloured due to the absence of polar polymerizing substances. This isolation method is majorly applied in extraction and purification of natural products for food and pharmaceutical applications. Its disadvantage is the high cost of the equipment and poor extraction of polar substances (Vankar et al., 2001; Patil et al., 2009; Talib et al., 2018)

## 2.2. MORDANTING OF NATURAL DYES

Natural dyes are not readily substantive or having very good affinity to textiles, this giving rise to the application of metallic salts or natural mordants that help in aiding or creating their affinity for both the colouring matter and the fibre (Ferreira et al., 2004).

Transition metal ions such as stannous chloride, alum, ferrous sulphate, chrome and copper sulphate are notably used as mordants as they offer strong coordinating abilities of producing weak to medium attraction or interaction forces that act as linkage of materials thereby creating substantivity for the selected textile fibre.

This salt forms matrix with the fibre producing an insoluble precipitate that fixes the dye and mordant into the textile fibre, giving rise to an appreciable fastness levels (Konar and Samanta, 2011; Samanta, and Agarwal, 2009).

Many reviews have already been documented showing development of mordanting agents which are non-toxic and ecofriendly this is because some mordants have some negative impact to the environment and life. Some of the approaches harnessed and reported include the use of metals which are considered ecologically safe such as alum and iron sulphates; natural oil products, tannins and other natural plant extracts (Raisanen, et al., 2001; Raja and Thilagavathi, 2008; Prabhu et al., 2011; Saxena and Raja, 2014, Okonkwo, et al. 2019).

Mordanting therefore, is the treatment of textile fabrics before, after or while dyeing with metallic salts or other complex forming agents with the aim of enhancing the ability of binding or creating affinity between natural dyes onto textile substrates. This process is applied using either pre, simultaneous (Insitu), or post mordanting, using different selective mordants that result into the development of various shades, and increased dye uptake and improved colour fastness behavior of any natural dye on the fabric (Okonkwo, et al. 2019).

Mordants are of different types which are classified according to metal salts, tannins/tannic acid and natural oils (Singh et al., 2000). Metallic salts such as aluminum, chromium, copper, Iron and tin has been the most used for the purpose of mordanting, amongst the other types of mordants which is the use of natural mordants like tannins and natural oils. Tannins/tannic acid are bitter and stringent substances gotten from excretions in plant parts such as barks, leaves, cutch, fustic, black oak, galls, pomegranate and fruits. (Konar and Samanta, 2011; Saxena and Raja, 2014). The main tannins used in place of tannic acid on account of their low prices are natural tannins like myrobolan, mango bark /leaves and tea.

Natural oil mordants have fatty acids such as palmitic, stearic, oleic, ricinoleic and glycerides. During mordanting process, the -COOH group of the fatty acids reacts with metal salt leading to the formation a COO-M, where M represents the metal (Palanisamy and Kumar, 2011). Amongst all of the natural oil mordants available, sulphonated oils are most notably used due to their better binding capacity between them and the fibre when compared with other natural oils, they are usually used in dyeing of madder to obtain Turkey red colour. All these mordants find application in the mordanting of numerous textiles such as silk, cotton, sisal, blends of fabrics, synthetic fabric and dyeing madder to obtain Turkey red colour (Samanta and Agarwal, 2009; Kumaresan et al. 2011; Saxena and Raja, 2014).

However, mordanting with salts of chrome, copper and tin have proven to be hazardous to health in the sense that they produce toxic waste which requires special disposal process. Regardless, merits because it offers the dye better fixation to fibre providing an alternate palette,but due to its toxic nature, it is not recommended for use (Cordon, 2010; Chengaiah et al., 2010). On the other hand, mordants such are alum, iron and tannins are safer and used for mordanting purposses. This mordants of alum, iron and tannins produces myriad colours when used in conjunction with the appropriate natural dye. This is so because they are naturally present in the environment in large amounts (Saxena and Raja, 2014; Cordon, 2010).

Mordanting can be attained by either pre mordanting (mordanting before dyeing), simultaneous (Insitu) mordanting (dyeing the fabric and mordanting at the same time) or post mordanting (mordanting after dyeing) using different types of mordants. The selection of mordant and mordanting techniques is dependent on the nature of the substrate, its affinity for the substrate and type of dye to be used. Scientific research and documentation made on the dyeing of textiles with natural dyes while adopting specific mordanting systems and mordnt best suits for a particular textile material. Most this work have been reported by the following (Gupta, et al 2004); Ferreira et al., 2004; Saikia and Bhuyan, 2005; Jansen and Cordon, 2005; Zhang et al., 2010; Saha and Sinha, 2012; Basak et al., 2012; Lokesh., 2013; Yim et al., 2013;).

### 2.2.1. MORDANTING METHODS USED IN DYEING WITH NATURAL DYES

#### a. Pre-mordanting

Pre-mordanting process involves primarily mordanting the fabric before dyeing operation occurs. The mordant is firstly applied to the fabric before it's subjected to dyeing. Pre-mordanting is the most conventional method of mordanting cotton, cellulosic and some animal fibres. This is because textile fibres in unmordanted form have low or no affinity for many natural dyes. The advantage of this method is that the standing baths is re-useable many times after replenishing with the mordants.

This makes the process economical with reduced pollution load hence enhancing suitable for large-scale application (Gümrükçü et al., 2008; Cordon. 2010). The procedures for pre-mordanting are;

i. Dissolve the mordant and add it to the dye bath containing specified amount of water.

ii. Add the substrate (fibre) and bring the whole mixture to boil for a period of about 45mins

iii. Cool the solution

iv. Remove the substrate (fibre) gently, and ensure even take-up of the mordant.

v. Substrate is rinsed to remove unfixed dyes, dry under room temperature and analyze. The fabric substrate is ready for dyeing. (Cordon. 2010)

The disadvantage with this method is that there is a lot of fabric handling.

**b. Simultaneous mordanting**

In this method or technique both the dyeing and mordanting process are carried out in the same dye bath and at the same time. In the handling of cotton and other cellulosics fabric/fibre, the mordant is usually added to the dye bath at the start of dyeing so that both mordanting and dyeing processes take place simultaneously (Chengaiah et al., 2010). The procedures for this method are;

i. The mordant in dissolved first in a separate bath.

ii. Mordant solution is then transferred to the dye bath followed by the addition of the wetted fabric.

iii. The whole mixture is boiled while stirring at chosen intervals of time using a stirring rod.

iv. Simmering is done until maximum dye uptake is achieved.

v. The dyebath is allowed to cool, fabric is removed and rinsed with mild detergent, dried and analyzed. This method gives a demerit as colours are not as permanent as pre-mordanted fabrics because mordanting is dissolved at a separate stage and later introduced into the dye solution, but this method is associated with less fabric handling (Chengaiah et al., 2010)..

**c. Post mordanting**

Post mordanting involves the treatment of the fabric with a mordant after dyeing operation has taken place. In this method, the final colour is developed at this last phase. Iron salts are notably applied using this method for producing grey and black colours (Gümrükçü et al., 2003). The procedures for post mordanting are as follows;

i. Dissolve mordant in specified amount of water.

ii. During simmering, which is after dyeing, add solution to dye bath at a specified time. For best practice, add to dye bath at the last five to ten minutes.

iii. Cool solution, and remove substrate.

iv. Rinse with cold water to remove unfixed dyes, dry and analysis.

After pre-mordanting or simultaneous mordanting using tin and iron they reclaimed mordants is reused using this mordanting method. This is because tin brighten and enhances colour, whereas iron dims or dulls colours. This effect is called blooming effect. This type of mordanting process is quite satisfactory in the dyeing of several skeins with different salts in the same dye bath, because once combined with the fibres, the metallic ions do not react with one another.

Many scientists have reported their use of these mordanting techniques in the dyeing of various natural fibres like cotton, silk, wool and synthetics such as polyamide and polyester (Vankar and Shanker, 2007; Kumaresan et al., 2012; Mongkholrattanasit et al., 2011). Some of the studies investigated and reported on these techniques are; Teli (2009) who in his study employed $CuSO_4$ and $FeSO_4$ to investigate influence of concentrations of mordants when turmeric dyes is used to dye cotton fabrics. Teli (2009) reported that when fabrics were treated with tannic acid which was the mordant and then dyed with metal salts, the depth and performance properties of the fabric such as fastness to light, washing, rubbing (dry as well as wet) significantly improved. Effects of mordant on a fabric substrate he reported was dependent on various factors such as its concentration, kind of mordant used, type of fabric substrate and the method employed for mordanting process and dyeing.

He concluded in his report that the type of mordant used significantly affects the fastness attributes of the dye and also affected the hue of the fabric after dyeing. If the action of the mordant on the cotton substrate is hard (acidic mordant with an acidic dye), the best technique to employ is either pre or post mordanting because they reduce the potency of damage to the substrate (Wikipedia. 2016). Simultaneous mordanting is suitable when the dyer want to achieve little or no loss of the dye properties. The mordant chosen has a marked effect on the final colour. However, each dye has different interactions with each mordant thus different shades can be obtained with the same mordant using different methods of mordanting (Elena. 2010; Asif et al., 2010).

Further reported works relating to the mordanting methods and dyeing of substrates with natural dyes include work done by Sundarajan (2011) who used tannin acid, cow dung, lemon juice and pomegranate rind as natural mordants to study the standardization of the dyeing effect of marigold and turmeric dyes on silk and knitted cotton fabric (Sundarajan et al., 2011).

The study established that all the mordanted fabric showed good dye uptake. Kumaresan (2012) dyed silk fabrics using extracts from the stems of Achras sapota and flowers of Spathodea campanulata. Dyeing was performed under varying conditions of mordanting techniques using pre-mordanting, simultaneous and post mordanting methods. He reported that the flowers of Spathodea campanulata with simultaneous method at three percent mordant concentration gave the best results. Under different dyeing conditions, different mordanting methods yield various results as most of the mordants used generally affect the hue (shade) and purity of colour (Kumaresan et al., 2012). Ali (2011) who studied the effect of pre-mordanting and post-mordanting of wool fibres with Aluminium sulfate, ferrous sulfate under different conditions reported that in his study, during pre-mordanting and post-mordanting with ferrous sulfate, there were significant changes in hue and a great deal of decrease in the chroma (purity of colour). The study concluded that, alum and iron did not have any effect on fastness as appreciable increase in fastness properties occurred (Ali et al., 2011).

## 2.3. CHARACTERIZATION OF DYES

Analyzing the dyes that will be used is essential in light of the importance of environmental issues and dye sustainability. Characterization of dyes is the process of studying or identifying dyes in the context of their chemical makeup as well as the presence of other compounds like formaldehyde, pesticide residues, chromium, and prohibited amines (Bhuyan and Saikia, 2008).

This type of study was started as early as 1930s. Various techniques which can be used for characterization of dyes notable among them are (Broadbent, 2001):

i) Thin layer and column chromatographic studies

ii) Ultra Violet-Visible Spectrophotometric studies

iii) Fourier Transform- Infra-red Studies

iv) High Performance Liquid Chromatographic Studies

v) Gas Chromatography-Mass Spectrophotometric Studies

In this study we were limited to the use of Ultra Violet-Visible spectrophotometer, and Fourier Transform-Infra-red in characterizing the natural dye from *peristrophe roxburghiana* plant.

### 2.3.1. CHARACTERIZATION OF FUNCTIONAL GROUPS IN DYE EXTRACTS

Infrared spectroscopy using the Fourier transform is a useful technique for locating functional groups in plant extracts. It facilitates the identification of the reactive areas and molecule's bond structure (Hazra, et al. 2007; Eberhardt, et al. 2007). There are numerous techniques to prepare samples for FTIR. The simplest method for liquid samples is to put one drop of the sample between two sodium chloride plates. A thin layer is created between the plates by the drop. Potassium bromide (KBr) can be used to mill solid materials, and the resulting thin pellet can subsequently be examined. As an alternative, solid samples can be dissolved in a solvent like methylene chloride, and then a few drops of the resulting solution are applied to a single High Attenuated Total Reflectance (HATR) plate, where the spectra are then recorded in terms of the percentage transmittance. According to the reference provided in the Varian FTIR instrument manual, the peaks at particular wave numbers were assigned by bonding and functional group. The FTIR was carried out at the university laboratory of Ahmad Bello University Zaria for the natural dye extract obtained from peristrophe roxburghiana, and the results are graphically displayed in Figure 4.1.

### 2.3.2. CHARACTERIZATION OF PHYTOCHEMICALS IN DYE EXTRACTS

It is extremely difficult to identify and characterize the many types of bioactive chemicals found in plant extracts since they have different polarity when they are separated. In order to acquire pure molecules, it is common practice to isolate these bioactive compounds utilizing several separation techniques, such as TLC, HPTLC, paper chromatography, column chromatography, gas chromatography, OPLC, and HPLC. Following that, the pure chemicals are utilized to determine the structure and biological activity (Sasidharan, et al. 2011). For the natural dye extract from *peristrope roxburghiana* this type of characterization was not done as the study isn’t concerned with the phytochemicals present in the plant extract.

## 2.4. DYEING

Dyeing is the process of applying a dye or pigment unto a chosen substrate and in most cases needs dyeing auxiliaries. Dyeing has been an old, ancient and medieval practice, which is regarded as an art and traditional practice(s). Mankind in the medieval time only knew and used naturally occurring colours. They harnessed these colours for designing and decorating their bodies, houses and a form of disguise to lure animals for hunt. Before the use of synthetic dye came to light and displaced its use in 1856 due to discovery of young William Henry Perkins and the development natural dyes have been a dominant colourant available and known to man. Dyeing using natural dye has been an art having some traditional inclinations as seen in its application in batik, aso eke and in tie-dye, in the south western part of Nigeria (Nnorom, et al. 2018). Natural dyes are used for textile dyeing as well as in food dyeing/colouration and to offers aesthetic beauty on things it's applied on. Dyeing in place of colouration is the term used scientifically and technically when impacting a colour unto a textile substrate or material alike and this colour impacting must be homogenous or/and uniform (Stintzing and  Carle, , 2004).

Dyeing processes use auxiliaries which are chemicals or formulating chemicals that enables process operation and enhances dye attributes in dyeing for more effectively results. Dyeing auxiliaries are chemical agents such as dye fixing, cationizing, dispersing and leveling agents etc. They are stabilizing the dye-bath by improving the exhaustion of dye and given satisfactory levels of fastness properties.

### 2.5. *PERISTOPHE ROXBURGHIANA* PLANT (PR)

*Peristrophe roxburghiana* is a perennial herbaceous plant which grows widely in cool and humid climate areas. Belonging to genius Acanthaceae family, it is distributed in Asia and South of Africa.  Based on the different colours of extracts and morphological characteristics, *Peristophe* appears in four colour varieties which are purple, purple-magenta, red, and yellow (Chi, 1999; Trinh, et al., 2003; Thao, et al., 2009). There are different species of *peristrophe* with *P.bivalis* predominate in Asia (Trinh, et al., 2003). The identification of these varieties is dependent on their phenotypes, such as the leaf shape and difference among colourants extracted from them. *Peristophe roxburghiana* has several biological and pharmaceutical attributes employed in the treatment of blood diseases, anti-hypertension, anti-hyperlipidemia, congestion, bronchrotis, fungistatic and antibacterial properties this  (Yang, et al 2002; Wiart, et al., 2004) reported.

A documented report show the effectiveness of *P. roxburghiana* ethanolic extracts on slowing down bacteria activities of Bacillus subtilis, Staphylococcus aureus, *Escherichia coli*, and *Pseudomonas aeruginosa* (Tanavade, et al 2012a; Tanavade, et al 2012b).

Thuy, et al.(2013a) reported a new use of *P. roxburghiana* when the alkaloid components from purple and red varieties growing in Vietnam is evaluated(Thuy, et al., 2013b). Phytochemical contents in *Peristrophe* specie varieties have been investigated and documentation made on it. The colours in these plants are attributed to pigments which are very diverse in structure and classification of which photosynthetic pigments and flavonoids are considered as the main groups responsible for colourful attributes of plant.

In their study, Nguyen Van Quan et al. (2016) stated that carotenoids, which are responsible for the colours red, orange, and yellow and also serve as accessory pigments in photosynthesis, are responsible for the colour green, with chlorophylls having the largest presence of Chl a and Chl b in plant cells. Anthocyanins, a subclass of flavonoids, derive their colour from the spectrum of red, purple, or blue depending on their pH. Flavonoids are a group of secondary metabolites with the broadest colour range, ranging from pale-yellow to blue. (Tanaka, et al 2008) and are sensitive to temperature and light (Bechoff, et al.,2010). And by spectral analysis, as reported by (Nguyen Van Quan, et al. 2016).

Thuy, et al.(2012b) in their work reported the isolation of the major component of the colour present in the aqueous extract of red *P. roxburghiana* leaves which they called *peristrophine*. In their study, the further reported that the colour extract components of *P. roxburghiana* varieties were identified as photosynthetic pigments and anthocyanins. The loss of carotenoids in P. roxburghiana was observed in a different study by (Bechoff, et al., 2010), who also explained that samples might be better understood by the impact of drying and storage. Water, ethanol, alcohol, or other aqueous solvents are frequently used to extract anthocyanins, which are pigments that can be extracted by water soluble means (Kong, et al., 2003; Patil, et al 2009). Moreover, the flavonoid concentrations can be used to explain the variations in colour since water-soluble flavonoids known as anthocyanins are crucial for giving P. *roxburghiana* its distinctive hue.

Furthermore, the categorization of P.*roxburghiana* can be determined by the considerable variations in total flavonoid contents. In addition to supporting the classification of *Peristrophe roxburghiana*, the results of phytochemical analysis and antioxidant activity evaluation can also be useful in a variety of other fields, such as the production of natural dyes and pharmaceutical preparations from *Peristrophe roxburghiana* by choosing the best extraction solvent.

## 2.6. EXTRACTION AND APPLICATION OF NATURAL DYE EXTRACT ON TEXTILE

In their research, Sentthil Kumar and Dhinakaran (2017) sought to accomplish the twin goals of efficient food industry waste recycling and the extraction and use of natural dyes from frit waste while also enhancing the performance characteristics of dye materials. They used the cold ethanol extraction procedure in three different ratios, reporting that the 1:1 ratio had the highest concentration of colour extract. Alum and sodium carbonate, two organic solvents, were utilized in pre-mordanting in three distinct ratios: 10%, 20%, and 30%. According to their report, the samples that were 30% mordanted had increased dye uptake.

They added that orange peel and lemon peel yields were seen to be higher with a 50ml ethanol extraction and that orange peel produced a larger yield of dye than lemon peel. They come to the conclusion that a 30% mordanting produced a better dye absorption. The cotton fabric dyed with extracts from orange peel and lemon peel demonstrates greater fastness to rubbing in dry and wet state, as well as fastness to washing, with a material to liquor ratio of 1:1 and 30% pre-mordanting.

Divya, et al. (2013) extracted, from the bark of C.*sappan*, seeds of B.*orellana* and combination of B.*orellana* and C.*sappan*, the dyes were extracted. The phytochemical compounds present in the extracts were analyzed as carotenoids in B.orellana and anthocyanin, phenolic acids, flavonoids in C. sappan using TLC.

In order to determine the effectiveness of the dye, the extracts were applied to cotton fabric using a variety of natural and artificial mordants, and their colour fastness against rubbing and washing was examined. According to their research, ethanol works better as a solvent to extract natural colours from plant materials. According to their research, the dyes were all dyes based on the greatest absorbance of the extracted dyes. The further reported that the colour fastness tests of the dyed fabrics revealed that the fabric dyed with extract from B. *orellana* dye using grape peel extracts as natural mordant showed very good to excellent washing fastness while the fabric dyed with C. *sappan* dye without the use of any mordants showed very good to excellent rubbing fastness.

In their study, Kundal, et al (2016) demonstrated the versatility of Ficus cunia as a plant that produced high-quality dyes. While mordanting wool and polyester cotton (PEC), they employed various mordants, including potassium aluminum sulfate, ferrous sulfate, stannous chloride, and tannic acid in addition to one natural mordant. They claimed that utilizing various natural and synthetic mordants, the extract of the natural dye produced various hues. They evaluated the dyed sample's washing, rubbing, and light fastness qualities and reported good to excellent fastness grades.

In their study, Israt Zerin and Foisal (2016) described using natural dye from Acacia Catechu to colour cotton woven garments. The optimum extraction technique for the colour was aqueous extraction, which they used on the scoured and bleached cotton. Three methods of mordanting were used: pre-mordanting, post-mordanting, and simultaneous mordanting and dyeing. They clarified that the materials had been treated with alum and copper sulphate as mordants. According to their investigation, materials pre-mordanted with copper sulfate and alum produced colours that were deeper in shade than those produced by other samples. According to them, colour fastness to wash and rubbing were both better for the post-mordanting process than colour fastness to rubbing alone. When mordanting was not performed, it was discovered that the reflectance % was higher, and the pre-mordanting process' K/S value was higher.

In the end, they came to the conclusion that the outcome of post-mordanting is a better method for catechu dyeing cotton woven cloth while employing alum and copper sulphate as mordants.

The effects of various techniques of application of chosen mordants on dyeing woven cotton with natural dyes from the leaves of *Vernonia amygdalina* were examined by Loum Janani and Lukyambuzi Hillary in (2013). Colour fastness to light, washing, wet and dry rubbing, and colour features on CIELab colour coordinates were the effects they examined.

They claim that aqueous extraction is the most effective method for getting rid of the colour. A few of the carefully selected mordants that were used for dyeing include alum, potassium dichromate, ferrous sulphate, iron water, and ash water. The mordanting methods included pre-mordanting, simultaneous mordanting, and post-mordanting.

According to their study, the following fastness ratings for washing (4R), dry rubbing (5), wet rubbing (5), and light were all extremely good (5). According to the, natural dye is a significant dye since it dries quickly without mordants. Nonetheless, they noted that using mordants increased colour fastness to light ratings from (5) to (6) for the majority of mordants, with post-mordanting techniques recording the greatest outcomes.

They also claimed that different mordants produced a variety of colours, supporting their claim that plant leaves contain polygenetic dye. The post-mordanting procedure showed the best colour saturation values C and the best colour strengths K/S values. The post-mordanting approach consistently produced the most vibrant fabrics with the best colour qualities and good colour fastness with all mordants.

### 2.7. KINETIC, THERMODYNAMIC STUDIES AND ISOTHERM RESPONSES OF DYE EXTRACT ON TEXTILES

In their work, Gumel et al. (2011) evaluated the colouring components they isolated from *henna* leaves and *roselle* (Zobo) pods and used to dye a 5g cotton cloth at 50°C and 70°C. Using spectroscopic and kinetic techniques, the dyeing activation energy and half-time of dyeing were calculated for each extract at these temperatures. They said that, at 50 and 90 0C, respectively, the $t_{1/2}$ values were found to be 43 and 28 for (Henna) and 30 and 23 for (Roselle). Combining them with the corresponding values (2.495 and 1.540 kcalmol-1), it was possible to determine that, at both temperatures, and the fabric had a higher affinity for the Roselle extract.

In their research, Habib-Allah Tayebi et al. (2015) reported on the isotherm, thermodynamics, and kinetic studies of acid dye adsorption on nylon 6 yarn with various *Titania* concentrations and various cross sectional shapes. Their findings demonstrated that adsorption is influenced by temperature, *Titania* concentration, pH, and cross-sectional shape. Also, the results of the adsorption isotherm demonstrated that the acid dye on nylon 6 is of the Langmuir type, highlighting that the process of acid dye adsorption on nylon 6 is exothermic. They also calculated the dye's partition ratio (K), standard affinity (°), dyeing heat (H°), and dyeing entropy (S°).

Researchers investigated the use of activated charcoal as an adsorbent to remove Azure C from aqueous solutions (Al-Rufaie, et al 2016). Their findings demonstrated that the dyes are removed in a quick manner. The equilibrium adsorption fit of the Freundlich, Langmuir, and Tempkin isotherms was used to determine the equilibrium and kinetic of the dyes adsorption at activated charcoal. Their kinetics study report demonstrated that the pseudo-second-order equation drove the adsorption process.

On wool fabric, kinetic and thermodynamic tests using the crude A. *nobilis* dye extract have been carried out (Anjali Arora, et al 2012). They observed that the diffusion coefficient of the A. *nobilis* dye was marginally lower when they compared the dyeing results of this dye with those of other natural dyes (*juglone, lawsone,* and *Rheum emodi*). The dyeing method conforms to the partition mechanism, confirming that their sample was a naphthoquinonoid based colourant. They stated that the dying process was exothermic and that it was absorbed by wool fabric as a dispersion dye. In addition, the rate of dye uptake, diffusion coefficient, standard affinity, heat of dyeing, and entropy were computed; the results showed that the heat of dyeing and entropy were negative.

Using polyester and nylon 6 substrates, Otutu (2012) studied the thermodynamic absorption properties of a number of disazo dyes produced from paminophenol and 4-aminobenzoic acid. According to what he found, dyes often have a stronger affinity for polyester fibres than they do for nylon 6 fibres.

The two dye-fibre systems' values for m°, H°, and S° indicate that the hydrogen bonding mechanism had a role in the binding forces between the dye and the fibre. The rate curves were a perfect fit to the experimental data, as seen by the extremely high correlation coefficient values he presented. Based on the findings of his investigation, it may be inferred that some intrinsic qualities, such as planarity and molecule volume, may be more helpful in evaluating activation energy of diffusion data.

In a study conducted by Jiping Wang et al (2018) reactive dye was used to dye cotton fabric. The dye adsorption kinetics in non-aqueous dyeing systems, and a conventional water base was examined. In their report, they excluded salts from the dyeing process because reactive dye had a great attraction for cotton fabric but was fully insoluble in non-aqueous media. The entire media was made recyclable thanks to a higher (>94%) uptake of dye compared to reactive dyeing in a conventional water base. The fixing of reactive dye was also higher (80%–90% for non–aqueous dyeing vs. 40%–50% for conventional dyeing), which led to cotton fabric acquiring a deeper shade after dyeing, as they further explained in their paper. They claimed that both conventional water dyeing systems and non-aqueous dyeing systems can effectively represent the adsorption and equilibrium of reactive dyes using the pseudo-second-order kinetic model. The adsorption rate of reactive dye was also considerably higher in non-aqueous dyeing systems than it was in a conventional water bath. They discovered that the reactive dye's adsorption equilibrium time in the siloxane non-aqueous dyeing system was 5–10 min at 25°C, whereas it required more time at 60°C in the water dyeing system. The adsorption rate of the dye was impacted by the surface tension of non-aqueous fluids. Reactive dye absorbed reactive dye more quickly and with higher ultimate absorption when the surface tension of non-aqueous medium was lower. In addition, they noted that successful results implied a reduction in the environmental pressure from reactive dyeing for cotton textiles in a source-control way due to the lack of salts, as well as higher dye uptake, lower dying temperature, and significant water savings.

In a study by Haque et al. (2015), three reactive dyes—Remazol Red, Remazol Yellow, and Remazol Blue were subjected to exhaustion, fixation, and adsorption isotherm analyses to determine compatibility. The extinction coefficients were determined by creating an absorbance versus concentration curve after testing the known solutions of each dye in a UV-visible spectrophotometer. For each of the dyes, 4 different dye concentrations (0.5%, 1%, 2%, and 3%) were used in the dyeing procedure. The UV-visible spectrophotometer was used to evaluate the post-dye and post-wash liquors, and the Beer-Lambert law was used to determine the dye concentrations in those solutions. The three colours' fixing and exhaustion percentages were evaluated, and adsorption isotherm models for each dye were created. The Freundlich isotherm model prevailed over the Langmuir model in this comparison.

Among the dyes, Blue RR was said to have a stronger exhaustion performance, despite the fact that it did not adhere to the fibre particularly well during fixation. Red RR performed admirably during the fixation and exhaustion rounds. They discovered and noted that there was little compatibility between these three colours at higher concentrations. But experimental data shows that introducing more electrolytes and reducing the temperature as well as the alkali amount can improve compatibility of these dyes.

Puttaswamy et al. (2010) found morin, a flavonoid, as the primary colouring agent they extracted from the G. *sepium* pods for their study. After that, they put it to silk, and the Langmuir, Freundlich, and Tempkin-Pyzhev models were used to determine the adsorption isotherm of morin on silk. They claimed that the morin's adsorption on silk was well compatible with the Langmuir and Freundlich isotherm. However, it was discovered that the Langmuir model provided a superior fit and suggested that a homogenous monolayer would form on silk.

In a study (Norasiha Hamid and Mimi Sakinah Abdul Munaim, 2017), the kinetics of betacyanin extract adsorption on spun silk and acrylic yarn were examined. According to the experiment data they provided, the adsorption process' equilibrium was found to follow a pseudo-second-order kinetic model, with activations of 55.7 kJ/mol for spun silk and 44.5 kJ/mol for acrylic yarn, respectively. They underlined and clarified that the chemisorption process is probably what regulates the adsorption of betacyanin pigment onto spun silk and acrylic yarn. The thermodynamic parameters for the adsorption process were established in the final section of their work. They clarified that low values of G° obtained showed that both yarn's adsorption process was spontaneous. The fact that H° was negative meant that energy was lost during the adsorption process. The negative values of S° demonstrated that as the temperature rose, there was less movement, which reduced the randomness of the dye's ability to adsorb onto the yarn.

Karmaker, S., Sintaha,F. and Saha, T.K. (2019) in their studied investigated the adsorption bahaviour of reactive red 239 (RR239) dye onto chitosan 8B in aqueous solution at various pHs, initial dye concentrations, ionic strengths and temperatures, respectively. The used diffuse reflectance electronic absorption spectra to evaluate the adsorption of dye onto chitosan 8B. the reported that the adsorption of RR239 onto chitosan 8B was largely influenced by pHs,concentrations of dye, temperatures and ionic strengths. pseudo first-,second-order, Elovich and intraparticle diffusion kinetic models were aplied to analyse its kinetics and mechanism of dye adsorption process. They found out that the adsorption kinetics of the dye followed a pseudo second-order model very well, explaining that the surface sorption and intraparticle diffusion mechanisms occurred in the sorption process. With equilibrium isotherm data fitting well with the Langmuir model rather than the Freundlich, Temkin and Dubinin-Radushkevich models. The maximum dye adsorption onto chitosan 8B they reported to be in at an estimated of 163.93 μmol/g at 45˚C, activation energy (Ea) as 23.30 kJ/mol and thermodynamic parameters investigated on confirmed that the adsorption of RR239 dye onto chitosan 8B was an endothermic physisorption process.

Nwanonenyi et al (2017) investigated the mode of adsorption of millet starch (MS) on the mild steel in other to understand the performance of millet starch (MS) in controlling the corrosion of mild steel in 0.5 M HCl solution at 30 ± 1°C. From their stud they reported that it obeyed Langmuir adsorption isotherm. The thermodynamic parameters (ΔH, ΔS, ΔG and Ea) for the inhibition process they calculated, and results obtained the reported supported the proposed physical adsorption mechanism. The mathematical simulation technique they used to evaluate the correlation between the inhibition efficiency of MS and its electronic molecular structure, showed that there is a satisfactory agreement between mathematical simulation technique and experimental data. The concluded that MS inhibited corrosion of mild steel in the acid solution and increase in inhibition efficiency was dependent on concentration.

## CHAPTER THREE

## MATERIALS AND METHODS

### 3.1 MATERIALS

i. Distilled water and Sodium chloride were obtained from Pac-Besh chemical stores, Ikenegbu Owerri Municipal Imo state.

ii. Cotton fabric of equal ends/picks (62warp-ends/62weft-picks) per square inch. The cotton sample was purchased from Nwaorie lane Douglas Market, Owerri, Imo state.

Plate 3.1: Cotton Fabric Sample

iii. *Peristrophe roxburghiana* plant leaves were obtained from and identified at the plant lab unit of Department of Pharmacy, University of Uyo, AkwaIbom State, Nigeria.

Plate 3.2: *Peristophe roxburghiana* plant (Tanaka and Van Ke, 2007)

**Equipments**

i. Soxhlex extractor Pyrex 500ML,

ii. Heater Mantle Model 500ML PEC Medicals,

iii. Electric blender Saisho Model S-748,

iv. Thermostatic water bath model HH-420 size 64 x 35 x 31 cm,

v. UV-VIS machine Cary300,

vi. FTIR machine Cary 630,

vii. Weighing balance,

viii. 50ml, 250ml, and 500ml beakers, 1000ml conical flask, pipette, stringy, clamping scissors, test lab tubes, pen, paper tape, corked lab tubes and polyethylene film envelop bag.

## 3.2 METHOD

### 3.2.1 PREPARATION OF *PERISTOPHE ROXBURGHIANA* (PR) SAMPLES:

The *Peristophe roxburghiana* plant leaves were well washed under running water and dried at room temperature. They were ground using electric blender into fine particle sizes of 100um. The finely ground plant sample was weighed out and kept in well labeled polyethylene film bag for further investigations.

### 3.2.2. DYE EXTRACTION OF *PERISTROPHE ROXBURGHIANA* (PR)

Extraction of dye from 2g of PR plant leave powder sample was done in a 500ml flask of Soxhlex extractor with distilled water as the solvent.. The extraction was done at 70ºC for one hour. The hot solution was filtered, centrifuged and a clear solution was obtained which was used for dye exhaustion on cotton fabric. After the extraction the plant sample in the soxhlex extractor apparatus was carefully removed and kept to dry under sun. The dry sample after extraction was weighed and data recorded. Also the volume of the solution after extraction was measured and recorded. Pictorial representation of some stages in the extraction process are shown in Plate 3.3 and 3.4 while in Plate 3.5 and 3.6 .

Plate 3.3: Rinsed leaves Plate 3.4: Extract from *Peristophe roxburghiana* plant

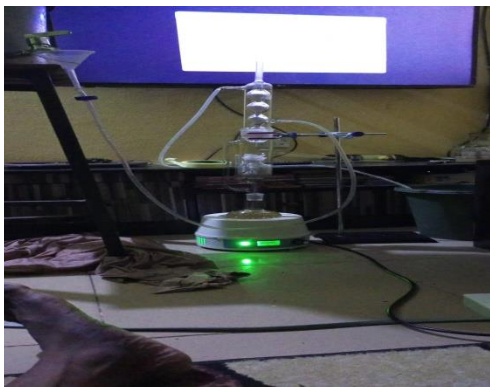


Plate 3.5 Soxhlex Extraction of dye from *PR* Plate 3.6: Extracted Dye From PR plant

Dyebath Recipe: Sodium chloride (NaCl), warm wetted cotton fibre, extracted PR dye

### 3.2.3. CHARACTERIZATION ANALYSIS OF *PERISTROPHE ROXBURGHIANA* DYE EXTRACT

For this study UV-Vis spectroscopy and Fourier transform Infra-red spectroscopy were used to examine the *Peristrophe roxburghiana* dye extract. 10ml of PR dye extract solution was introduced into a cuvette with a width of 1 cm and blanked with same amount with distilled water adsorption spectrum reading was taken and recorded.

### 3.2.4 ADSORPTION OF *PERISTOPHE ROXBURGHIANA* DYE ON COTTON SAMPLE

#### 3.2.4.1 TEMPERATURE STUDY ON *PERISTOPHE ROXBURGHIANA* DYE ON COTTON SAMPLE

The water bath was standardized at the three temperatures of 50°C, 60°C and 70°C, and 50ml of the dye extract solution was introduced into 250ml beakers with 0.3% on the weight of fabric (owf) of sodium chloride as the dyeing auxiliary followed by fully immersion of the cotton sample for the dyeing time range of 5, 10, 15, 20, 25, 30, 35, 40, 45 min respectively. Before any dyeing process commenced, the initial adsorption reading of PR dye extract solution was taken and recorded using the UV-VIS machine and at the expiration of each time of dyeing at the three temperatures, the residue PR dye bath adsorption value was determined. Values or data are tabulated for use in the study.

Plate 3.7: Pictoral representation of dyed Cotton fabric sample with *Peristrophe roxburghiana* dye extract solution.

#### 3.2.4.2 CONCENTRATION STUDY OF *PERISTOPHE ROXBURGHIANA* DYE ON COTTON SAMPLE

Extraction from PR plant leave powder sample was done by varying the weight of the powder sample 2, 2.5, 3, 3.5, 4, 4.5 and 5g with a constant volume of solvent of 500ml. The extract solution for each extraction was used for dyeing.  Dyeing was done in a water bath at a fixed equilibrium time of 40mins at three temperatures 50°C, 60°C and 70°C. Initial absorbance before dyeing was recorded and at the end of the dyeing absorbance reading was also taken and recorded this data was used to determine their individual Qe in the study.

### 3.2.5 ADSORPTION KINETICS OF *PERISTOPHE ROXBURGHIANA* DYE ON COTTON SAMPLE USING ISOTHERMS

Rate of dye exhaustion is the amount or weight of PR dye, which was absorbed or diffused in the fibre surface from the dye bath per unit time of dyeing at a maximum dyeing temperature. While kinetic study is aimed at creating an understanding of the reaction rates of PR dye on cotton and in this case how temperature and concentration affects it. UV/Vis spectrophotometer was employed to investigate the measure of exhaustion and fixation of the PR dye extract on cotton. By measuring the concentration of dye bath before and after the dyeing process, the initial concentration of the dyebath was determined and value recorded was designated as $C_i$. After the expiration of each individual time of dyeing, the PR natural dyed cotton sample is removed and the residue dyebath concentration was checked for its final concentration by determine its absorbance using a UV-spectrometer and the value obtained designated as $C_f$. the removed PR natural dyed cotton sample was then mildly rinsed with distilled water and allowed to dry at room temperature. This process is repeated for the three temperatures and at 580nm. The percentage of exhaustion determined using the equation below; the equation 3.1 is used to determine the equilibrium point at which the cotton took up dye and beyond which adsorption didn't occur.

$$Q_e = \frac{(C_o - C_e)V}{W} \qquad 3.1$$

Where $C_o$ and $C_e$, are concentrations of the PR dye bath before (initial) and after (equilibrium) dyeing processes (g/l), Qe is amount of adsorbed dye by the Cotton fabric sample (mg/g), V is the volume of dye bath (ml) and W is the weight of Cotton fabric sample (g). The equation 3.1 above was used in the analysis and computation of equilibrium and kinetic study. The unabsorbed dye molecules in the dye solution is determined using Beer-Lambert equation (see Appendix 1).

# CHAPTER FOUR

# RESULTS AND DISCUSSIONS

## 4.1 CHARACTERIZATION OF PERISTOPHE ROXBURGHIANA (PR) EXTRACT SAMPLE

The extract dye sample from PR plant was characterized using Ultra violet visible infarad spectrometry (UV-Vis) and Fourier transform infarad spectrometry (FTIR)

### 4.1.1 UV-VIS SPECTROSCOPY CHARACTERIZATION OF *PERISTOPHE ROXBURGHIANA* (PR) EXTRACT SAMPLE

UV-Vis spectroscopy of the *Peristrophe roxburghiana* extracted dye was scanned at a wavelength range of 300-800 nm using a Cary 300 UV-Vis machine and the data obtained were plotted on a graph below.

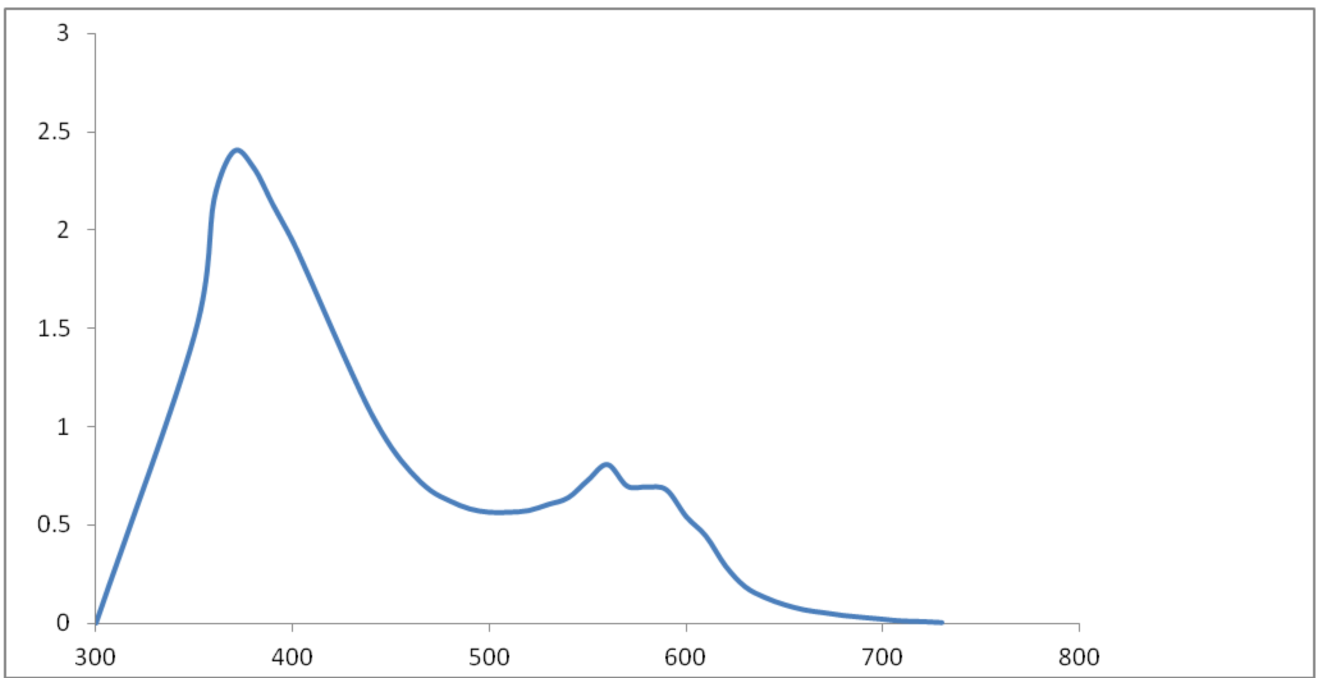



Figure 4.1: UV-VIS Spectrum of PR dye extract showing Maximum wavelength of 580nm.

From Figure 4.1 the aqueous dye extract of *Peristophe roxburghiana* plant showed maximum absorption at peaks of 440nm and 580 nm which fall within the visible spectral range for an extract to be categorized as a dye. This extract fell in the spectral range of a class of dye referred to as flavonoids. The possible chemical structure responsible for the bright red in the plant extract sample has been reported to be anthocyanin as such 580nm (Aluko, et al., 2019).

### 4.1.2 FOURIER TRANSFORM INFARAD SPECTROSCOPY CHARACTERIZATION OF FUNCTIONAL GROUPS IN PR EXTRACT SAMPLE

FTIR evaluation of the *Peristrophe roxburghiana* extracted dye was subjected to Cary 630 FTIR machine within a wave number range of 4000-650 cm-1and its plot obtained in a digital graph shown in Fig 2

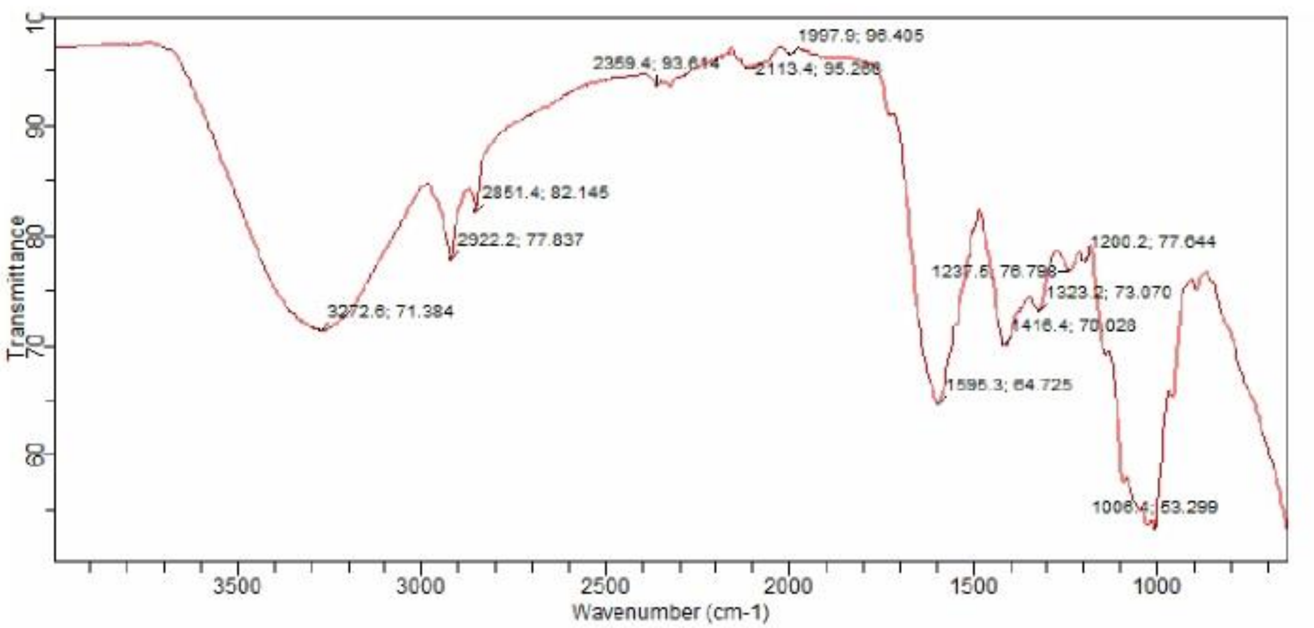



Figure 4.2: FTIR spectral of PR dye extract.

The FTIR evaluation was done at Ahmad Bello University Zaria, Kano state and a digital plot was obtained having peaks representing the functional active sites in the plot as shown in Figure 4.2.

From Figure 4.2 the FTIR analysis of the PR dye extract helps to understand the functional groups on the surface of the natural dye to help deduce which lass of dye it belongs based on dye chemical structure. From the FTIR spectroscopy analyses of the PR dye extract sample in Figure 4.2, IR- peak 1200.2 $cm^{-1}$ there are possible presence of C-O, C-C sing bond stretches showing presence of benzene ring present.  1.277.5 $cm^{-1}$, 1.323.3 $cm^{-1}$ show C-H carboxylic acid group, at peak of 1595.3 $cm^{-1}$ shows the presence of O=C stretching in the PR dye extract still carboxylic acid. The peak at 1997.3 $cm^{-1}$ describes the presence of C=C asymmetric stretch of the PR chain at peak 2113.4 $cm^{-1}$ and 2309 $cm^{-1}$ there is more asymmetric stretch as there is reduced intensity of the symmetric nature of PR dyes due to C-H and C-C alkyne bonds (Soriano A., Pérez-Juan P.M., Vicario A., González J.M., Pérez-Coello M.S., 2007; Dharmasoth Rama Devi and Ganga Rao Battu 2019). Then at peaks 2922.2 $cm^{-1}$ and 3272.6 $cm^{-1}$ where conjugated C=O and O-H free bonded broadly of H exist there is abundant presence of alcohol and phenol groups present. These peaks seen explain a likelihood of the PR dye extract sample having attributes of a favonoids, becaused of the presence of hydroxyl groups, ketones and phenols in it agreeing that the dye is an anthocyanin which is similar to works done by (Mehdi Mehran, Saeed Masoum, Mohammadreza Memarzadeh, 2020).

## 4.2 ADSORPTION MECHANISM OF *PERISTOPHE ROXBURGHIANA* DYE ON COTTON SAMPLE

In determining the equilibrium study, the individual time at which equilibrium was achieved was calculated and recorded in Table 1. (see appendix 1)

The equilibrium concentrations and adsorption $C_e$ and Qe for the three temperature ranges obtained are represented in a tabular form in table 1.

Table 1: Result of equilibrium concentration of PR dye on Cotton sample

| **580nm** | | |
|---|---|---|
| **TEMPERATURE** | **$C_e$ (g/l)** | **Qe (mg/g)** |
| 50°C | 0.674 | 0.076 |
| 60°C | 0.257 | 0.285 |
| 70°C | 0.228 | 0.30 |

### 4.2.1. EFFECT OF TEMPERATURE ON EQUILIBRIUM ADSORPTION OF PR DYES ON COTTON SAMPLE AT 50°C, 60°C AND 70°C

Table 2: Data of Equilibrium Study PR dyes on cotton sample at 50°C, 60°C and 70°C

| **Equilibrium Study** | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **50°C** | | | | **60°C** | | | **70°C** | | |
| **Time** | **$Abs_{50}$** | **$C_t$(g/l)** | **$Q_t$ (mg/g)** | **$Abs_{60}$** | **$C_t$(g/l)** | **$Q_t$ (mg/g)** | **$Abs_{70}$** | **$C_t$(g/l)** | **$Q_t$ (mg/g)** |
| 5 | 1.376 | 0.736 | 0.045 | 0.549 | 0.293 | 0.267 | 0.445 | 0.238 | 0.294 |
| 10 | 1.343 | 0.719 | 0.0535 | 0.544 | 0.291 | 0.268 | 0.438 | 0.234 | 0.296 |
| 15 | 1.341 | 0.717 | 0.0545 | 0.530 | 0.284 | 0.271 | 0.434 | 0.232 | 0.297 |
| 20 | 1.324 | 0.708 | 0.059 | 0.528 | 0.283 | 0.272 | 0.427 | 0.228 | 0.30 |
| 25 | 1.305 | 0.698 | 0.064 | 0.525 | 0.281 | 0.273 | 0.427 | 0.228 | 0.30 |
| 30 | 1.298 | 0.694 | 0.066 | 0.481 | 0.257 | 0.283 | 0.427 | 0.228 | 0.30 |
| 35 | 1.261 | 0.675 | 0.0755 | 0.481 | 0.257 | 0.283 | 0.427 | 0.228 | 0.30 |
| 40 | 1.259 | 0.674 | 0.076 | 0.481 | 0.257 | 0.283 | 0.427 | 0.228 | 0.30 |
| 45 | 1.259 | 0.674 | 0.076 | 0.481 | 0.257 | 0.283 | 0.427 | 0.228 | 0.30 |
| 50 | 1.259 | 0.674 | 0.076 | 0.481 | 0.257 | 0.283 | 0.427 | 0.228 | 0.30 |

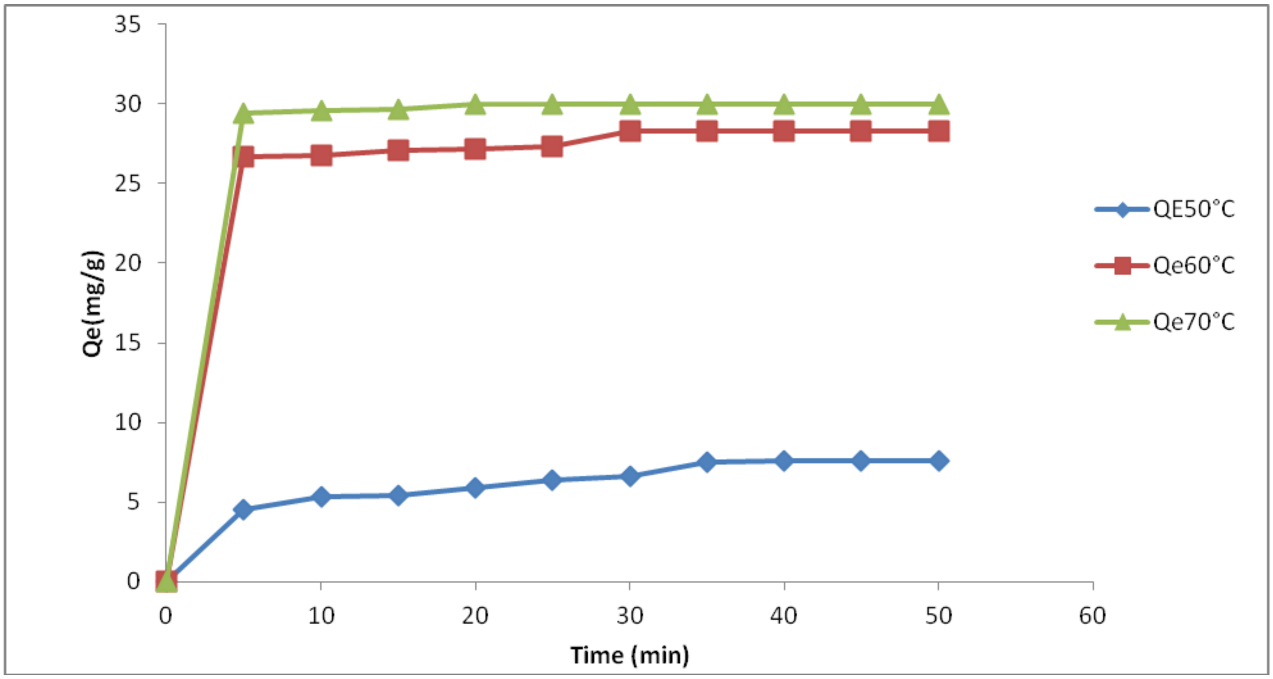



Figure 4.3: Effect of Temperature on Equilibrium Adsorption Responses of PR Dye on Cotton Fabric Sample

From the graph above Figure 4.3, it was observed that the  temperature influenced the mobility of the dye into the cotton as at 50ºC and 60ºC the equilibrium of adsorption was achived at 40mins and 30mins respectively, while 70ºC it was attained more sharply at 20mins, indicating that the dye extract from PR diffused faster when temperature was elevated.. Temprature increased the rate of reaction between cotton and the dye. Mobility of dye molecules was enhance by temperature as dye molecules tend to move faster into it the surface of the cotton. Pillai (2020) reported that increase in temperature enhances molecular interaction between substrates interacting, until at a point were maxumium adsorption of hue or colour shade of the dye is reached. This was in agreement with a similar reported ,made by (Chai, 2021).  Nnorom O.O et al (2021) in their study of inhibitive effect of NaCl and Citric Acid on the Colour Yield of Acid Dye on Nylon Fabric gave a positive results that temperature affects movement of dye molecule into the nylon until at a point were it saturates. Adsorption is a widely used technique employed to separate dissolved impurities (organic or metals) in a solution like water (Simonin,2016). This technique in recent times have been considered and used notably as an excellent techniques to treat wastewater from synthetic dyes, heavy metals, and other substances such as phenols, pesticides, pharmaceuticals.

**4.2.2. EFFECT OF CONCENTRATION ON THE EQUILIBRIUM ADSORPTION OF PR DYE ON COTTON SAMPLE**

The effect of concentration of PR dye on cotton fabric sample was shown in Table 3 and graphically in Figure 4.4

Table 3: Result of Effect of Concentration of PR Dye on cotton sample

| PR dye concentration (g/l) | Qe(mg/g) | | |
|---|---|---|---|
| | 50°C | 60°C | 70°C |
| 2 | 0.076 | 0.285 | 0.299 |
| 2.5 | 0.370 | 0.367 | 0.381 |
| 3 | 0.420 | 0.430 | 0.411 |
| 3.5 | 0.486 | 0.483 | 0.461 |
| 4 | 0.551 | 0.541 | 0.530 |
| 4.5 | 0.550 | 0.551 | 0.551 |
| 5 | 0.550 | 0.551 | 0.551 |

The result tabulated in table 3 were uanalysis graphically in figure 4.4

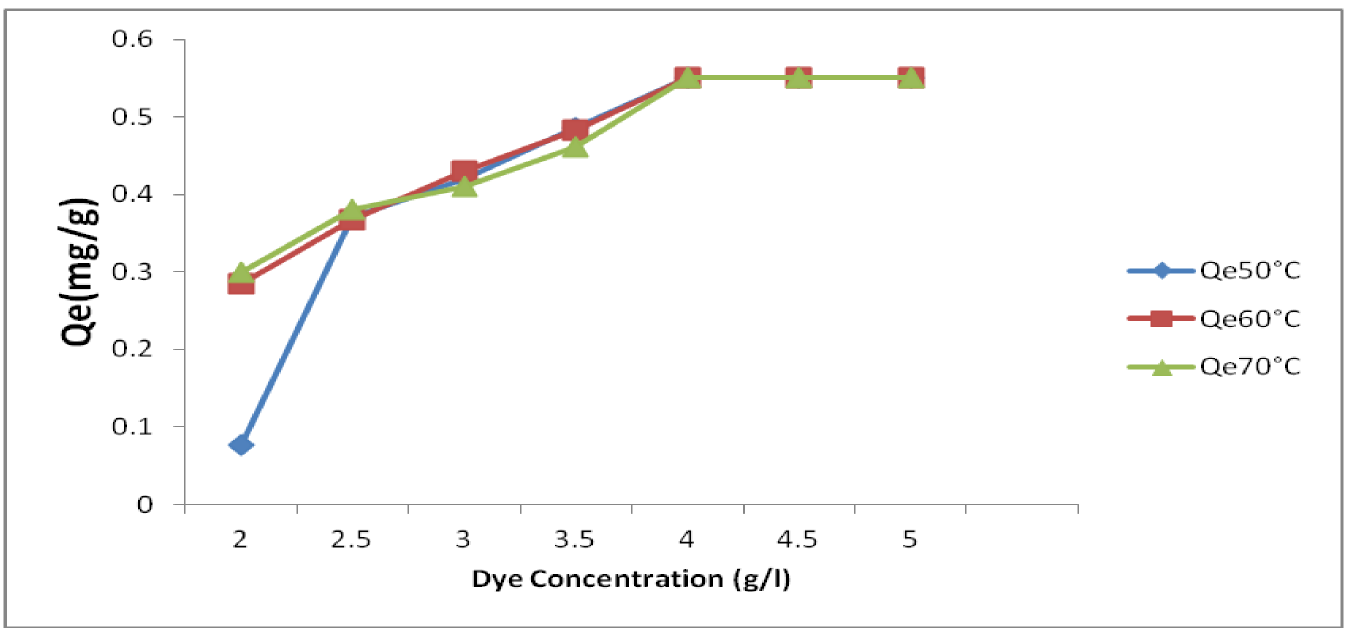



Figure 4.4: Graph of Effect of Concentration on Equilibrium Adsorption of PR Dye on cotton fabric sample

From Figure 4.4 it shows that adsorption at concentration of 2g/l was slow across the temperatures of investigation. But gradually increased as the concentration was increased from 2g/l to 4g/l after which it linearized. This can be due to availability of more dye molecules to enter the cotton sample as concentration was increased regardless of the temperature of investigation. But from the plot there was a lag in the curve between 3g/l to 4g/l at 70°C which may be  due to possible clog at the pore sites of the fabric because many excited dye molecules moving too fast and at the same time rushing into the surface of the cotton got stucked, blocking the pores available. This observation was in agreement with (Anjali et al 2012) who reported that concentration of the dye extract played a part to colour hue. Al-Rufaie et al. (2016) also in their study of adsorption kinetics and thermodynamics of Azure C dye from aqueous solution onto activated charcoal reported that enhanced concentration affects positively on adsorption kinetics.  This findings was also in accordance with (Anjali et al 2012) in their work on the kinetics and thermodynamics of dye extracted from Arnebia nobilis Rech.f. on wool were concentration increased adsorption. Tayebi, et al (2015) reported that adsorption of this kind is commonly modeled using pseudo-first and pseudo-second order rate laws.

## 4.3. ADSORPTION KINETICS OF *PERISTOPHE ROXBURGHIANA* DYE ON COTTON FABRIC SAMPLE

### 4.3.1 PSEUDO FIRST ORDER OF ADSORPTION KINETICS OF PR DYE ON COTTON SAMPLE

From Figure 4.5 70°C showed the best kinetic response and the result for pseudo first order kinetics was determined and tabulated in Table 4 (see appendix 1).

The fitting of the pseudo first-order-kinetic model was done using Langergren's equation in (Nnorom et al. 2020)

$$In(Qe - Qt) = InQe^{\cdot} - KT \qquad 4.1$$

$Q_t$ (mg/g) and $Q_e$ (mg/g) are quantity of dye adsorbed at different time t

(min) of dyeing and at equilibrium, k is the rate constant of the pseudo first order kinetic model which was obtained from a plot of In($Q_e$ – $Q_t$) against time.

The results in table 4 were used in a graphical analysis of the pseudo first order kinetic of adsorption of PR dye on cotton fabric sample with a plot of In (Qe -qt) against time of dyeing.

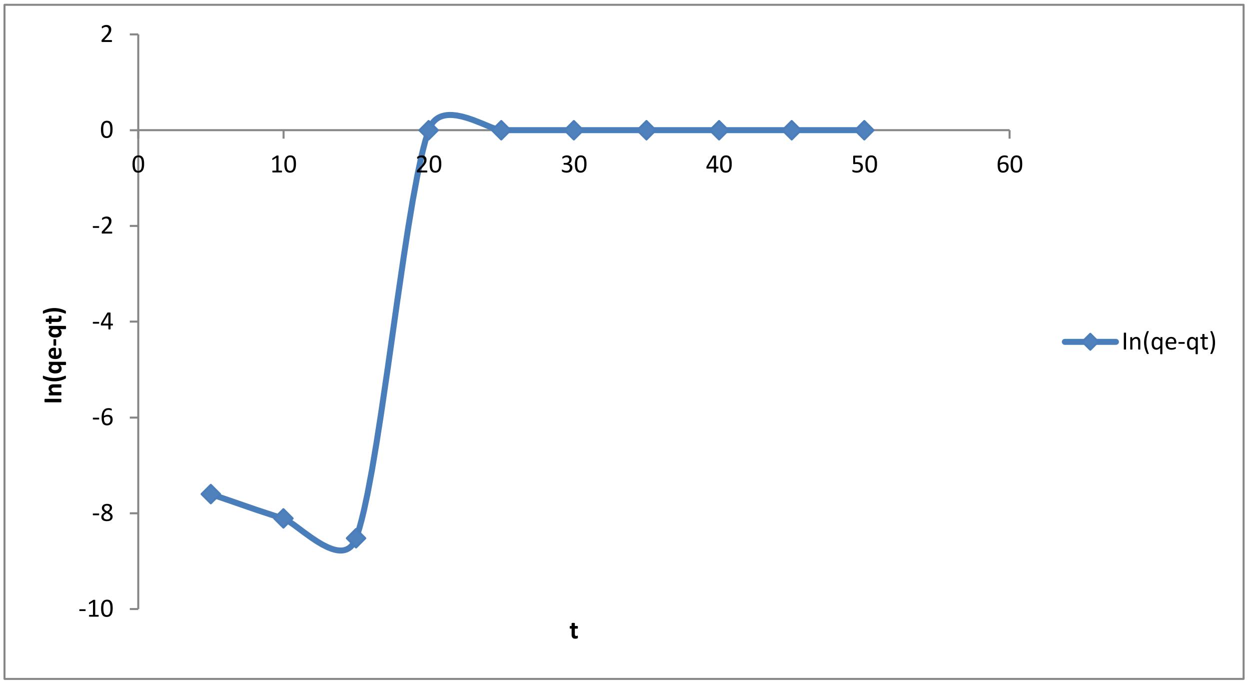



Figure 4.5: Graph of pseudo first order adsorption of *Peristrophe roxburghiana* on Cotton sample

Pseudo first-order reaction can be referred as a second-order or bimolecular reaction that acts like a first-order reaction. To a layman is a reaction that appears fake in likeness or mimicking first order reaction where rate of reaction is always directly proportional to the concentration. But this reaction happens when one reacting material is more when compared to the other substance it is reacting with. A graph of ln( Qe – qt) versus t(mins) was plotted as shown in Figure 4.5 which was used to calculate $R^2$ the correlation coefficient. The $R^2$ value is 0.6207 with $Q_e$ and k representing the intercept and slope as 8.02 mg/g and 0.2034 respectively. From the plot it can be seen that dye extract of PR on cotton had adsorption capacity, giving insights to the fact that there exist in this PR dye extract an adsorption mechanism Nnorom et al. (2020). In this study pseudo 1st order adsorption kinetics is of need in industry for designing and optimizing adsorption processes, such as in the removal of pollutants from wastewater or the purification of gases. Understanding the kinetics of adsorption of dye extract of PR is important for the efficient development and handling of PR dye applying a cost-effective adsorption processes.

### 4.3.2 PSEUDO-SECOND –ORDER ADSORPTION KINETICS OF PR DYES ON COTTON SAMPLE

Table 5: Results of Pseudo-Second –Order Adsorption Kinetics of PR dyes on Cotton sample

| **Time** | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 |
|---|---|---|---|---|---|---|---|---|---|---|
| **Qt** | 0.294 | 0.296 | 0.297 | 0.300 | 0.300 | 0.300 | 0.300 | 0.300 | 0.300 | 0.300 |
| **T/Qt** | 170.1 | 330.7 | 500.50 | 660.67 | 830.33 | 1000 | 1160.67 | 1330.33 | 1500 | 1660.67 |

The values in Table 5 was used to plot a graph of t/qt against time to determine the adsorption pattern of PR dye on cotton using pseudo second order adsorption kinetics as shown in Figure 4.6

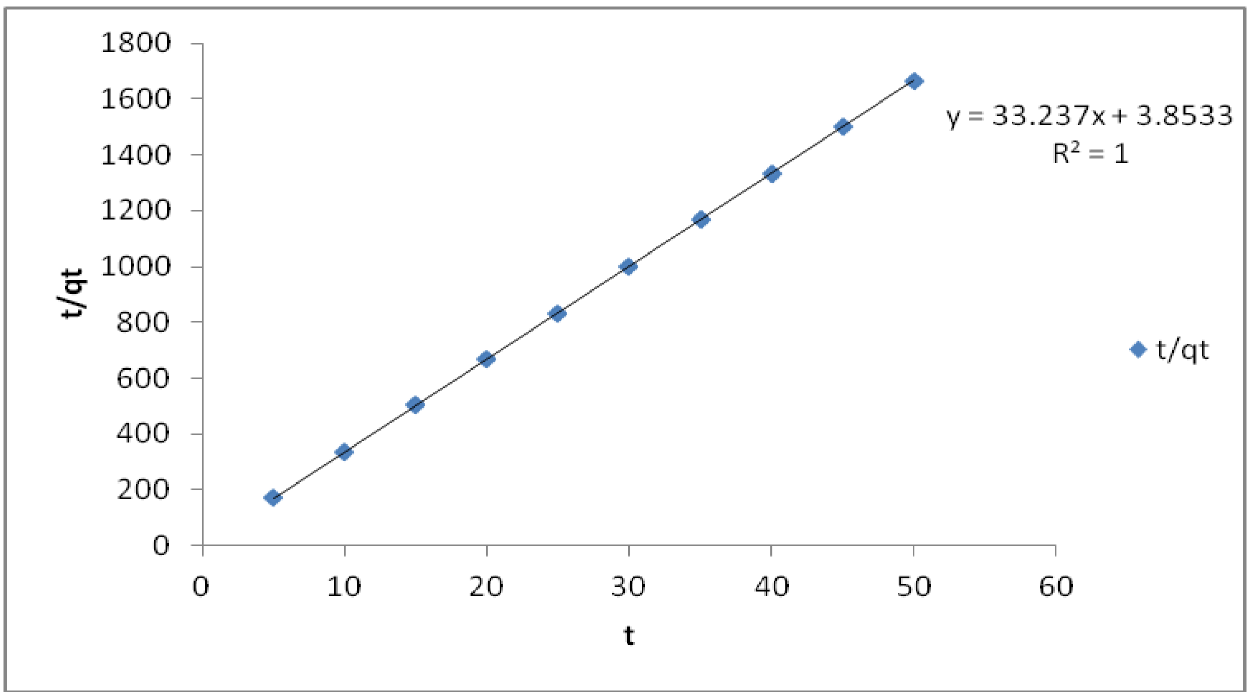



Figure 4.6: Graph of pseudo-second –order of dye extract *Peristrophe roxburghiana* (PR) on cotton fabric sample

In the graph plot of t/qt vs t showing the pseudo second order adsorption kinetic model in Figure 4.6, the slope and intercept were used to determine $k_2$ (3.853) and Qe (33.24mg/g). The pseudo-second-order kinetic model better describes the PR dye's adsorption mechanism, and this is evident from the $R^2$ value of 1. This is consistent with reports on acid dyeing nylon 6 fabrics by Tayebi, et al. (2015) and Nnorom et al. (2020) stating this model best describes this kind of adsorption behaviour. The pseudo-second-order kinetic model predicts behavior over the whole adsorption range and is based on the presumption that chemical sorption or chemisorptions is the rate-limiting step. Explaining the adsorption kinetics of naturally extracted dyes using this model are usually suitable for both conventional and non-conventional extractions. (Rakotondramasy-Rabesiaka et al. 2009). It provides a suitable illustration of solid-liquid extraction process; as such it fits to describe PR dye solution on cotton fabric sample used. If the pseudo-first order reaction plot shows an $R^2$ value of 1 or near to 1, the reaction is more likely to result in physiosorption. In a similar vein, a reaction that closely resembles a pseudo-second order model suggests a propensity for chemisorption. Chemisorption is initially followed by a number of reactions, and that too in a relatively short amount of time. Importance of this pseudo second order adsorption kinetics is it offers a more robust and accurate explanation of adsorption kinetics and helps understand the mechanism of adsorption, whilst evaluating adsorption capacity, which in turn optimizes the design of adsorbent materials (PR dye). Rakotondramasy-Rabesiaka et al. (2009) and Qu et al. (2010) in their studies have shown that adsorption behavior that fits the Pseudo-Second-Order model well mostly can be described by diffusion-based mechanisms.

Pseudo-first and second order models can be considered as simplifications of Langmuir kinetics for batch adsorption (Rakotondramasy-Rabesiaka et al. 2009; Qu et al. 2010)

### 4.3.3 THERMODYNAMIC PARAMETERS OF PR DYES ON COTTON FABRIC SAMPLE

Thermodynamics parameters used in this study includes standard affinity, heat of dyeing, and entropy of dyeing, used to evaluate the thermodynamic behavior of dye on cotton (see appendix 5,6 and 7).

#### 4.3.3.1. Standard Affinity of PR Dye on Cotton Sample

The result from calculation is represented in appendix 5.The standard affinity values were obtained at 50°C, 60°C and 70°C. It was found that the value of standard affinity decreased from12.74 kJ/mol to 10.53 kJ/mol as the dyeing temperature increases from 50°C to 60°C, on further increase in temperature by 10°C there was a further decrease in the standard affinity to 10.02 kJ/mol. This trend is evidence that PR responses to adsorption isotherms as there was mobility of dye into the cotton fabric sample but is affected by temperature. This proves that PR dye mobility is temperature dependent and comparable with respect of findings of other studies conducted by (Das D. et al., 2008; Gulrajani M.L et al., 2002).

### 4.3.3.2. Heat of Dyeing of PR Dye on Cotton Sample

The calculation of heat of dyeing is represented in appendix 6. The enthalpy of heat (ΔH°) of PR dye on cotton gave a positive value of 3438.4KJ/Mol this could mean that energy was depleted as new dye-cotton bonds were formed and energy was absorbed from the environment which assisted the reaction. Enthalpy behavior of this reaction gave the information on the type of adsorption that occurs; which is not just physical which but also chemical. The greater or higher the value of energy of bonds formed between the fibre and the dye, the more stability the dyeing efficiency will be. And when this value is greater than the energy of broken bonds; that is the dye bonds breaking out to form new bonds with cotton fabric. When the heat of dyeing is negative and energy is absorbed as such endothermic and if the value is lower the heat of dyeing becomes positive and exothermic. Thus, there are lesser new formed bonds between the PR dye and the cotton fabric once equilibrium is attained as such causing an exothermic reaction this is in consonance with reports from studied conducted by (Gulrajani M.L et al., 2002).

### 4.3.3.3. Entropy of Dyeing of PR Dye on Cotton Sample

The thermodynamic behavior of PR dye to its entropic (ΔS°) response gave a calculated value of entropy is -9.991 J/ mol/K. The entropy of dyeing using PR dye on cotton fabric is seen to be negative. The negative ΔS° value suggests a possible decrease in the randomness at the solid/solution interface during the PR dye adsorption onto cotton fabric sample. Vinod et al. (2010) reported that this attribute can also be a possible uniformity in the orderly distribution of PR dye onto the cotton fabric sample that was dyed as temperature increased. This is to say that when the dye molecules of PR dye were absorbed by the fibre (cotton), they arrange themselves in a less orderly manner which is loosely held on the axis of the fibre (cotton). This means that there would be less fastness with more tendencies to bleed out in use if mordant aren’t applied.

This behaviours helps to understanding the molecular motion of the PR dye to understand the molecular disorder, or randomness in the dyebath across the temperatures of 50°C, 60°C, 70°C by measuring possible energy lost that took no part in the dyeing operation. The equation used is presented in appendix 7 .

## 4.4 ADSORPTION ISOTHERM OF PR DYE ON COTTON FABRIC SAMPLE

Here the tabulated results in Tables 6-13 gives the values of results obtained from the Langumuir and Freundlich isotherm evaluations and graphically represented in Figures 4.7 – 4.15

### 4.4.1 LANGMUIR ISOTHERM TYPE 1 OF PR DYES ON COTTON FABRIC SAMPLE

Table 6: Results of Langmuir Isotherm Type 1 of PR dye on Cotton fabric sample

| **C (g/l)** | 2 | 2.5 | 3 | 3.5 | 4 | 4.5 | 5 |
|---|---|---|---|---|---|---|---|
| **$C_e/Q_{e\ 50°C}$** | 1.6 | 5.6 | 5.9 | 6.6 | 7.3 | 7.3 | 7.3 |
| **$C_e/Q_{e\ 60°C}$** | 4.2 | 5.5 | 6.0 | 6.6 | 7.3 | 7.3 | 7.3 |
| **$C_e/Q_{e\ 70°C}$** | 4.7 | 6.0 | 5.6 | 6.0 | 7.3 | 7.3 | 7.3 |

The results of langmuir type 1 represented on table 6 were used in the graphucally analsis of the model. A plot of $C_e/Q_e$ against C was plotted as shown in Figure 4.7

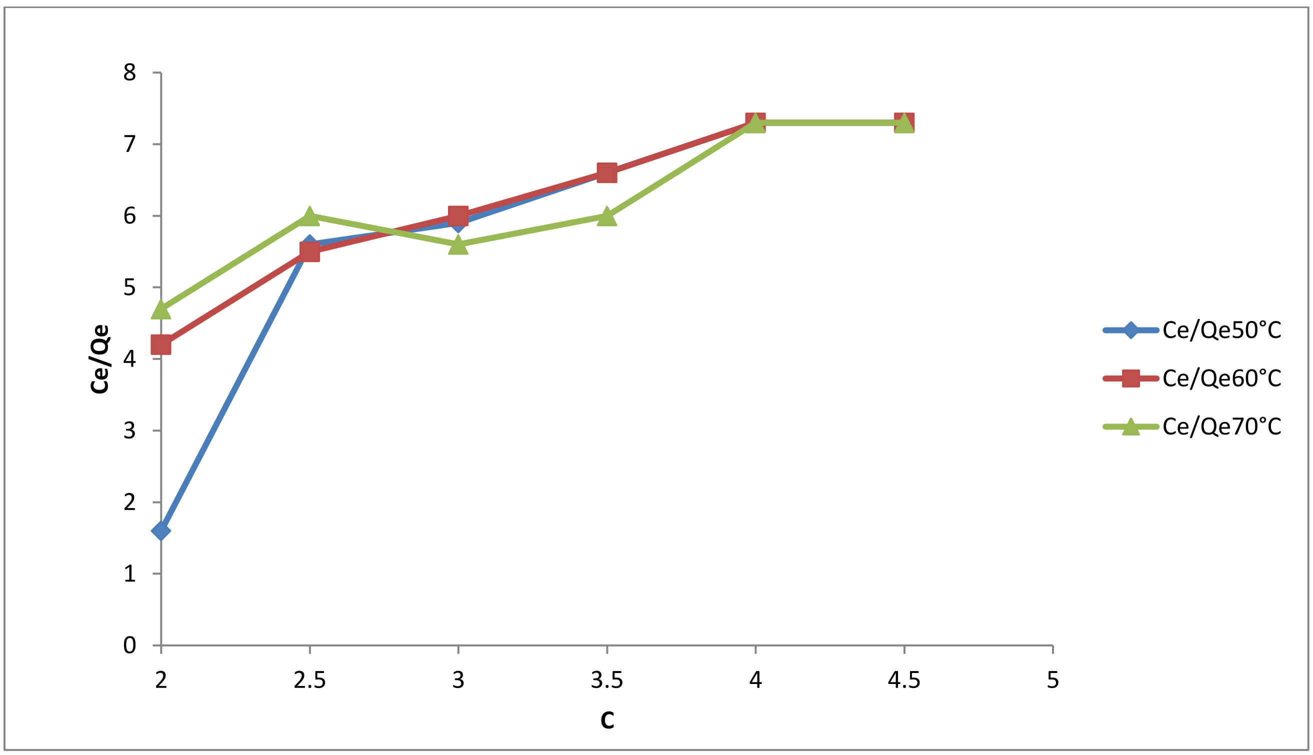



Figure 4.7: Graph of type 1 langmuir isotherm of PR dye on cotton fabric sample at 50°C,60°C and 70°C

From Figure 4.7, adsorption isotherm tries to bring to light the relation between the extent of adsorption to bulk concentration at constant temperature and pH. In Langmuir adsorption isotherm is concerned with the theoretical explanation of how adsorbate and adsorbent system (s) got to equilibrium. In type 1 Langmuir model is concerned with solid matter that have fixed site whereby each site can only contain one molecule with no interaction between adsorbed molecules. Here it is concerned in finding out if PR dyes have microporous surface and if it has like in activated carbon used in wastewater management can the PR dye form a monolayer. Graphically is seen if the graph gives linear graph. From the Figure 4.7 the plot show that $R^2$ at 50°C was (0.8392), at 60°C (0.9307) and 70°C (0.7375). PR dyes found sites in the cotton where they could fix themselves and form a mono-layer better at 60°C (Mimi Sakinah Abdul Munaim et al 2016). The value of Qe depicts that the amount of PR dye required forming a complete monolayer equilibrium (Vinod, 2010), from the study, results showed in table 10 that as the temperature increased, the amount of PR dye extracted onto the cotton Qe fluctuated.

### 4.4.2 LANGMUIR ISOTHERM TYPE 2 OF PR DYE ON COTTON FABRIC SAMPLE

Table 7: Results of Langmuir Isotherm Type 2 of PR dye on Cotton fabric sample

| | | | | | |
|---|---|---|---|---|---|
| **$1/C_e$** | 0.5 | 0.4 | 0.3 | 0.286 | 0.25 |
| **$1/Qe_{50°C}$** | 0.794 | 2.25 | 1.95 | 1.89 | 1.85 |
| **$1/Qe_{60°C}$** | 2.08 | 2.20 | 2.01 | 1.88 | 1.78 |
| **$1/Qe_{70°C}$** | 2.34 | 2.41 | 1.87 | 1.72 | 1.58 |

Table 7 represents the results for langmuir type 2 and the values obtained were used in a plot of 1/Qe against $1/C_e$ as shown graphically in figure 4.8

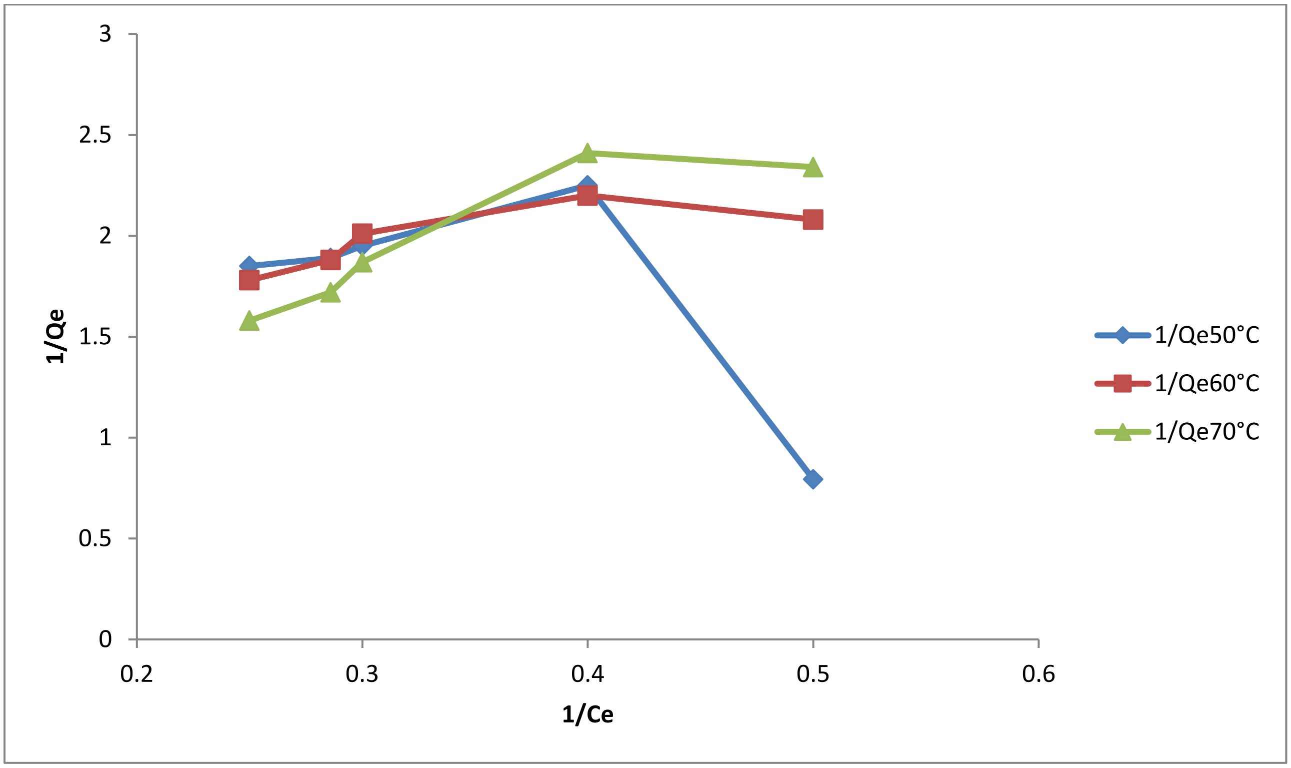



Figure 4.8: Graph of type 2 langmuir isotherm of PR dye on cotton fabric sample at 50°C, 60°C and 70°C

From Figure 4.8, This model type of Langmuir tries to explain the non-porous or macroporous solids and how multilayers can be formed. Here it tries to describe systems with wide range of pore sites with no saturation limits. From the plots in figure 4.8 it didnt distinctively follow the plot for type2 Langmuir model, but the regression coefficient of the PR dye at 50°C was (0.8234), 60°C (0.5762) and 70°C (0.4239) gave lower coefficient of detremination. Cotton interaction showed that the type 2 depicts a favorable path as the coefficient is less than 1. From the study, results showed in Table 7 that as the temperature increased, the amount of PR dye extracted onto the cotton Qe this was supported by (Habib-Allah Tayebi, et al., 2015) who did similar investigation using acid dye on nylon 6.

#### 4.4.3 LANGMUIR ISOTHERM TYPE 3 OF PR DYE ON COTTON FABRIC SAMPLE

Table 8: Results of Langmuir Isotherm Type 3 of PR dye on Cotton fabric sample

| Qe 50 | Qe /Ce50 | Qe 60 | Qe /Ce60 | Qe 70 | Qe /Ce70 |
|---|---|---|---|---|---|
| 1.3 | 0.63 | 0.48 | 0.24 | 0.43 | 0.21 |
| 0.44 | 0.18 | 0.45 | 0.18 | 0.42 | 0.17 |
| 0.51 | 0.17 | 0.5 | 0.17 | 0.54 | 0.18 |
| 0.53 | 0.15 | 0.53 | 0.15 | 0.58 | 0.17 |
| 0.54 | 0.14 | 0.56 | 0.14 | 0.63 | 0.16 |

Table 8 represents the combined results for langmuir type 3 at the three temperatures of 50°C, 60°C and 70°C obtained and used in a plot of Qe against Qe /Ce at 50°C, 60°C and 70°C as shown graphically in figure 4.9., 4.10, 4.11.

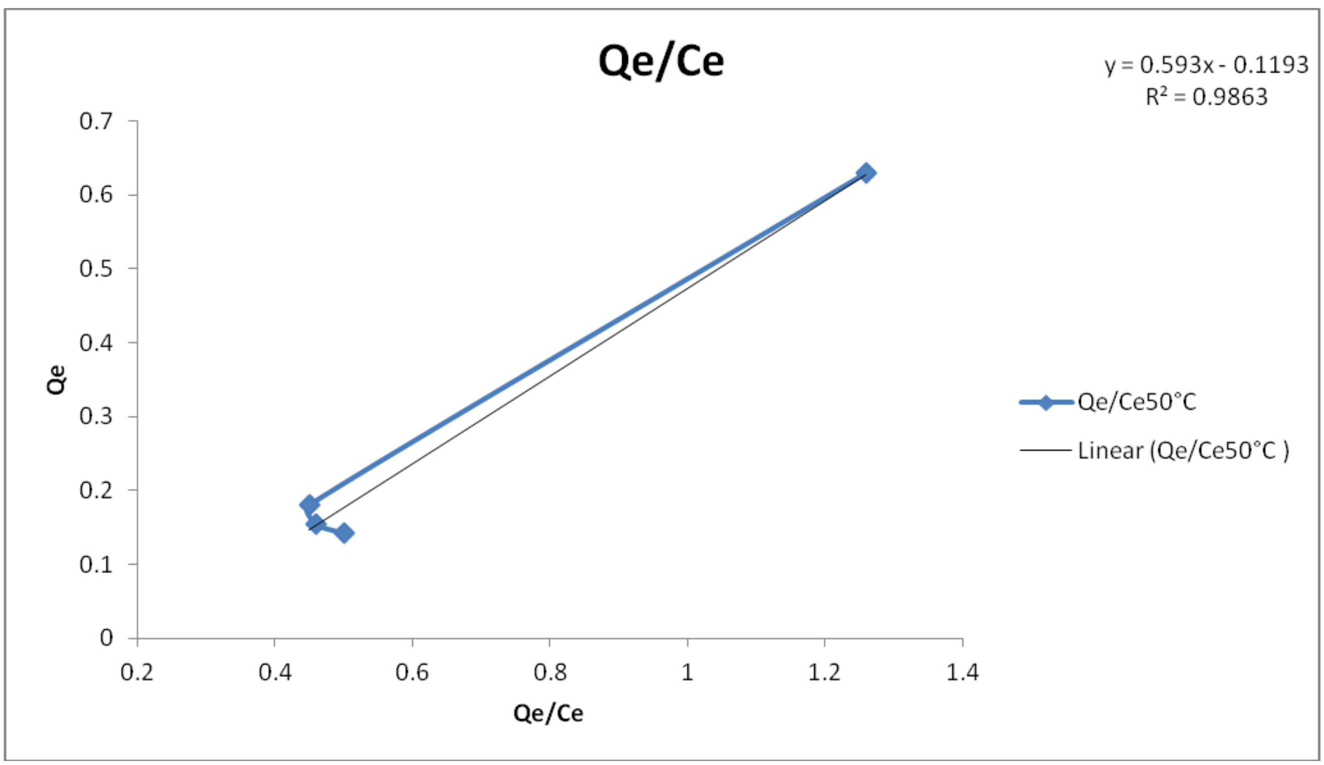



Figure 4.9: Graph of type 3 langmuir isotherm of PR dye on cotton at 50°C

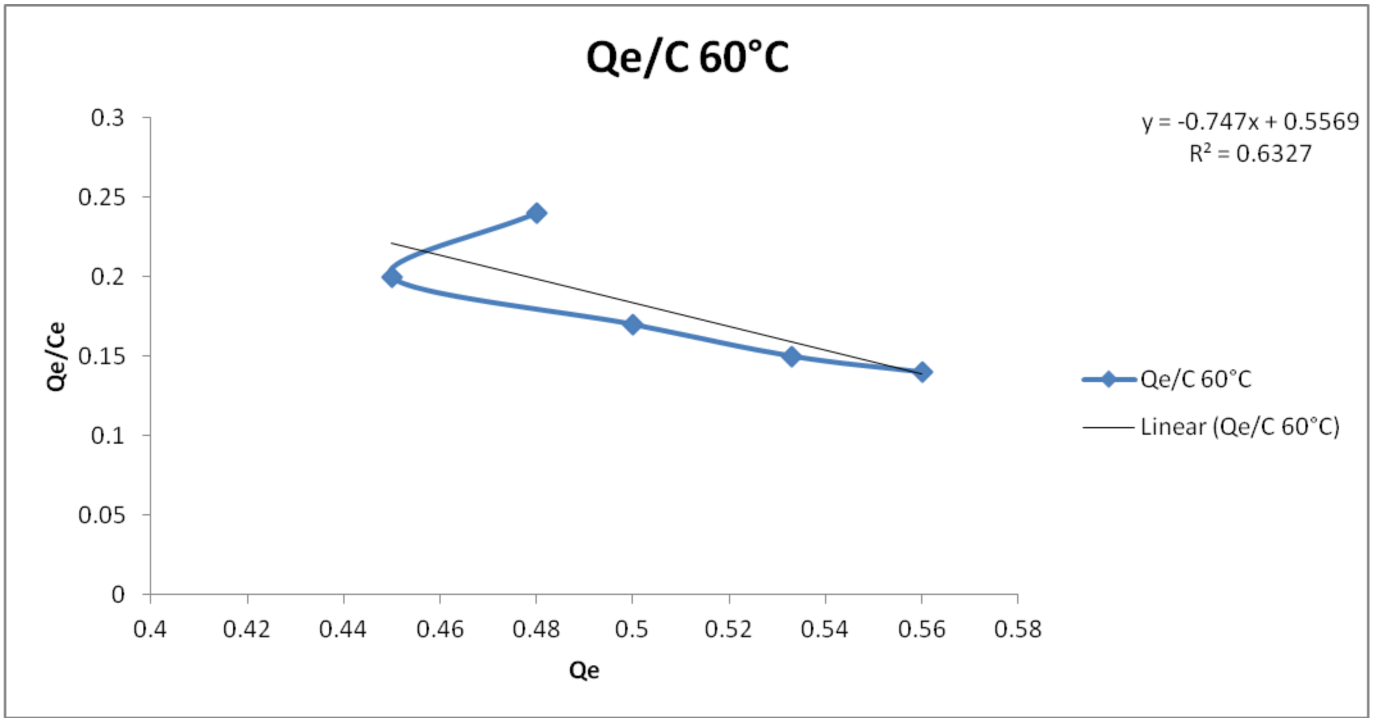



Figure 4.10: Graph of type 3 langmuir isotherm of PR dye on cotton sample at 60°C

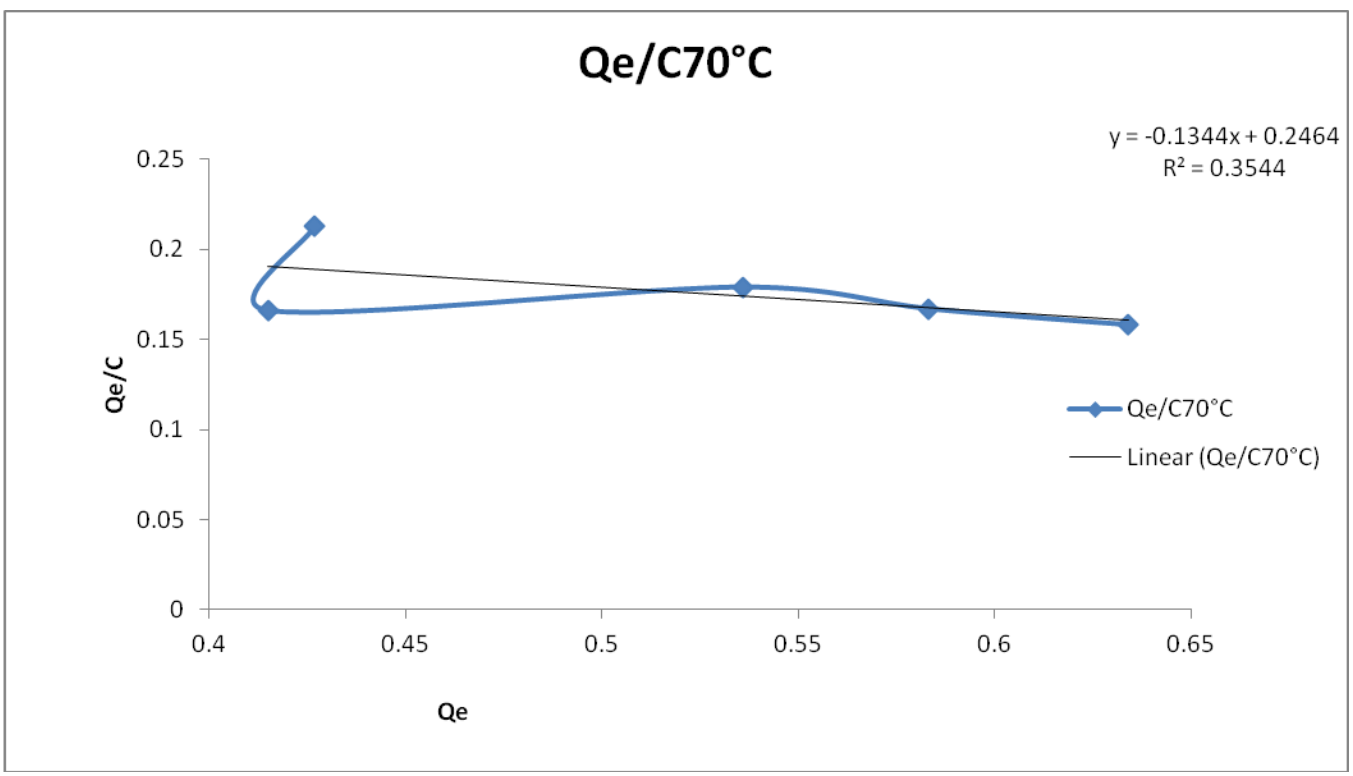



Figure 4.11: Graph of type 3 langmuir isotherm of PR dye on cotton sample at 70°C

From Figure 4.9 to 4.11**,** this type3 model of Langmuir tries to explain the non-porous or macroporous solids and how multilayers can be formed. Here it tries to describe systems with wide range of pore sites with no saturation limits. From the plots in Figure 4.9-4.11 it didnt distinctively follow the plot for type3 Langmuir model, but the regression coefficient of the PR dye and cotton interaction showed that in type 3 at 50°C (0.9669), 60°C (0.4516) and 70°C (0.3443) across the temperatures depicts a favorable path as the coefficient is less than 1 except at 50°C which had highest coefficeint determination. From the study, results showed in table 10 that as the temperature increased, the amount of PR dye extracted onto the cotton Qe this is in harmony with a study done by (Hamid, Abdul Munaim, & Abu Seman, 2016) on the extracts from the dragon fruit peel onto the Spun Silk Yarn investigating its regression analysis for the adsorption isotherms of the dye.

### 4.4.4 LANGMUIR ISOTHERM TYPE 4 OF PR DYE ON COTTON SAMPLE

Table 9: Results of Langmuir Isotherm Type 4 of PR dye on Cotton sample

| **C** | 2 | 2.5 | 3 | 3.5 | 4 |
|---|---|---|---|---|---|
| **Qe /C50** | 0.63 | 0.18 | 0.17 | 0.15 | 0.14 |
| **Qe /C60** | 0.24 | 0.2 | 0.17 | 0.15 | 0.14 |
| **Qe /C70** | 0.22 | 0.17 | 0.18 | 0.17 | 0.16 |

Table 9 represents the combined results values for langmuir type 4 obtained for the three temperatures 50°C, 60°C and 70°C were used in a plot of Qe /Ce against Ce as shown graphically in figure 4.12

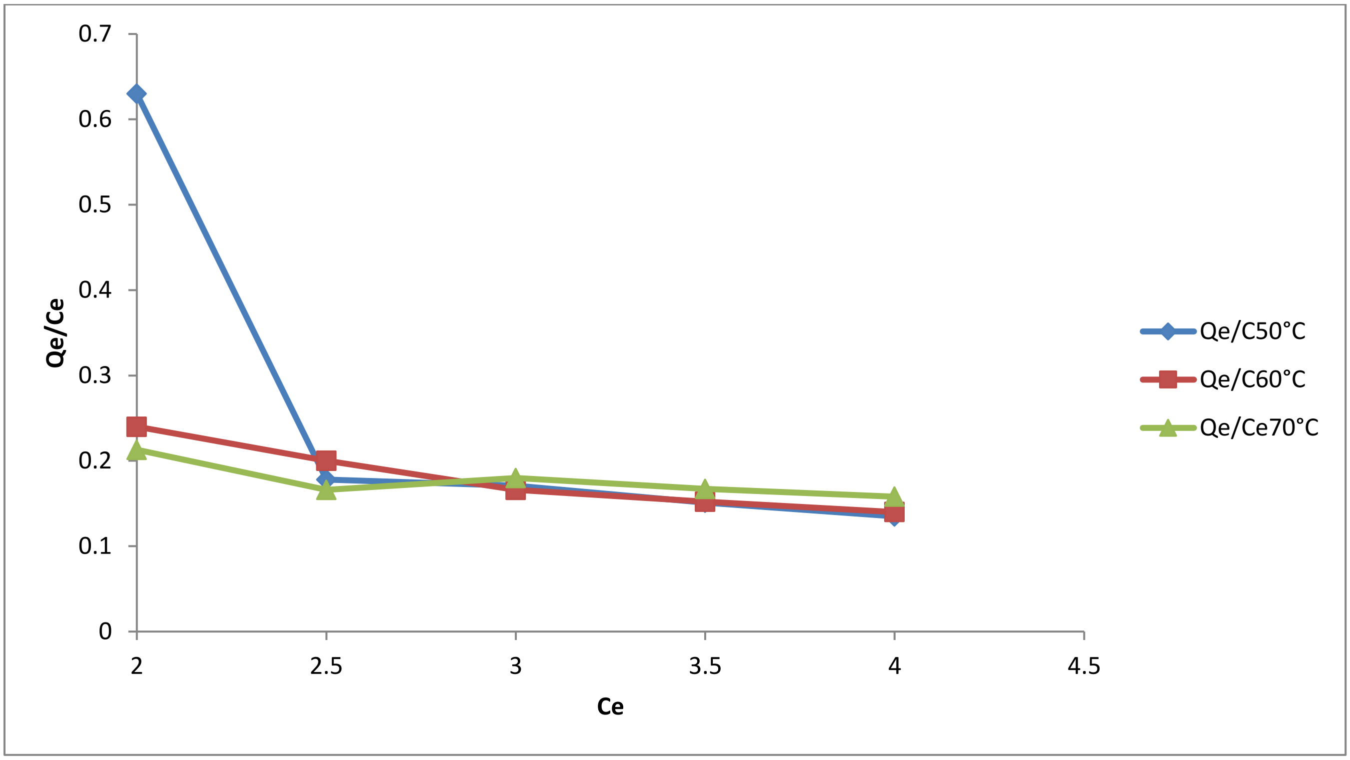



Figure 4.12: Graph of type 4 langmuir isotherm of PR dye on cotton sample at 50°C, 60°C and 70°C

In Figure 4.12, this type 4 model of Langmuir tries to explain the non-porous or macroporous solids and how multilayers can be formed. Here it tries to describe systems with wide range of pore sites with no saturation limits. From the plots in figure 4.12 it didnt distinctively follow the plot for type4 Langmuir model, but the regression coefficient of the PR dye and cotton interaction showed that the type 4 at 50°C(0.9348), 60°C (0.62920) 70°C (0.5784) indicating that there could be polutant adsorbed homogenously on the surface by forming monolayer. From the study, results showed in table 10 that as the temperature increased, the amount of PR dye extracted onto the cotton as Qe this was supported by (Hamid et al 2016) While at the other two temperature the coefficient shows a favorable path as the coefficient is less than 1, depicting that there is surface interaction and that there is capacity for adsorption to occur between the PR dye and the cotton fabric sample.

In contrast, Langmuir isotherm tries to provide us with;

i. more details about the adsorption process

ii. show the adsorption mechanism or pathway of the adsorbate and adsorbent

iii. explain the surface properties of the matters interacting

iv. give us an understanding of the maximium adsorption capacity of the adsorbent

v. help in designing the adsorption system for any two matter interacting.

Table 10: Summary of Langmuir Isotherm Type 1-4 PR dye values for Qe , K, R2

| **TYPE 1** | **50°C** | **60°C** | **70°C** |
|---|---|---|---|
| **Qe (mg/g)**<br>**K (ml/g)**<br>**$R^2$** | 3.8<br>1.203<br>0.6615 | 1.74<br>1.210<br>0.9545 | 2.14<br>1.211<br>0.7872 |
| **TYPE 2** | **50°C** | **60°C** | **70°C** |
| **Qe (mg/g)**<br>**K (ml/g)**<br>**$R^2$** | 0.8336<br>1.210<br>0.8234 | 1.564<br>1.211<br>0.5762 | 2.9783<br>1.211<br>0.4239 |
| **TYPE 3** | **50°C** | **60°C** | **70°C** |
| **Qe (mg/g)**<br>**K (ml/g)**<br>**$R^2$** | 0.1501<br>1.210<br>0.9669 | 0.4934<br>1.211<br>0.4516 | 0.2464<br>1.212<br>0.3443 |
| **TYPE 4** | **50°C** | **60°C** | **70°C** |
| **Qe (mg/g)**<br>**K (ml/g)**<br>**$R^2$** | 0.3284<br>1.210<br>0.9348 | 0.2422<br>1.211<br>0.6297 | 0.8632<br>1.213<br>0.5784 |

It can be seen that but experimentally and calculated values of Langmuir model for the four types that type1 fits the best for *Peristophe Roxburghiana* dye extract on cotton fabric sample.

### 4.5. FREUNDLICH ISOTHERM RESPONSE FOR PR DYE ON COTTON FABRIC SAMPLE

Table 11: Results of Freundlich Isotherm for PR dye on cotton sample at 50°C

| | | | | | |
|---|---|---|---|---|---|
| **InQe** | 0.23 | -0.81 | -0.67 | -0.64 | -0.61 |
| **InCe** | 0.69 | 0.92 | 1.10 | 1.25 | 1.39 |

Table 11 represents the adsorption results of Freundlich isotherm model for PR dye on cotton fabric sample at 50°C. the values were used to plot a graph of InQe against InC

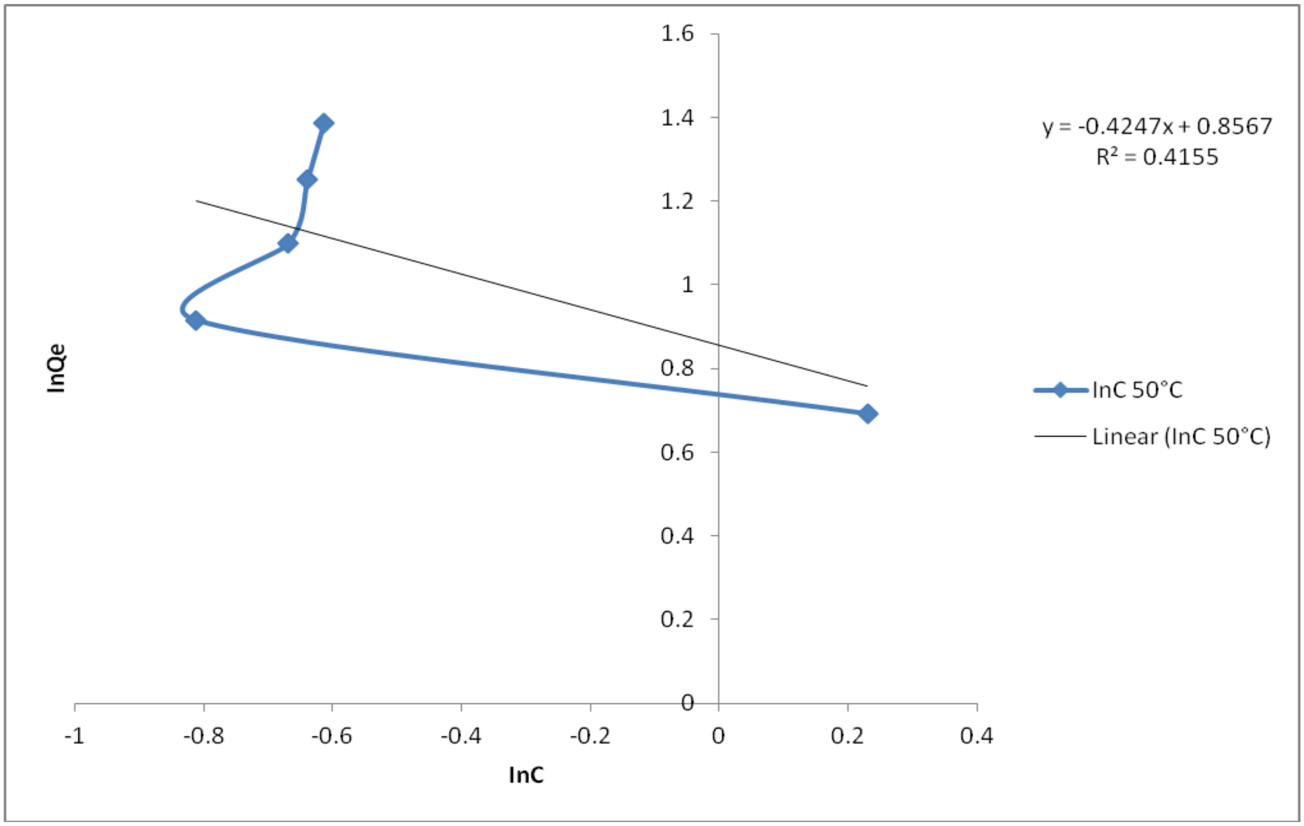



Figure 4.13: Graph of Freundlich isotherm of PR dye on Cotton sample at 50°C

Table 12: Results of Freundlich Isotherm for PR dyes on cotton at 60°C

| | | | | | |
|---|---|---|---|---|---|
| **InQe** | -0.73 | -0.80 | -0.70 | -0.63 | -0.60 |

| | | | | | |
|---|---|---|---|---|---|
| **InCe** | 0.69 | 0.92 | 1.10 | 1.25 | 1.39 |

Table 12 represents the adsorption results of Freundlich isotherm model for PR dye on cotton fabric sample at 60°C. the values were used to plot a graph of InQe against InC

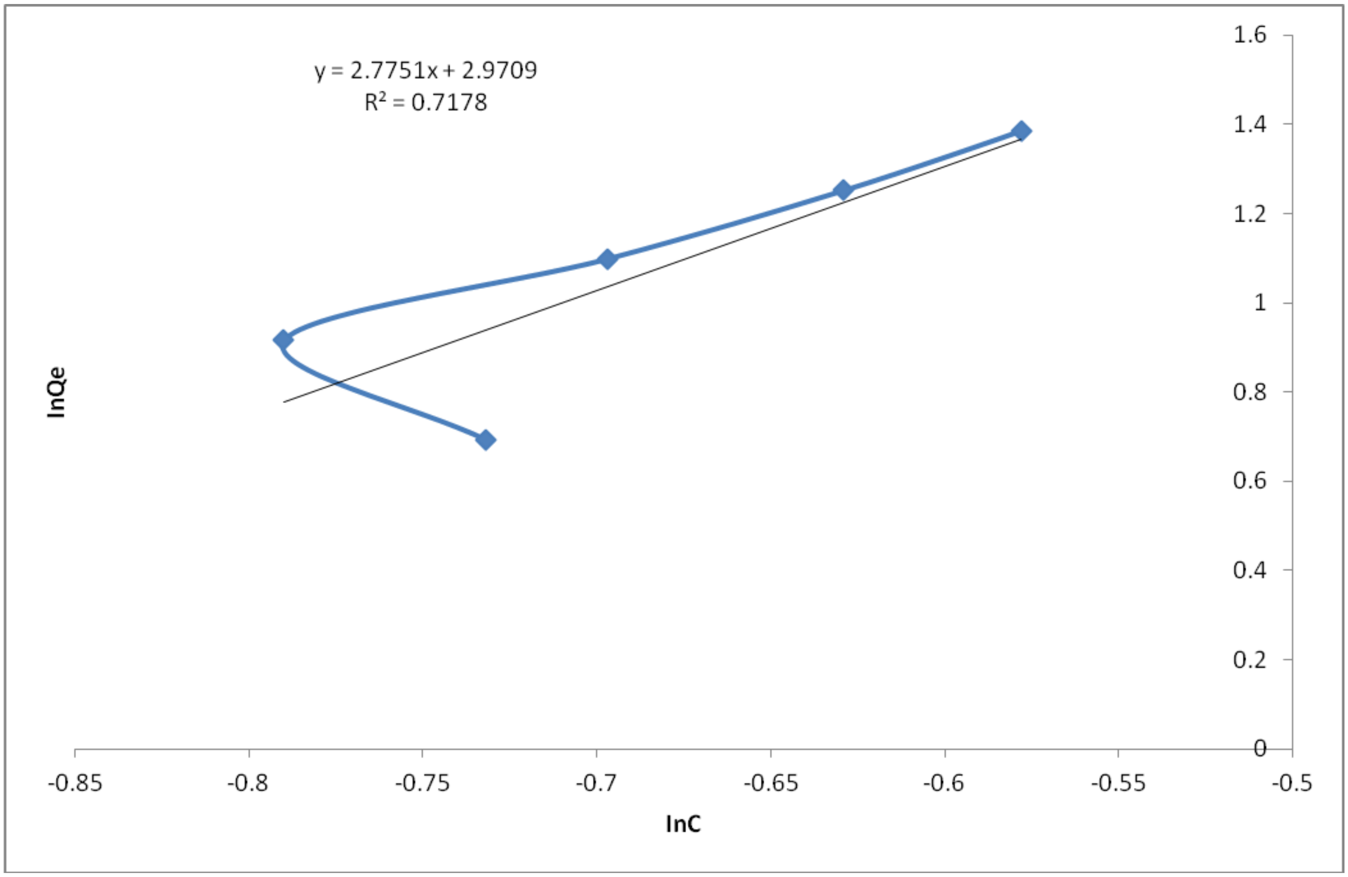



Figure 4.14: Graph of Freudlich Isotherm for PR dye on cotton sample at 60°C

Table 13: Results of Freundlich Isotherm for PR dyes on cotton at 70°C

| **InQe** | -0.85 | -0.88 | -0.63 | -0.54 | -0.46 |
|---|---|---|---|---|---|
| **InCe** | 0.69 | 0.92 | 1.10 | 1.25 | 1.39 |

Table 13 represents the adsorption results of Freundlich isotherm model for PR dye on cotton fabric sample at 70°C. the values were used to plot a graph of InQe against InC

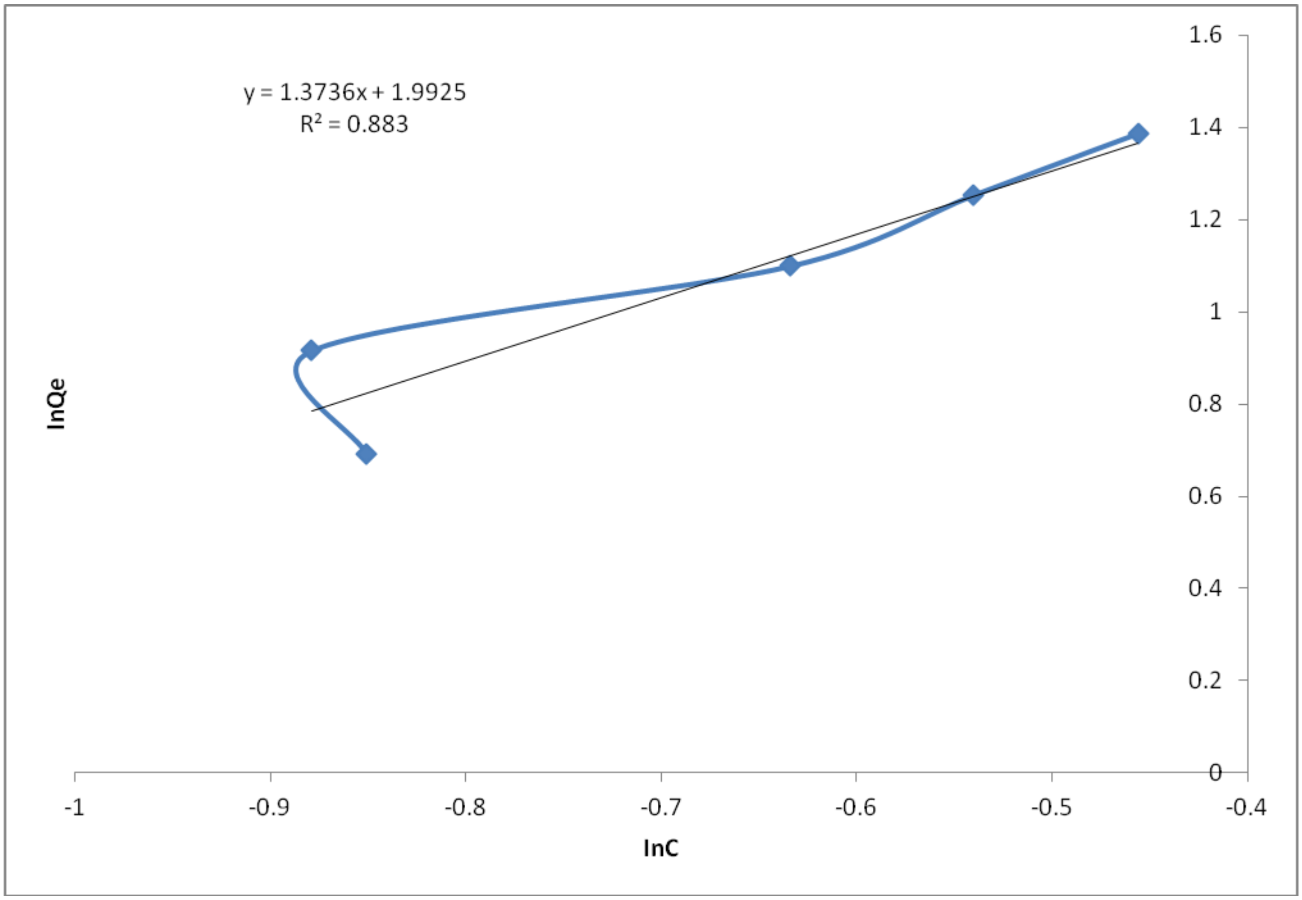



Figure 4.15: Graph of Freudlich Isotherm for PR dye on cotton sample at 70°C

From Figure 4.13 to 4.15, this study showed that their $R^2$ coeffiients were for plot at 50°C (0.4155), at 60°C (0.7178), and at 70°C (0.883) while K at the temperatures were 0.8567, 2.979, and 1.993 respectively. The importance of the Freundlich isotherm lies in its ability to explain a wide range of adsorption systems as in the case of PR dye, which is a heterogeneous and non-ideal systems. It is also helps in predicting the adsorption behavior of PR dye onto cotton.

From the experimenatl values, Freundlich isotherm of PR dye showed  moderate surface area. Therefore, Freundlich isotherm is an important tool for understanding and predicting the adsorption behavior of PR dye onto solid surfaces like Cotton fabric sample.

# CHAPTER FIVE

## CONCLUSION

From the research work aimed at the determination of kinetic, thermodynamic behavior and isotherm responses of dye extract from PR on cotton fabric sample, they following were the conclusion obtained.

Firstly, *Peristophe roxburghiana* plant is suitable for obtaining natural dye for dyeing textile fibre, and can be extracted using aqueous extraction method with the use of soxhlex extractor to enhance efficiency of the process. The optimum extraction time and temperature are 40mins and 70°C respectively. On dyeing cotton fabric the reaction had very good kinetic response same as the equilibrium rate which was achieved at different times for different temperature. The optimum equilibrium time was 40mins at this point thermal degradation may not occur to the extracted dye molecule. Thermodynamics behaviours showed that the dye were affected by temperature, and was exothermic in nature and at equilibrium there was decreased mobility with the negative values of entropy. Concentration of the process affected dye molecule uptake by the cotton as more material of the solute. The reaction obeyed the pseudo first and second order adsorption isotherm with second order having best experimental fit. The adsorption isotherm that was investigated using Langmuir and Freundlich isotherm showed PR dye interaction with cotton fabric sample obeying Langmuir isotherm type 1 across the temperature and selectively for other types with respect to temperature. Effect of temperature and concentration helps users of natural dye to know how best to use them to obtain good shade as a result.

Finally, care should be taken when choosing other solvent for extracting it because the dye have tendency to change colour with respect to the solvent medium.

## 5.1. CONTRIBUTION TO KNOWLEDGE

I. The study having established the adsorption kinetics that PR dye on cotton followed type 1 Langmuir isotherm and pseudo second order perfectly.

II. The adsorption mechanism model show that the reaction of the dye on cotton is a chemisorption process and exothermic in nature.

III. The study have armed natural dye handlers with the knowledge on how to efficiently handle this dye obtained from bio-diverse environment as a suitable substitute of synthetic dye for dyeing natural fabrics like cotton.

## 5.2. RECOMMENDATION

I. I recommend a comparison of the kinetics and thermodynamics adsorption responses of this dye extract using other solvents.

II. I recommend that researchers investigate the suitability of dye extract from *Peristophe roxburghiana* plant as acid-base indicator and sensitizer for dye-solar cells.

III. I recommend that other isotherm model should be employed in the analysis and determination of adsorption pattern of dye extract from *Peristophe roxburghiana* plant for a better understand of adsorption response.

This study has proffered a guide on the determination of adsorption pattern of previously reported natural dyes extracted from other plant sources.

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# APPENDIX

## APPENDIX1: EXTINCTION COEFFICIENT OF PR DYE EXTRACT ON COTTON FABRIC SAMPLE

To be able to effectively determine the kinetic behavior of PR dye, its extinction co-efficient was determined by first obtaining its concentration using the equation below;

$$Concentration = \frac{Mass\ o\ dissolved\ solute}{volume\ of\ solution\ ater\ isolation} \quad 3.2$$

Mass of dissolved solute = mass of PR sample before extraction – mass of PR sample after extraction/isolation

M= 2g – 1.6g = 0.4g

V= $V_o$ – $V_f$ , where $V_o$ is initial volume of distilled water before extraction 500ml and $V_f$ is the final volume after extraction which was 484ml

Therefore, Co= 0.4g/0.484L = 0.826g/L

With the above, determination of the extinction co-efficient of PR dye at 440nm and 580nm was obtained respectively using the formulas below

$$\boldsymbol{A} = \Sigma * \boldsymbol{L} * \boldsymbol{C} \quad 3.3$$

$$\Sigma * \boldsymbol{L} = \frac{\mathbf{A}}{\mathbf{C}} \quad 3.4$$

Where L=1cm

C=concentration, A= Absorbance, $\Sigma = \text{Dye extinction co} - \text{efficient}$

Co = Mass of dissolved solute/ Volume of solution after isolation

M = mass of PR dry sample before extraction – Mass of PR after isolation

M= 2g – 1.6g = 0.4g

V = volume remaining after isolation 484ml = 0.484 liters

Therefore, Co = 0.4g/0.484litres = 0.826g/l

W = mass of fabric used 1l

Ce= $A/\Sigma L$

3.5

Where A is absorbance at 580nm before dyeing (1.544)

Ƹ is extinction co-efficient which is A/CL

Ƹ at 580nm = 1.544/0.826*1 = 1.869cm

The equilibrium PR dye uptake by the contain fabric was observed at 40mins at 580nm

Therefore, Ce at 580nm = Absorbance at 40mins for peak 580nm after dyeing/ 1.869 * 1cm=

Ce = $\frac{1.259}{1.869*1}$ = 0.674g/l

The equations above were used to obtained results in Table 1and 2 in chapter 4 for the equilibrium concentration, to get the individual concentrations and adsorption and to get the graph of the kinetic behavior of the PR dye on cotton fabric sample in Figure 4.3 at different times from 5min to 50 min at the three temperatures 50°C, 60°C and 70°C

From 3.2.4, the equilibrium was determined in Table 1 and 2 in chapter 4 the values of the results were used in the determination of the kinetic behavior of the dye extract from PR on cotton fabric using pseudo first order of adsorption and pseudo second order of adsorption respectively.

Pseudo first order reactions are reactions that at first glance seem to be second order but, upon closer inspection, approximate a first order reaction.

**A + B —–> C + D**

Although the concentrations of both A and B are necessary for this reaction, one of the components is present in significant excess, so its concentration barely varies as the reaction progresses. Therefore, the reaction is considered to be pseudo-first order with respect to component A if component B is in large excess and the concentration of B is very high in comparison to that of A, and pseudo-first order with respect to component B if component A is in large excess and the concentration of A is very high in comparison to that of B. the component A for this study is the PR dye while component B is the cotton.

Table 4: Results of Pseudo-First–Order Adsorption Kinetics of PR dyes on Cotton sample

| **Time** | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 |
|---|---|---|---|---|---|---|---|---|---|---|
| **In(Qe - Qt)** | -7.60 | -8.11 | -8.52 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

The second-order rate law had been used over the years to model solvent extraction of a number of substances from plants, leaves, seeds, and nuts (Qu et al. 2010).

Pseudo second order was investigated using the equation in below (Nnorom et al. 2020);

$$\frac{T}{Qt} = \frac{1}{K2Qe} + \frac{1}{Qe}T \qquad 3.17$$

## APPENDIX 2: ISOTHERM MODEL USED IN ADSORPTION KINETICS OF PR DYE EXTRACT ON COTTON

The sorption capacity of a given sorbent may depend on a series of properties. Sorption isotherms are often non-linear. Classification of isotherms has been reported and each isotherm has its own interpretation by a specific model. Some of these isotherm models such as Langmuir, BET, and Gibbs models mostly describe sorption data in water phases sufficiently and only Freundlich and linear models seem to have a better fit for sorption datas (Habib-Allah Tayebi1 et al, 2015). But all these isotherm models approaches linear model at low sorbate concentration.

In this study, the determination of the isothermic behavior of PR natural dye, was investigated by employing Langmuir type 1-4 and Freundlich isotherms. The values obtained were used to get the plot for each model represented in 4.7 in chapter 4.

## APPENDIX3: LANGMUIR ISOTHERM MODEL

The Langmuir model is a notably and widely used isotherm model with type 1-4. Developed to show chemisorptions on a set of distinctively localized adsorption site. It explains the adsorption behavior which assumes that equilibrium is attained when a monolayer of the adsorbate molecules saturates the adsorbent.

The four types of Langmuir isotherms are represented below:

Type1:

$$\frac{\mathbf{Ce}}{\mathbf{qe}} = \frac{\mathbf{1}}{\mathbf{qm}}\,\mathbf{Ce} + \frac{\mathbf{1}}{\mathbf{Kl\ qm}} \qquad 3.8$$

Type2:

$$\frac{1}{qe} = \frac{1}{KlqeCe} + \frac{1}{Klqm}$$ (H. Tayebi et al. 2015)

Type3 :

$$Qe = Qm\frac{Qm}{KlCe}$$ (H. Tayebi et al. 2015) 3.10

Type 4:

$Qe/C_e = K_l\ Q_m - K_L Qe$ (H. Tayebi et al. 2015) 3.11

Where Ce (mg/l) is the equilibrium concentration, Qe (mg/g) is the amount adsorbed at equilibrium, $K_L$ is the Langmuir constant and $Q_m$ (mg/g) is the maximum adsorption capacity. The values of $Q_m$ and $K_L$ was calculated from the slope and intercept of the plotting for Type 1: Ce /Qe versus Ce, Type2: 1/Qe versus $1/C_e$, Type 3: Qe versus Qe $/C_e$, Type4: Qe $/C_e$ versus $C_e$/Qe

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless separation factor or equilibrium parameter, $R_L$ which is defined by;

$$\mathbf{R_L} = \frac{\mathbf{1}}{\mathbf{1 + KL\ Co}} \qquad 3.12$$

Where $C_o$ is initial concentration and $K_L$ = Langmuir constant (L/mg). The value of $R_L$ shows the shape of the isotherm to be either unfavorable when ($RL > 1$), linear ($RL = 1$), favorable ($0 < RL < 1$) or irreversible ($RL = 0$)

**APPENDIX4: FREUNDLICH ISOTHERM MODEL**

This isotherm model explains adsorption behavior that happens on a multiple or heterogeneous surface. Freundlich isotherm model is not thermodynamically consistent but it tries to help explain better than Langmuir in predicting equilibrium of mixture using the power law offering a good empirical correlation of equilibra of gas mixtures (Qada et al. 2006). Freundlich isotherm is calculated using the equation:

$Qe = K_F Ce^{1/n}$ 3.13

KF = Freundlich isotherm constant and n is the heterogeneity factor or adsorption intensity.

To determine the linear form of the isotherm a logarithmic form of the Freundlich isotherm is applied which is represented as follows;

$In\ Qe = In\ Kf + 1/n\ In\ Ce$ 3.14

where Kf is roughly an indicator of the adsorption capacity and 1/n is the adsorption intensity. The values of Kf and 1/n can be determined from the linear plot of ln Qe versus ln Ce. The slopes gives the value of 1/n which is the magnitude of the exponent indicating if adsorption is favourable. Values of n>1 represent favourable adsorption condition**.**

$Qe = K_F Ce^{1/n}$ 3.15

$Log\ Qe = LogKl + 1/n\ Log\ Ce$ 3.16

$InQe = InKl + 1/n\ InCe$ 3.17

## APPENDIX 5: STANDARD AFFINITY OF PR DYE ON COTTON FABRIC SAMPLE

Standard affinity of PR dye on cotton is evaluated using $-\Delta\mu = RT\ln K$

4.8

But K =$[\frac{Dd}{V}] * [Ds]$ where

4.9

Dd= Concentration of the dye in the fibre

Ds= Concentration of dye in solution.

V= Volume of water in the substrate

$R = 8.315 J.mol^{-1}K^{-1}$

$T_{(k)} = T_{(°C)} + 273.15$

Boltzmann constant= $1.381*10^{-3}$ $J.K^{-1}$

But K value is obtained from the slope of pseudo-second order using y=mx +c for 50°C, 60°C and 70°Cas follows:

y= 114.55x + 847.15; $R^2 = 0.9855$

y=44.671x + 133.73; $R^2 = 0.9956$

y= 33.237x + 3.853; $R^2 = 1$

Therefore, for 50°C, 60°C and 70°C are as follows: $K_{50}$= 114.55, $K_{60}$ =44.671, $K_{70}$ = 33.33, In $K_{50}$ = 4.74, In $K_{60}$ = 3.799, and In $K_{70}$ = 3.51 using the equation:

$-\Delta\mu = RT\ln[\frac{Dd}{V}] * [Ds]$

4.10

$\Delta\mu_{50°C}$ = 8.315*323.15*4.74 = <u>12.74kJ/mol</u>

$\Delta\mu_{60°C}$ = 8.315*333.15*3.99 = <u>10.53 kJ/mol</u>

$\Delta\mu_{70°C}$ = 8.315* 343.15*3.51 = <u>10.02 kJ/mol</u>

**APPENDIX 6: HEAT OF DYEING OF PR DYE ON COTTON SAMPLE**

$\Delta H° = T\ \Delta\mu$

$\Delta H° = 343.15 * 10.02 = \underline{3438.4 kJ/Mol}$

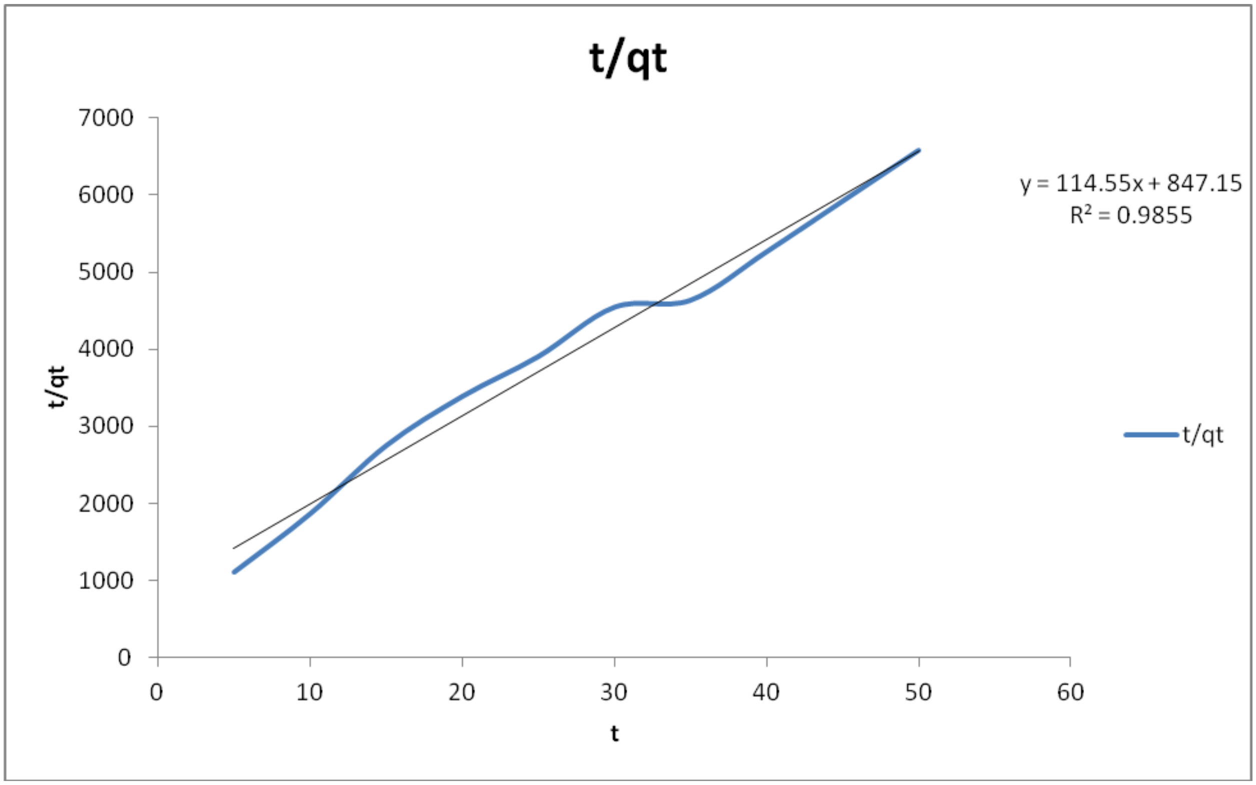
**APPENDIX 7: ENTROPY OF DYEING OF PR DYE ON COTTON SAMPLE**

$\Delta U = \Delta H - T\Delta S$ 4.11

$\Delta\mu° = \Delta H° - T\ \Delta S°$

Where - $\Delta S° = \frac{\Delta\mu° - \Delta H}{T} = \frac{10.02 - 3438.4}{343.15}$ = <u>-9.991 mol/K</u>

**APPENDIX 8: PSEUDO SECOND ORDER ADSORPTION AT 50°C FOR PR DYE ON COTTON FABRIC SAMPLE**



**APPENDIX 9: PSEUDO SECOND ORDER ADSORPTION AT 50°C FOR PR DYE ON COTTON FABRIC SAMPLE**