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PREPARATION OF ACTIVATED ADSORBENT FROM WATER TREATMENT SLUDGE FOR REMOVAL OF PHOSPHATE IMPURITIES IN WATER: OPTIMIZATION, CHARACTERIZATION, ISOTHERM AND KINETICS STUDIES

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BAHIR DAR UNIVERSITY
BAHIR DAR INSTITUTE OF TECHNOLOGY
SCHOOL OF GRADUATE STUDIES
FACULTY OF CHEMICAL AND FOOD ENGINEERING
Environmental Engineering

MSc Thesis on:

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BY

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AUGUST, 2023
BAHIR DAR, ETHIOPIA

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A Thesis Submitted to the Department of Environmental Engineering, College of Engineering, Bahirdar University, in a Partial Fulfilment of the Degree of Master of Science in Environmental Engineering

Advisor: D/r Metadel Kassahun (PhD)

AUGUST, 2023

BAHIR DAR, ETHIOPIA

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Declaration

This is to certify that the thesis entitled "**Preparation of activated adsorbent from water treatment sludge for removal of phosphate impurities in water: optimization, characterization, isotherm and kinetics studies**", submitted in partial fulfillment of the requirements for the degree of Master of Science in (Specialization) under (Faculty),Bahir Dar Institute of Technology, is a record of original work carried out by me and has never been submitted to this or any other institution to get any other degree or certificates. The assistance and help I received during the course of this investigation have been duly acknowledged.

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APPROVAL SHEET

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Approval of thesis for defense result

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ABSTRACT

Nature is a self-regulatory in terms of protecting the environment. The advent of technology, however, is up against, in some cases, to nature and remains constant threat to the environment and entities within by producing hazardous chemicals that are beyond the permissible limits. Banana peel is a waste material that can be used to treat dye molecules effluvia particularly from textile industry. A banana peel, thus, was activated both thermally and chemically at different conditions. It was subjected to 0.5–2.5 M sulfuric acid concentration, and 50–90 °C temperature for 1–5 hrs activation time. Based on this study, banana peel activated at 1.5 M acid concentration, 70 °C and for 3 hrs showed efficacy of about 90%. The synthesized activated banana peel at the specified condition was characterized using different techniques such as SEM and BET that showed that it is a porous material with 302 m^2/g. To further scrutinize the capacity of the adsorbent, adsorption of dye molecules in a range of different variables, namely adsorption time from 20–140 min, pH 1.0–7.0, adsorbent dose 1–4 g/L and initial dye concentration 20–80 mg/L was conducted. The process of this adsorption was optimized using design expert statistical software an optimal removal efficiency 90.5%was obtained at adsorption time of 60 min, pH 3, adsorbent dose of 2 g/L and initial dye concentration of 40 mg/L over a wide range of adsorption time (10–160 min) .adsorption kinetics using pseudo first and second order models was studied at 2 g/L adsorbent dose 40 mg/L dye concentration for period of 10–160 min was performed. Besides, the isotherm study was conducted at 2 g/L adsorbent dose for a wide range of 20–125 mg/L dye initial concentration and fitted the data to Langmuir and Freundlich models. As a result, pseudo second order kinetics model and Langmuir isotherm model were the best fit to describe the adsorption process. The reusability test conducted showed that activated banana peel can be used repeatedly five times before its performance declines below 50%. All told, the results so obtained are litmus test that the activated banana peel bio-adsorbent can be used in industry, if not, in pilot scale to treat textile effluents.

Keywords: Banana peel, Dye, Activation, Adsorption, Optimization

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LIST OF ABBREVIATION

PZC	Point of zero charge
FTIR	Fourier transforms infrared radiation
SEM	Scanning electron microscope
TGA	Thermogravimetry Analysis
XRD	X-Ray Diffraction
UV/Vis	Ultra-violet spectrometry
AC	Activated carbon
ANOVA	Analysis of variance
ASTM	American Society for Testing and Materials
BET	Brunauer Emmett Teller
CCD	Central composite design
k1	pseudo first order rate constant
k_L	Langmuir equilibrium constant
K2	pseudo second order rate constant
PFO	Pseudo first order
PSO	Pseudo second order
qe	Amount of sorbatesorbed at equilibrium

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CHAPTER ONE

1 INTRODUCTION

1.1 Background

Due to the release of various industrial effluents, environmental degradation has gotten worse in recent years. Large amounts of untreated solid and liquid waste are carelessly dumped into rivers and streams, especially those that pass-through cities, towns, and different production sectors. As a result, a large number of pollutants have extensively contaminated the water body. Additionally, pollution lowers the amount of water that is available and boosts the cost of water filtration. Thus, in order to prevent pollution, it is advised that all wastewater kinds that are most likely to be released into the environment should be treated(Ibrahim O., Raphael O. and Onyebuchi N.J, 2012).

Major water contaminants include a variety of organic and inorganic substances such as heavy metals and industrial compounds. They have the potential to harm human health and obstruct industrial or agricultural water use. When the level of a pollutant in the water supply exceeds an acceptable threshold for a certain water usage, such as drinking or industrial water supply, the water is termed unsafe. (Ahalya N. and Ramachandra T.V., “Restoration of wetlands, 2020). Dyes are organic pollutants that are made up of synthetic aromatic organic chemicals that bind to textiles or surfaces to give them color. Synthetic dyes are common water contaminants due to their high solubility, and they are frequently detected in trace amounts in industrial wastewater. (C.I. Pearce, J.R LIoyd, and J.T. Guthrie, 2003). Industries such astextile, cosmetics, food, and paper sectors all utilize dyes. However, if dyes are not properly disposed of after usage in these sectors, they can be harmful to the environment.

The reason for this is because dyes are generally colored and so can tint surface water. It is well acknowledged that the color of water has a significant impact on public impression of its quality. Color is the first contaminant to be detected in wastewater. Water with very small quantities of colors (less than 1 ppm for some colours) is very visible and unpleasant. Furthermore, dye-using businesses consume a significant amount of water. As a result, they produce a large quantity of colorful effluent(F. Banat, S. Al Asheu and L.A. Makhadmeh, 2003).

Dyes may have a major impact on photosynthetic activity in aquatic life because to the presence of aromatic metals, chloride, and other chemicals. One of the most problematic aspects of dye treatment is that the majority of dyes used in industry are resistant to light, oxidation, and aerobic digestion. Dyes, on the other hand, are typically synthetic and have a complex aromatic molecular structure that makes them more stable, making them non-biodegradable (H. chen and J. zhao, 2009). Because of their high chemical and biological oxygen demands, suspended particles, turbidity, and hazardous components, dyes in wastewater undergo biological and chemical transformations, which deplete dissolved oxygen(M. Oacar and I.A. Sengil, 2003). Because reactive dyes account for 20-30% of the entire dye market, a substantial portion of reactive dyes (10-50%) is lost during the dyeing process, and traditional treatment procedures have been shown to be ineffective in completely eliminating many reactive dyes. (Z.AksuandS.Tezer, 2005).As a result, an effective treatment of wastewater containing dyes is required. Chemical reduction, ion exchange, evaporation, reverse osmosis, and chemical precipitation are some of the methods for treating wastewater containing colors. The drawbacks of utilizing these approaches include the high capital and operating costs, as well as the disposal of leftover sludge(Kumar*etal*, 2012).The bio-adsorption technique is an appealing option for treating contaminated water, especially if the adsorbent is affordable and does not require any extra processing prior to use(P. Janes , H.Buchtova, and M.Ryznarova, 2003).Adsorption is a superior technology that is becoming increasingly important because to its ease of use and low cost of application and removal(E. EREN and B.Afsin, 2007). For the treatment of colored wastewater, many treatment plants use activated carbon as an adsorbent. However, because of its high cost, the application of such activated carbon is limited, necessitating the development of low-cost adsorbents capable of adsorptive color removal. (S. Tunali, A.S. Ozcan, A. Ozcan andT.Gedikbey, 2006).

1.2 Statement of the Problem

Chemical-based textile dyes, in contrast to natural dyes, have become increasingly popular in the textile and dyeing sectors due to their cost-effectiveness and great stabilitytowards many parameters such as high temperature and light. As a result, extremely contaminated effluents are discharged from those sectors. These water-soluble textile dyes have had a significant impact on the fragile ecosystems surrounding the industries, and they pose serious environmental issues.

Those compounds dyes are often poisonous and carcinogenic. If dyes are left untreated, they can survive in the aquatic environment for a long time due to their great thermal and light stability.

The color and organic content of wastewaters from textile dyeing and finishing activities are often high. The effluent from the textile sector is known to be brightly colored, contain a significant number of suspended particulates, have a wide pH range, be hot, and have a high chemical oxygen demand. The first contaminant detected in this effluent is color. A relatively little amount of dye in water is extremely visible and limits light penetration in water systems, causing photosynthesis to suffer. Reactive colors are known to cause allergic dermatoses and respiratory disorders. Adsorption of azo dyes and their breakdown products (toxic amines) through the gastrointestinal system, skin, and lungs, as well as creation of hemoglobin adducts and disruption of blood formation, pose a significant health concern.

As a result, wastewater treatment is a major concern in the textile sector. Traditional dyes in textile effluents may necessitate costly processes to achieve a reasonable level of treatment. This is primarily owing to the effluent streams' heterogeneous composition. Chemical and physical treatment method for dyes in effluent includes adsorption, coagulation, precipitation, filtration, membrane separation and oxidation. Dye-containing wastewaters are difficult to treat because the dyes are refractory molecules (especially azo dyes), resistant to aerobic digestion, durable to oxidizing agents, and may be present in small amounts. Traditional color removal processes may be cost-prohibitive and/or technically challenging.

The goal of this study is to determine the banana peels adsorptive capacity for removing reactive dye (reactive blue) from aqueous solution. Banana peel is a waste product that can be found in great quantities. In addition to treating the dye effluent, converting scrap banana peel into usablebioadsorbent reduces the amount of home garbage. The impacts of initial pH, contact time, initial dye concentration, and adsorbent dose were investigated, and the best experimental conditions were identified.

1.3 Objectives of the Research

1.3.1 General Objective

The general objective of this study issynthesis of activated carbon from banana peel for removal of dye from an aqueous solution.

1.3.2 Specific Objectives

The specific objectives of this study are:

- To prepare bio-adsorbent from banana peels at different acid concentration, activation time and time
- To characterize the physic-chemical properties of the activated banana peel bio-adsorbent.
- To investigate adsorption process and effect of operating parameters such as adsorption time,pH, adsorbent dose and initial dye concentrationon the removal of reactive dye from aqueous solutions.
- To study the adsorption kinetics and isotherm processes at different times and initial dye concentrations
- To determine the reusability performance of the activated banana peel bio-adsorbent

1.4 Significance of the research

This research envisionedto remove reactive dye biosorption using a bio-adsorbent made from discarded banana peels that is reliable, efficient, easy, and cost-effectivematerial. Using waste banana peel to treat effluents, per se, signifies that the waste material is turned into useful one which would otherwise pollute the environment. Better yet, it can be used as potential candidate alternative for dye treatment and ploys role in pollution reduction.

1.5 Scope of the research work

The scope of this work is to synthesize the bio-adsorbent from waste banana peel for the effective removal of reactive dye from an aqueous solution using waste banana peels. Operating parameters like pH, initial dye concentration, adsorption time and adsorbent dosagewere conducted to the conditions for optimum dye removal. Also, the adsorption isotherms and kineticsparticularly Langmuir and Freundlich, first and second order models were scrutinized and theappropriate modelswere selected.

1.6 Limitation of the thesis

This thesis dealt with synthesizing of activated carbon from waste banana peel in a given range parameters like acid concentration, activation time and temperature. The activated banana peel was aimed to adsorb some level different dye concentration prepared in a laboratory. The variables considered to affect the adsorption process dye molecules on the surface of the activated banana peel bio-adsorbent were adsorption time, pH, adsorbent dose and initial dye concentration, putting aside others variables such as temperature and pressure. More to this point, the adsorption process was limited to synthetic dye concentrations, not tested using real dye effluent from textile industry.

CHAPTER TWO

2 LITERATURE REVIEW

2.1 Characteristics of dyes

The development of new dyes is unavoidable in today's fast-paced society. Some of the characteristics of those new dyes include being less expensive to create, being brighter, having more color, and being easy to apply to cloth. Dye-using companies' effluents contain a variety of synthetic dyestuffs, making wastewater containing dyes extremely difficult to treat since dyes are recalcitrant organic molecules that resist aerobic digestion and are stable to light, heat, and oxidizing agents (M.N. Kumar, T.R. Sridhari, K.D. Bhavani, P.K. Dutta, 1998 and Q. Sun and L.Yang, 2003). Dyes can be classified according to their chemical structure or according to their use.

2.2 Classification of dyes

Dye molecules are made up of two primary components: chromopores, which are responsible for color generation, and auxochromes, which not only add the chromopore but also reduce the molecule's solubility in water and improve its affinity for fiber. (Christie, 2001Soluble dyes, such as acid, mordant, metal complex, direct, basic, and reactive dyes, and insoluble dyes, such as azoic, sulfur, vat, and disperse dyes, are divided into two categories based on their solubility. (Dos Santos *et al*., 2007).characteristics of bright color, being easily water soluble, cheaper to produce, and easier to apply to fabric (D. Karadag, E. Akgul, S. Tok, F. Erturk, M.A. Kaya, M. Turan, 2007 and S. Karcher, A. Kornmüller M. Jekel, 2002 and Purkait, M.K., DasGupta, S., De, S., 2005). In aqueous solution, anionic dyes carry a net negative charge due to the presence of sulfate (SO3-) groups, while cationic dyes carry a net positive charge due to the presence of protonated amine or sulfur containing groups (Netpradit S, Thiravetyan P, Towprayoon S., 2004). Dyes usually have a synthetic origin and complex aromatic molecular structure, which make them more stable and more difficult to biodegrade. The chromophores in anionic and non-ionic dyes are mostly azo groups or anthroquinone types. Anthraquinone based dyes are more resistant to degradation due to their fused aromatic structures and thus remain colored in the wastewater.

Table 2.1: Classification of dyes based on application classes & their chemical types

Class	Principal Substrate	Method of Application	Chemical Types
Acid	Nylon, wool, silk, paper and leather	Usually from neutral to acidic dye baths	Azo (including premetallized), anthraquinone,triphenylmethane,azine, xanthene, nitro &nitroso
Base	Paper, polyyacrylonitrile, modified nylon, polyester and inks	Applied from acidic dyebaths	Cyanine,hemicyanine,diazahemicynanine, diphenylmethane, trialrylmethane, azo, azine, xanthene, acridine, oxazine, and anthraquinone
Direct	Cotton, rayon, paper, leather and nylon	Applied from neutral or slightly alkaline baths containing additional electrolyte	Azo, anthraquinone, styryl, nitro and benzodifuranone
Disperse	Polyester, polyamide, acetate, acrylic and plastics	Fine aqueous dispersions often applied by high temperature/pressure or lower temperature	Azo, anthraquinone, styryl, nitro and benzodifuranone
Reactive	Cotton, wool, silk, and nylon	Reactive site on dye reacts with functional group on fibre to bind dye covalently under influence of heat and pH (alkaline)	Azo, antraquinone, phthalocyanine, formazan, oxazine and basic
Solvent	Plastics, gasoline, varnishes, lacquers, stains, inks, fats, oils and	Dissolution in the substrate	Azo, triphenylmethane, antraquinone, and phthacyanine

	waxes		
Sulfur	Cotton and rayon	Aromatic substrate vatted with sodium sulfide &reoxidized to insoluble sulfur containing products on fiber	Indeterminate structures
Vat	Cotton, rayon and wool	Water-insoluble dyes solubilized by reducing with sodium hydrogensulfite, then exhausted on fiber and reoxidized	Antraquinone including polycyclic quinones and indigiods

2.2.1 Reactive dyes

Reactive dyes are colored compounds which contain one or two groups capable of forming covalent bonds between a carbon or phosphorus atom of the dye ion or molecule and an oxygen, nitrogen or sulfur atom of a hydroxyl, an amino or a mercepto group, respectively, of the substrate. Such covalent bonds are formed with the hydroxyl groups of cellulosic fibers, with the amino, hydroxyl and mercapto groups of protein fibers and the amino groups of polyamides. Due to their strong interaction with many surfaces of synthetic and natural fabrics, reactive dyes are used for dyeing wools, cotton, nylon, silk, and modified acrylics (Mottaleb M, Littlejohn D., 2001). Reactive dyes are used extensively in textile Industries regarding favorable characteristics of bright color, water-fast, simple application techniqueswith low energy consumption (Y.S. Al-Degs,M.I. EI-Barghouthi, A.H. EI-Sheilh and G.M.Walter, 2008).A considerable amount of research on wastewater treatment has focused on the elimination of reactive dyes essentially for three reasons;

•Firstly, reactive dyes represent an increasing share of the total dye market, because they are used to dye cotton fibers, which makes up about half of the world's fiber consumption (Orfao J, Silva A, Pereira J, Barata S, Fonseca I, Faria P, et al., 2006); •Secondly, large fractions of reactive dyes (10-50%) are wasted during the dyeing process due to the dye hydrolysis in alkaline dye bath(PiasKowsKi, ŚwidersKa, and Paweł K. 2018); •Thirdly, conventional wastewater treatment methods, which rely on adsorption and aerobic biodegradation, were found to be inefficient for complete elimination of many reactive dyes which lead to colored water ways (Robinson T, McMullan G, Marchant R, Nigam P.).Water soluble reactive and acid dyes are problematic; as they pass through the conventional treatment system unaffected, posing problems. Hence, their removal is also of great importance Traditional wastewater treatment technologies have proven to be markedly ineffective for handling wastewater of synthetic textile dyes because of the chemical stability of these pollutants. Thus, it has been verified that, of the 18 azo dyes studied 11 compounds passed through the activated sludge process practically untreated, four of them (Acid Blue 113, Acid Red 151, Direct Violet 9, and Direct Violet 28) were adsorbed on the waste activated sludge and only three (Acid Orange 7, Acid Orange 8, and Acid Red 88) were biodegraded (Shaul, G.M., Holdsworth, T.J., Dempsey, C.R. and Dostal, K.A.,22).

2.2.2 Toxicity of dyes

The chemical based textile dyes due to their cost-effectiveness and high stability of various parameters like temperature and light in contrast to natural dyes have increasingly been used in the textile and dyeing industries. This leads to discharge of highly polluted effluents. These textile dyes which are readily soluble in water have resulted in negative effects on the fragile ecosystems around the industries and represent serious environmental problems (Keharia, H., and Madamwar, D. 2003).The biggest threat to the environment is presence of untreated dyes in water bodies because many of these reactive dyes hinder the photosynthetic process of hydrophytes by blocking the light to penetrate, which further leads to synthesis of toxic substances (Bhatia, Raj, Sharma, Singh and S. Kanwar, 2017).

For instance, toxic aromatic amines are formed under the oxygen deficient environment in receiving media due to the discharge of untreated dye effluent. Because of the high BOD, the untreated textile wastewater can cause rapid depletion of dissolved oxygen if it is directly discharged into the surface water sources. The effluents with high levels of BOD and COD are toxic to biological life (Bhatia, Raj, Sharma, Singh and S. Kanwar, 2017).

During the decomposition process of organic pollutants the dissolved oxygen in the receiving water may be consumed at a greater rate than it can be replenished, causing oxygen depletion and having severe consequences for the stream biota (Q. Sun and L. Yang, 2003). Estimation of LC50 values of many commercial dyes at different time intervals on fish was done by Zahahriaet.al. (Zaharia, C.; Suteu, C. and Muresen, 2011).

Dyes are also problematic because the families of chemical compounds that make good dyes are also toxic to humans. Each new synthetic dye developed is a brand new compound, and because it’s new, no-one knows its risks to humans and the environment. Allergic dermatoses and respiratory diseases are known to be caused by reactive dyes. Contact dermatitis and asthma due to exposure to dyes were also studied by Weisburger et al. (J.H. Weisburger, 2002). Other researchers have shown textile industry workers exposed to reactive dyes to have changes in their immunoglobulin levels. Wollin et al. (Wollin .T, Börnick, H. & Schmidt, T.C., 2006) showed several azo dyes to have genotoxicity. Moreover, various azo dyes, mainly aromatic compounds, show both acute and chronic toxicity. High potential health risk is caused by adsorption of azo dyes and their breakdown products (toxic amines) through the gastrointestinal tract, skin, lungs, and also formation of hemoglobin adducts and disturbance of blood formation. LC50 values reported for aromatic azo dyes range between 100 and 2000 mg/kg body weight (Wollin .T, Börnick, H. & Schmidt, T.C., 2006).

2.3 Treatment options for dye effluent

Nowadays, the concern is primarily focused on developing economic and effective methods to treat wastewater discharge from the textile industries to protect the aquatic life in water bodies. Therefore, the methods could be physio-chemical, biochemical or the combination of both which can provide effective technologies in removing contaminants from wastewater coming from the textile industries.

2.3.1 Biological dye removal method

In most countries, the typical biological method is the commonly and extensively utilized dye removal method to treat dye wastewater. Generally known the conventional method, combination of aerobic and anaerobic process is carried out before dye effluents are released to the environment. This method was chosen as the go-to dye removal method mainly because it is very cheap and can be accomplished easily (Katheresan, Kansedo, and Lau, 2018). Biological based methods employed for degradation of the effluent from the textile industries have been successfully used. The biological degradation (i.e., bioremediation) is economically feasible, environmental-friendly and generates less volume of sludge when compare with other techniques.

It causes the degradation of synthetic dyes to a comparatively less toxic inorganic compound because of breakdown of bond (i.e., chromophoric group) and finally helps in removal of color(Bhatia,Sharma,Singh,S.Kanwa,2017).the conventional method does treat the chemical oxygen demand present in the wastewater, it does not make the water dye-free or toxic free. Side this method, other conventional biological dye removal methods are adsorption by microbial biomass, algae degradation, enzyme degradation, fungal cultures, microbial cultures as well as pure and mixed culture. Biological dye removal methods incorporate some form of living organism in its process. Since this method deals with living things, its major disadvantage is its growth rate. System instability is common in biological dye removal process as predicting its growth rate and reactions can be tricky at times(Katheresan, Kansedo, and Lau, 2018). Lewinsky and Lin and Lo, gave the insight that biological process is efficient in reducing the COD and turbidity but inefficient in removing the color.Muda et al. reported success and benefit of the two-phase process. In developing biological methods for decolorization in a future where the first phase involves anaerobic processes followed by aerobic process (Bhatia,Sharma , Singh , S. Kanwa,2017). .

2.3.2 Fungal biodegradation of dyes

Different fungal species have been reported and have been tried for treating the wastewater discharge from dying industries (Aust, S. D. 1990). Combinations of aerobic and anaerobic treatment by different microbes have shown promising results for biological degradation of textile dyes (Lade, H., Govindwar, S., and Paul, D. 2015).Several studies on fungal based dye decolorization have been conducted to replace present chemical and physical treatment methods.

2.3.3 Microbiological Decomposition

The application of microorganisms for the biodegradation of synthetic dyes is an attractive and simple method by operation. However, the biological mechanisms can be complex. Large number of species has been tested for discoloration and mineralization of various dyes. The use of microorganisms for the removal of synthetic dyes from industrial effluents offers considerable advantages. The process is relatively inexpensive, the running costs are low and the end products of complete mineralization are not toxic (Ademoroti, C.M.A., 1979). Stolz reviewed the various aspects of the microbiological decomposition of synthetic dyes. Besides the traditional wastewater cleaning technologies, other methods have been employed in the microbial discoloration of dyes. The application of microorganisms for the biodegradation of synthetic dyes is an attractive and simple method. Unfortunately, the majority of dyes are chemically stable and resistant to microbiological attack. The isolation of new strains or the adaptation of existing once to the decomposition of dyes will probably increase the efficiency of microbiological degradation of dyes in the near future (Stolz, A., 2001).

2.3.4 Chemical dye removal method

Chemical dye removal methods are methods utilizing chemistry or its theories in accomplishing dye removal. Conventional chemical dye removal methods are advanced oxidation process, electrochemical destruction, Fenton reaction dye removal, oxidation, ozonation, photochemical ultraviolet irradiation, coagulation and flocculation. Most of the chemical dye removal methods are costly compared to biological and physical dye removal methods with an exception to the electrochemical degradation dye removal method (Katheresan, Kansedo, and Lau, 2018).

2.3.5 Coagulation and flocculation

Flocculation is an essential process in water and in industrial wastewater treatment. Several studies have been reported on the performance and optimization of coagulants, determination of pH and investigation of flocculants addition. Coagulation – flocculation process has been found to be cost effective, easy to operate and energy saving treatment alternatives. Coagulant dosage varies in a wide range aiming at maximum removal efficiency of pollutants using minimum doses at optimum pH. Coagulation can be interpreted as the conversion of colloidal and dispersal particles in to small visible flock upon addition of a simple electrolyte (Ahmed, Chuo, and Khatoon, 2015).

Increasing the concentration of the electrolyte results in a compression of the electrical double layer surrounding, each suspended particle decreases in the magnitude of the repulsive interactions between particles and destabilization of the particles. The most common coagulant used in wastewater treatment is alum $Al_2(SO_4)_3.4H_2O$ and PAC (Poly Aluminum Chloride). Flocculation is used to describe the process whereby the size of particles increases as a result of particle collisions. The purpose of flocculation is to produce particles, by means of aggregation, that can be removed by inexpensive particle separation procedures such as gravity sedimentation and filtration. The combined action of coagulation, flocculation and settling is named clariflocculation. Settling needs stillness and flow velocity, so these three processes need different reactions tanks (Ahalya N. Ramachandra T.V. and Kanamadi R.D. 2002).

2.3.6 Chemical oxidation

Chemical operations can oxidize the pigment in the printing and dyeing wastewater as well as bleaching the effluent. Currently, Fenton oxidation and ozone oxidation are often used in the wastewater treatment. Oxidative processes represent a widely used chemical method for the treatment of textile effluent, where decolorization is the main concern.

2.3.6.1 Fenton's reaction

Among the oxidizing agents, the main chemical is hydrogen peroxide (H_2O_2), variously activated to form hydroxyl radicals, which are among the strongest existing oxidizing agents and are able to decolorize a wide range of dyes. A first method to activate hydroxyl radical formation from H_2O_2 is the so called Fenton reaction, where hydrogen peroxide is added to an acidic solution (pH=2-3) containing Fe^{2+} ions. Fenton reaction is mainly used as a pre-treatment for wastewater resistant to biological treatment or/and toxic to biomass. The main drawbacks of the method are the significant addition of acid and alkali to reach the required pH, the necessity to abate the residual iron concentration, too high for discharge in final effluent, and the related high sludge production (Z. wang, M. Xue, K. Huang and. Liu., 2002).

2.3.6.2 Ozone oxidation

Ozone oxidation is a very effective and fast decolorizing treatment, which can easily break the double bonds present in most of the dyes. Ozonation can also inhibit or destroy the foaming properties of residual surfactants and it can oxidize a significant portion of COD. Moreover, it can improve the biodegradability of those effluents which contain a high fraction of non-biodegradable and toxic components through the conversion (by a limited oxidation) of recalcitrant pollutants into more easily biodegradable intermediates. As a further advantage, the treatment does increase neither the volume of wastewater nor the sludge mass (Z. wang, M. Xue, K. Huang and Liu, 2002).

2.3.7 Physical dye removal method

Physical dye removal methods are usually straightforward methods commonly accomplished by the mass transfer mechanism. Conventional physical dye removal methods are adsorption, coagulation or flocculation, ion exchange, irradiation, membrane filtration, Nano filtration or ultra-filtration and reverse osmosis. Among the three methods (biological chemical and physical), branches of physical dye removal are the most commonly used methods. These methods are often chosen for its simplicity and efficiency. By far, this method requires the least amount of chemicals compared to the biological or chemical dye removal methods. This method does not deal with living organisms hence is considered to be more predictable than the other two dye removal methods(Katheresan, Kansedo, and Lau, 2018)..

2.3.7.1 Membrane Technology

Various separation techniques, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), have been applied in the textile industry for the recovery of sizing agent from effluent. Some of these methods constitute effective treatments for removal of color from wastewater regardless of the type of dyestuff used. MF is of no use for wastewater treatment because of its large pore size. Membrane can act as a physical barrier to specific components in wastewater without degradation of these components. The specification of a membrane system treating dye waste is guided by a number of factors including the dyeing process, the type of dye to be removed, the chemical composition of the waste stream and above all the maximum allowable expenditure. The membrane used for color remove must have reasonable chemical and thermal stability, allowing operation at high flux, and capable of withstanding wide ranges of pH, temperature and solvents, and thus have been found to be suitable for the separation of organic dyes from the textile effluents(Singh and Arora, 2011).

2.3.7.2 Adsorption

Adsorption is an exceptional dye removal technique as it does not require any additional special equipment and is easy to conduct (Wang, Huang, Xue, Liu, 2011). Besides that, no pre-treatment is required for the commencement of adsorption. Sometimes the adsorption technique is used as post-treatment after using the conventional method to decolorize dyes effluents. The adsorption process is best conducted with porous materials so that dye removal is efficient. One desirable quality of the adsorption technique is that no additional hazardous materials will results at the end of the process making it suitable for pollution control applications (B. Bouabidi, El-Naas, Cortes, McKay, 2017). To ensure the production of high quality treated effluents, proper design of adsoption system is crucial. Furthermore, in order to ensure a higher rate of adsoption, the factors affecting adsoption should be acknowledged and used as guidance.

Dyeadsorption is a result of two mechanisms (adsorption and ion exchange) and is influenced by many factors as dye/adsorbent interaction, adsorbent's surface area, particle size, temperature, pH, and contact time. The removals of dyes from effluent using adsorption process provide an alternative treatment, especially if the adsorbent is inexpensive and readily available. Physical adsorption techniques are generally considered as the preferred means for removing and purifying organic substances due to their high efficiency and ability to separate a wide range of chemical compounds (Rosemal H. Mas Haris and Kathiresan, 2009).

Adsorption is a surface phenomenon with common a mechanism for both organic and inorganic pollutants removal. When a solution containing absorbable solute comes into contact with a solid with a highly porous surface structure, liquid–solid intermolecular forces of attraction cause some of the solute molecules from the solution to be concentrated or deposited at the solid surface. The solute retained (on the solid surface) in adsorption processes is called adsorbate, whereas, the solid on which it is retained is called as an adsorbent. This surface accumulation of adsorbate on adsorbent is called adsorption. This creation of an adsorbed phase having a composition different from that of the bulk fluid phase forms the basis of separation by adsorption technology (Katheresan, Kansedo, and Lau, 2018).In a bulk material, all the bonding requirements (be the ionic, covalent, or metallic) of the constituent atoms of the material are filled by other atoms in the material. However atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbate. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as physicsorption (characteristic of weal Van Der Waals forces) or chemisorptions (characterstic of covalent bonding). It may also occur due to electrostatic attraction (Tang, Yu, Pang, Zeng, Deng, Wang, Ren, Ye, Peng, Feng, 2017).

Table 2.2: Available processes of dye removal

Technology	Advantage	Disadvantage
Coagulation and Flocculation	Simple, economically feasible	High sludge production, handling and disposal problems
Biodegradation	Economically attractive, publicly acceptable treatment	Slow process, necessary to create an optimal favourable environment, maintenance and nutrition requirements
Adsorption on activated carbon	The most effective adsorbent, great, capacity, produce a high-quality treated effluent	Ineffective against disperse and vat dyes, the regeneration is expensive and results in loss of the adsorbent, non-destructive process
Membrane Separation	Removes all dye types, produce a high-quality	High pressures, expensive, incapable of treating large

	treated effluent	volume
Ion-Exchange	No loss of sorbent on regeneration, effective	Economic constraints, not effective for disperse dyes
Oxidation	Rapid and efficient process	High energy cost, chemicals required
Biosorption	Economically attractive, regeneration is not necessary, high selectivity	Requires chemical modification, non-destructive process

2.3.7.3 Bioadsorption

The accumulation and concentration of substances from aqueous solutions by the use of biological materials is termed as bioadsorption. Such substances can be organic and inorganic, and insoluble or insoluble forms. Bioadsorbentsfunction almost the same way regular adsorbent do, by accumulating and attaching roaming dye molecules from an adsorbate onto its surface through process a called reactive adsorption. There is existing research papers proving reactive adsorption an efficient as well as cost-effective process in dye removal processes (Srinivasan, Viraraghavan, 2010 and T. Yagub, KantiSen, Afroze, H.M. Ang, 2014). The biosorbents and their derivatives contain a variety of functional groups which can complex dyes. The biosorbents are often much more selective than traditional ion-exchange resins and commercial activated carbon adsorbents, and can reduce dye concentration to ppb levels (Comte S, Guibaud G and Baudu M, 2008).

Basic advantages of bioadsoption over other methods

In comparison to various physical, chemical and biological methods available for the treatment of textile industry effluent, adsorption is an effective and economical method for dye removal due to simple, flexible design and easy operation. Today, researchers have come out with study that has been focused on the low-cost biosorbents that are mainly obtained from agriculture waste and industrial by product since they required little processing which reduces the procedure cost and abundant in nature (Talwar B., Goyal S. and patnala P., 2012).Additionally this process provides an attractive alternative for the treatment of contaminated waters, especially if the sorbent is inexpensive and does not require an additional pre-treatment step before its application (A. Dabrowski, 2001)**.** Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost and insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substances (Bhattacharyya,K.G.,Gupta,S.S.Kaolinite, 2006)**.** The process of adsorption has an edge over the other methods due to its sludge free clean operation and completely removed dyes, even from the diluted solution (Velmurugan, P. "Rathinakumar, V. and Dhinakaran, G, 2011)**.**The main advantage of adsorption technique is the opportunity to improve the nature and properties of adsorbent particles used. The trend of recent research leads to the application of cost-effective materials, which can adequately adsorb the dyes from solutions even presenting slightly lower capacities. The need of the market is to limit the procedure costs regarding the environmentally-friendly nature of the techniques suggested (George Z. Kyzas, Jie Fu and Kostas A. Matis., 2013)**.**

2.4 Categories of adsorbents

The Categories of adsorbents used in sorption process are activated carbon, naturally occurring materials, synthetic polymers, agro waste materials, industrial waste, activated carbon from agro waste materials and bioadsorbents.

2.4.1 Adsorption using commercially activated carbon

Among all the sorbent materials available, activated carbon is the most popular for the removal of pollutants from wastewater (Babel and Kurniawan, S. Babel and T.A. Kurniawan, 2003). In particular, the effectiveness of adsorption on commercial activated carbons for removal of a wide variety of dyes from wastewaters has made it an ideal alternative to other expensive treatment options (R. Ramakrishna and T. Viraraghavan, 1997). This capacity is mainly due to their structural characteristics and their porous texture which gives them a large surface area, andtheir chemical nature which can be easily modified by chemical treatment in order to increase their properties. However, activated carbon presents several disadvantages (Babel and Kurniawan, S. Babel and T.A. Kurniawan, 2003).it is quite expensive, the higher the quality, the greater the cost, non-selective and ineffective against disperse and vat dyes. The regeneration of saturated carbon is also expensive, not straightforward, and results in loss of the adsorbent. Commercially available activated carbons are usually derived from natural materials such as wood, coconut shell, lignite or coal, but almost any carbonaceous material may be used as precursor for the preparation of carbon adsorbents (F. Rozada, L.F. Calvo, A.I. Garcia, J. Martin-Villacorta and M. Otero, 2003,F. Rodriguez-Reinoso, and M. Otero, 2003 and F. Rodriguez-Reinoso, 1997). Coal is the most commonly used precursor for AC production (F. Carrasco-Marin, M.A. Alvarez-Merino and C. Moreno-Castilla, 1996) for its availability and cheapness.

2.4.2 Natural materials

Some of the natural materials that are considered for adsorption are: clay, siliceous material, and zeolites. Natural clay minerals are well known and familiar to mankind from the earliest days of civilization. Because of their low cost, abundance in most continents of the world, high sorption properties and potential for ion-exchange, clay materials are strong candidates as adsorbents. They are classified by the differences in their layered structures. There are several classes of clays such as smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pylophyllite (talc), vermiculite and sepiolite (T. Shichi and K. Takagi, 2000). The adsorption capabilities results from a net negative charge on the structure of minerals. This negative charge gives clay the capability to adsorb positively charged species. Their sorption properties also come from their high surface area and high porosity ([M. Alkan, Ö. Demirbas, S. Celikçapa and M. Dogan, 2004). In addition, the use of natural siliceous sorbents such as silica beads, glasses, alunite, perlite, and dolomite for wastewater is increasing because of their abundance, availability and low price.Among inorganic materials, silica beads deserve particular attention (T.N.T. Phan, M. Bacquet and M. Morcellet, 2000), considering chemical reactivity of their hydrophilic surface, resulting from the presence of silanol groups. Their porous texture, high surface area and mechanical stability also make them attractive as sorbents for decontamination applications. However, due to their low resistance toward alkaline solutions their usage is limited to media of pH less than 8 (Ahmed and Ram, 1992 M.N. Ahmed and R.N. Ram, 1992).

Zeolites are highly porous aluminosilicates with different cavity structures. Their structures consist of a three dimensional framework, having a negatively charged lattice. The negative charge is balanced by cations which are exchangeable with certain cations in solutions. Zeolites consist of a wide variety of species, more than 40 natural species. High ion-exchange capacity and relatively high specific surface areas, and more importantly their relatively cheap prices, make zeolites attractive adsorbents (Bernal MP, Lopez-Real JM., 1993).

2.4.3 Synthetic polymer

These are materials processed to suit the purpose of adsorption. For example, cyclodextrin is a polymer produced by cross linking of starch with a coupling agent (e.g chitosan) to form water insoluble networks (Oladipo, M.A., Bello, I.A., Adeoye, D.O., 2013).

2.4.4 Bioadsobents

✓**Biological (microbial) material -** Such as chitin, chitosan, peat, yeasts, fungi or bacterial biomass, are used as chelating and complexing sorbents in order to concentrate and to remove dyes from solutions.

✓**Agro waste materials -** These are waste materials from forest and poultry industries. They are available in large quantities and may have potential as a sorbent due to their physico-chemical properties and low cost. They contain various organic compounds such as lignin, cellulose and hemicellulose with polyphenolic groups that might be useful for binding dyes through different mechanisms. Examples are sawdust, wood, hen feather, sheep wool, corn cob, rice husk, coir pith, rice bran, wheat bran etc. (Oladipo, M.A., Bello, I.A., Adeoye,D.O., 2013).

✓**Activated carbon -** These are substances produced by carbonization of lignocellulosic materials. They are produced by placing the wastes in the furnace at a temperature of about 450^0C to drive away all other component except carbon. Materials that can be used are coconut shell, rice husk, sawdust, coir pith, date pits, bamboo, cassava peel, nutshells etc (Oladipo, M.A., Bello, I.A., Adeoye, D.O., 2013).

2.5 Industrial waste

These are materials collected after a particular product processing. They are otherwise called spent materials or by-products. Examples are carbon nanotubes, fly ash, bagasse, ash, sludge etc. (Oladipo, M.A., Bello, I.A., Adeoye, D.O., 2013).

2.5.1 Bioadsorpion mechanism

Biosorption is a physico-chemical process and includes such mechanisms as absorption, adsorption, ion exchange, surface complexation and precipitation. Bioadsorption mechanism is rather difficult to define because many mechanisms may contribute to the overall process depending on the substance to be sorbed, the biosorbent used, environmental factors and the presence or absence of metabolic processes in the case of living organisms. Adsorption is the physical adherence or bonding of ions and molecules onto the surface of another molecule, i.e. onto a two-dimensional surface. In this case, the material accumulated at the interface is the adsorbate and the solid surface is the adsorbent. If adsorption occurs and results in the formation of a stable molecular phase at the interface, this can be described as a surface complex. The variety of structural components present in biomass means that many functional groups are able to interact with dye species, e.g. carboxyl, phosphate, hydroxyl, amino, thiol, etc., to varying degrees and influenced by physico-chemical factors. Most solids, including microorganisms, possess functional groups like – SH, – OH, – COOH on their surfaces. Deprotonated ligands, e. g – RCOO-, behave as Lewis bases and adsorption of dye cations can be interpreted as competitive complex formation (Comte S, Guibaud G and Baudu M, 2008).In another case if adsorption occurs and continues through the formation of a new three-dimensional surface species, this new species can be defined as a surface precipitate. A number of different systems clearly exist in the continuum from adsorption and precipitation (Kiran B and Kaushik A, 2008).Precipitation, where bound species can act as loci for subsequent deposition, can lead very high uptake capacities. It should be noted that precipitation can occur even in simple laboratory biosorption systems depending on the substance and chemical conditions used (Ozdemir G, Ceyhan N and Manav E, 2005).also ion exchange is a mechanism of sorption which is the replacement of an ion in a solid phase in contact with a solution by another ion in the solution.ion exchange either cation exchange in which case exchange of positively charged ions (cations) occurs anion exchange in which case exchange of negatively charged ions (anions) occurs (Gadd GM and White C, 1989).

2.5.2 Factors affecting the bioadsoption process

There are many factors affecting dye adsorption such as temperature, solution pH, initial dye concentration, and chemical treatment, and contact time, dosage of adsorbent, agitation speed, and effect of competitive anions. Thus, the effects of these parameters are to be taken into account. Optimization of such conditions will greatly help in the development of industrial scale dye removal treatment process. In the next section, some of the factors affecting adsorption of dyes are discussed.

2.5.3 Effect of pH

One of the most important factors affecting the capacity of adsorbent in wastewater treatment is solution. The efficiency of adsorption is dependent on the solution pH, since variation in pH leads to the variation in the degree of ionization of the adsorptive molecule and the surface properties of adsorbent (Nandi B,GoswamiA,Purkait M.,2009).The surface properties of adsorbents, ionic state of functional groups and species of dyes are dependent on pH condition. Because hydrogen and hydroxide ions are adsorbed quite strongly, the adsorption of other ions is influenced by the pH of the solution. Bioadsorption of dye cationsis often reduced at low pH values because competition between cations and protons for binding sites arises. Conversely for anionic species, increased bioadsorption may be seen at lower pHvalues (Ho YS, Ng JCY and McKay G, 2000).

2.5.4 Effect of competitive Anions

Competition will also occur between cations or between anions of the dye species and such an effect can also depress bioadsorption of the dye of interest. This is because the adsorption of one substance will tend to reduce the number of open sites, hence the "concentration" of adsorbent available as a driving force to produce adsorption of the other substance, mutually depressing effects on rates of adsorption may be predicted (Ho YS, Ng JCY and McKay G, 2000).

2.5.5 Effect of chemical treatment

Chemically treating a bioadsorbent by acidic activation chemical may increase bioadsorption of anionic species by enhancing binding of the negatively-charged anions on the protonated surface. Similarly, chemically treating a bioadsorbent with a basic chemical may increase bioadsorptionofcationic species by enhancing binding of the positively charged cations on to the newly
deprotonated surface (Ho YS, Ng JCY and McKay G, 2000).

2.5.6 Effect of contact time

Removal of dye molecules will be very rapid initially and then slows down at later times because the binding sites will shortly become limited due to adsorption of ions on to adsorbent and the remaining vacant surface sites are difficult to be occupied by remaining ions due to the formation of repulsive forces between the dye ions on the solid surface and the liquid phase (Ho YS, Ng JCY and McKay G, 2000).

2.5.7 Effect of bioadsorbent dose

Bioadsorbent dosage is an important process parameter to determine the capacity of an adsorbent for a given amount of the adsorbent at the operating conditions. Generally the percentage of dye removal increases with increasing adsorbent dosage, where the quantity of sorption sites at the surface of adsorbent will increase by increasing the amount of the adsorbent. The effect of adsorbent dosage gives an idea for the ability of a dye adsorption to be adsorbed with the smallest amount of adsorbent, so as to recognize the capability of a dye from an economical point of view (Mustafa,Sen., Afroze, Ang, 2014). Dosage has a direct proportionality to removal efficiency while it has an inverse proportionality to adsorption capacity or maximum specific uptake (qm).increasing dosage increases ratio of binding sites to dye ions which results in more ions being adsorbed, hence a greater removal percentage. Conversely, specific uptake, which is the measure of amount of ions adsorbed per unit weight of adsorbent, decreases (Ho YS, Ng JCY and McKay G, 2000).

2.5.8 Effect of initial dye concentration

Increase in the concentration of the dye ions will result in an increase in the specific uptake until saturation of all the available binding sites is reached. In contrast, at low initial dye ion concentration, not all the binding sites on the adsorbent are fully bound. However removal percentage decreases with increasing initial dye concentration (Ho YS, Ng JCY and McKay G, 2000).in general, the percentage of dye removal decreases with an increase in the initial dye concentration, which may be due to the saturation of adsorption sites on the adsorbent surface. On the other hand the increase in initial dye concentration will cause an increase in the capacity of the bioadsorbent and this may be due to the high driving force for mass transfer at a highinitial dye concentration (Bulut Y, Aydin H.A 2006).

2.5.9 Effect of agitation speed

Adsorption efficiency increases as agitation speed is increased because of increasing kinetic energy between the dye molecules and the adsorbent. However, the effect of agitation usually plateaus at about 150rpm. This effect can be attributed to the increase in turbulence and the decrease in boundary layer thickness around the adsorbent particles as a result of increase in the degree of mixing (Fil B.A., Karcioglu Karakas z., 2013).

2.5.10 Effect of temperature

Effect of temperature is another significant physic-chemical process parameter because temperature will change the bioadsorption capacity of the adsorbent (Argun, Mehmet Emin., 2008). If the amount of adsorption increases with increasing temperature then the adsorption is an endothermicprocess. This may be due to increasing mobility of the dye molecules and an increase in the number of active sites for the bioadsorption with increasing temperature. Whereas the decrease of adsorption capacity with increasing temperature indicates that the adsorption is an exothermic process. This may be due to increasing temperature decreasing the adsorptive forces between the dye species and the active sites on the adsorbent surface as a result of decreasing the amount of adsorption(Salleh MAM, et.al, 2011).

CHAPTER THREE

3 Materials and Methods

3.1 Raw material and chemicals

Raw banana peel was used to prepare activated banana peel bio-adsorbent. The reactive blue dye was chosen as a model pollutant(adsorbate). All chemicals, consumables and reagents used in this studywere analytical grades bought from local markets in Addis Ababa, Ethiopia. A0.1M of H_2SO_4(99% pure) used to activate banana peel adsorbent.A0.1M HCl(Purity 99%) and 0.1 M of NaOH(99% pure) were used to adjust the desired level of pH during the experiments. Distilled water (5 µS/cm)was used throughout the experimental studies which was used for preparation and dilution of solutions.

3.2 Equipment and Instruments

Rotary orbital shaker was used to thoroughly mix the content of adsorbent and adsorbate solution. Magnetic stirrer hot plate was used for the batch adsorption experiments. Dry air Oven, with temperature control was used to dry raw material.pH meter was used to measure the level acidicity of the solutions.VIS-UVSpectrophotometer was used to measure the absorbance of adsorbent. Furnace was used to dry and determine the proximate composition of the samples. For the characterization of the adsorbent the following instruments were used: Scanning electron microscopy (SEM) to investigate the morphology of the material, Fourier transform-infrared spectrometer (FTIR)to determine the functional groups of the sample, thermal gravimetric analysis (TGA)to investigate the mass loss of the samples during thermal decomposition and to knowto what extent the adsorbent material resists or decompose upon heating,Brunauer-Emmett-Teller(BET) to quantify the surface area of the adsorbent synthesized.

3.3 Sample collection and preparation

The main raw material, waste banana peel was collected from juice house in Addis Ababa, Ethiopia. The banana peel was separated from unnecessary waste components manually. The peel was then washed with tap water approximately and rinsed with distilled water to remove the remaining dust materials. After the cleaning, the size of the peel was reduced manually approximately to 1cm to 2cm in order to accelerate the drying process. After all the dripping water was dried using sun drying, the peel was placed in an oven(Cooper technology, TD-1315/v/c, 2016) for 24hrs at 105 °C. The dried peel was powdered using attrition mill. The powdered banana peel was sieved (IC-205/EV) and the particle size below 125 μm was retained. It was then weighed and packed in an air tight plastic bag(Lin et al., 2021; Shrestha et al., 2021). The raw banana peel collected is depicted in Figure 3.1.

Figure 3.1. Raw banana peel collected from juice houses

3.4 Synthesize of activated banana peel bio-adsorbent

In this research, a two-stage activation process was followed; a physical activation succeeded by chemical activation. These two action methods would produce an enhanced porosity and hence relatively large surface area of activated banana peel bio-adsorbent. The physical activation particularly was a thermal treatment to vent out volatile components so that leaves vacant space on the precursor (banana peel)(Jjagwe et al., 2021). To effect this process, 20 grams of sample was subjected to 350 °C at a rate of 10 °C/ min for 3 hrsin furnace under N_2 environment as shown in Figure 3.2(Zamora-Ledezma et al., 2021). Having being cooled off and size reduced to 125 μm, the sample was further activated chemically at different operating conditions.

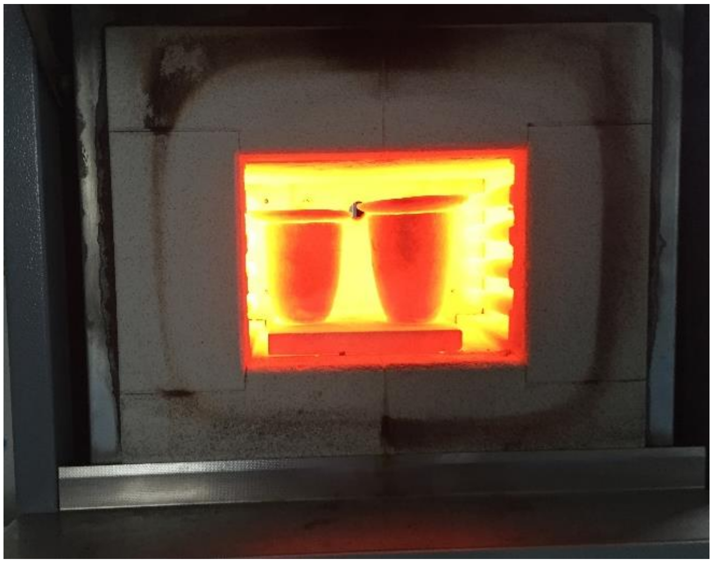

Figure 3.2. Thermal activation of banana peel

Acid activation is one of the most common chemical treatments and hasbeen used to increase the specific surface area and the number of acidic centers, modify the surface functional group and to obtain solids with high porosity (Shuma et al., 2019, S. Kumar et al., 2013a). The parameters considered for theactivation process are acid (sulfuric acid) concentration, activationtemperature andactivation time. These parameters were studied in a range of different levels to scrutinize the respective effect and to see at which operating condition the bio-adsorbent best can be synthesized. With this intention in mind,20 grams of banana peel powder particles were treated with different acid concentrations (H_2SO_4) of 0.5, 1.0, 1.5, 2.0 and 2.5M in 1000ml beakerand then kept in magnetic stirrer at fixed temperature of 70 °C and 3 hoursto investigated dye adsorbing capacity of the bio-adsorbent as acid concentration varied. To see the effect of activation temperature, the same sample was subjected to different temperatures of 50, 60, 70, 80 and 90 °Cat fixed acid concentration of 1.5M and activation time of 3 hours. Similarly, the effect of activation time was studied by varying it to 1, 2, 3, 4 and 5 hours at fixed acid concentration of 1.5M and activation temperature of 70 °C. After the solution was allowed to settle for 2 hours, then each sample was washed with distilled water to neutralize the pH and filtered with filter paper. The solid part was dried in oven at 105 ^{o}C for 24 hours. The setup of acid activation of bio-adsorbent samples is shown in Figure 3.3.

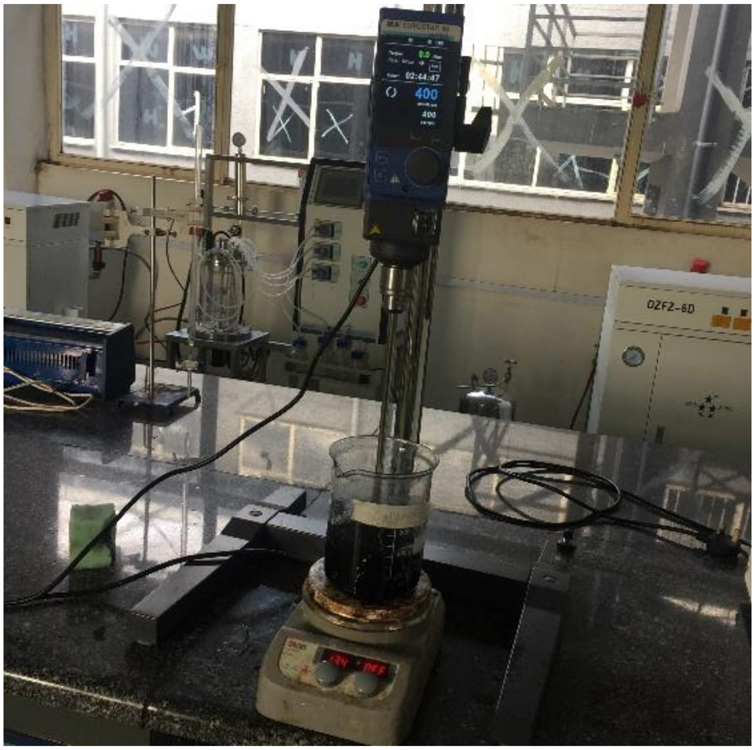

Figure 3.3. Laboratory setup for chemical activation process of banana peel bio-adsorbent

Now that the bio-adsorbent is produced, its capacity for dye adsorption was examined. For all experiments, 40 mg/L of dye was allowed to be adsorbed on each acid treated sample at contact time of60 minutes, pH of 3.0 and 2.0 gram of adsorbent dose. The filtrate after adsorption was analyzed in UV-spectrometer and the response (removal efficiency) was determinedagainst calibration curve (**Appendix A**).The sample with better removal efficiency was selected and characterized using different methods.

The summaryof parameters varied andfixed during acid activation of banana peel bio-adsorbent experiments are shown in Table 3.1.

Table 3.1. Parameters range of acid activation of banana peel bio-adsorbent

Varying parameter	Range of parameter					Fixed parameter
Acid concentration (M)	0.5	1.0	1.5	2.0	2.5	at 70 °c and 3 hours
Temperature (°C)	50	60	70	80	90	at 1.5 M and 3 hours
Time (hr)	1	2	3	4	5	at 70 °c and 1.5 M

3.5 Physicochemical Characterization of Adsorbent

The synthesized banana peel bio-adsorbent was characterized using scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET), XRD, thermal gravimetric analysis (TGA), Fourier-Transform infrared spectroscopy (FTIR), differential scanning calorimeter (DSC). Besides, proximate analyses and point zero charge determination had been performed.

3.5.1 Proximate determination of activated banana peel bio-adsorbent

The physio-chemical properties of the raw and activated banana peel samples were conducted to determine moisture content, volatile matter, fixed carbon and ash content using ASTM standard procedures. To determine the moisture content, 2 grams of sample was dried in oven at 105±3°C for 24 hrs. The mass of the samples before and after drying was weighed and the moisture content was calculated using **Eq**. 3.1.

$$MC = \frac{(M_0 - M_f)}{M_0} * 100\% \quad \text{Eq. 3.1}$$

Where, M_C is moisture content of the sample, %

M_0 is the mass of sample before drying, gram

M_f is the mass of the sample after drying, gram

The ash content of the samples was evaluated by igniting 2 grams of sample at 650 °C for 3 hrs in a furnace. It was determined by dividing the residue mass by the initial mass as is given in **Eq**. 3.2.

$$AC = \frac{M_r}{M_0} * 100\% \quad \text{Eq. 3.2}$$

Where, AC is the ash content of the sample, %

M_r is the residual mass of sample after burning, gram

M_0 is the mass of sample before burning, gram

Similarly, a 2 gram of sample was burnt in a furnace at 950 °C for 7 min to determine the volatile content of the sample by comparing the mass difference (**Eq**, 3.3).

$$VMC = \frac{W_0 - W_f}{W_0} * 100\% \quad \text{Eq. 3.3}$$

Where, VMC is the volatile matter content of the sample, %

W_0 is the weight of sample after drying, gram

W_f is the weight of sample before drying, gram

The fixed carbon content of the sample was calculated by subtracting the sum of moisture content, volatile content and ash content altogether from 100%.

3.5.2 pH of Point of Zero Charge Determination

Point zero charge is the point at which the net charge on the adsorbent surface is zero (Saruchi & Kumar, 2019). The surface charge of the adsorbent depends on the pH of the solution and its pH of point zero charge, pH_{pzc}(Liu et al., 2010). The adsorbent surface will be negatively charged when $pH > pH_{pzc}$ and positively charged if the $pH < pH_{pzc}$(Belachew & Hinsene, 2020).

A1.5-gram adsorbent was added in to 45 mL of 0.1N KNO_3 solution in the pH range of 2, 4, 6, 8, 10, 12, and 14. The initial pH solution was adjusted by adding drops of 0.1N NaOH and HCl solutions. Each flask was sealed and shaken thoroughly for 48 hr at room temperature. Finally, the pH was measured and recorded. The net charge (ΔpH) on acid and base activated kaolin surface was determined by the difference between initial pH and pH after 48 hrs. The pH values are plotted along the x-axis and ΔpH along y-axis, the data obtained from the experiment are plotted and the intersection point is taken as a reference for determining the pH_{PZC}.

3.5.3 Scanning Electron Microscopy (SEM) of raw and activated banana peel

To have a close look at the morphology of a prepared raw and activated banana peel bio-adsorbent were plated on aluminum stub coated with carbon conductivity tape sample holder and put into SEM (FEI, INSPCT-F50, Germany). The operating conditions used to observe the SEM image were 20 kV, 16 mm working distance, more than 5000x magnification, 20 µm scale and vacuum pressure.

3.5.4 Brunauer-Emmett-Teller (BET) surface area analyzer

A 0.4 gram of sample was weighed using analytical electronic balance (AD-300-3, 0.001 resolution) and placed in a sample holder. The sample was put in to the preparation unit of the surface analyzer (Horiba 96000 series) where the sample was subjected to 150°C temperature for 2 hour to remove (degas) the moisture content. After being cooled off, the sample was weighed again and the weight was recorded. The prepared sample was transferred to the surface area test part of the BET. The environment of the system was filled with helium gas used as carrier by replacing the air available in the sample holder. The system was calibrated each time it runs by injecting 1 cc (cubic centimeter) nitrogen gas. Thereafter, a mixture of 20, 30, and 50% of nitrogen and helium of 2 bar each were injected into the system intermittently as required. Simultaneously, the sample was cooled indirectly by liquid nitrogen at temperature of -196 °C during which nitrogen gas in the sample behaved like liquid and was adsorbed to form monolayer on the surface of the sample. When the cooling system was removed the adsorbed nitrogen molecules desorbed and were counted by conductivity meter detector. Based on the single nitrogen molecule surface area and the nitrogen adsorbed-desorbed of the multipoint data, the surface area of the sample was determined.

3.5.5 Thermal gravimetric analyses (TGA) of banana peel

Some 20 grams of raw andactivated banana peel bio-adsorbent samples weighed and placed in to ceramic sample holder separately. The sampleswere then put in to a temperature-controlled TGA cell (DTG-60H) and were set to decompose from ambient temperature to 800 °C.The percentage of mass loss as function temperature was recorded and analyzed.

3.5.6 Fourier-Transform Infrared Spectroscopy (FTIR)

Functional groups present in the well prepared raw and activated banana peel bio-adsorbent were analyzed using FTIR (Thermo Scientific iS50 ABX) instrument equipped with ATR (attenuated total reflection) accessory, Potassium bromide (KBr) beam splitter and detector. After the background was taken, the samples were placed on the sample holder and IR light source was applied to collect data at 32 resolution& 16 number of scans. Infrared solution was analyzed in the range of 4000 and 400 cm^{-1} wavenumber.

3.6 Experimental design and optimization of adsorption processes

3.6.1 Dye solution and calibration curve preparations

In the present study batch adsorption experiments were carried out to achieve the optimum operating conditions for the removal of the selected dye (Banerjee, Chattopadhyaya, 2013).Reactive blue dye solution with a concentration of 1000mg/l was prepared as a stock solution. In order to know the maximum wave length absorbency of Reactive blue dye, 25mg/L of the dye solution was taken and scanned using UV-Vis spectrophotometer (DR 5000). The maximum wave length (λmax)and absorbance of the dye was taken and scanned from 300 to 700nm using UV/VIS spectrometer and it was found at 660 nm.Anda series of batch experiments was made by diluting this solution. Reactive blue dye solutions with concentration ranging from 0–100mg/l wasprepared by dilution of the stock solution.

3.6.2 Batch adsorption studies

A preliminary and optimization of interactive parameters using Response Surface Methodology (RSM) have been studied to examine the adsorption capacity of the activated banana peel bio-adsorbent at different operating conditions. With these methods employed, the preliminary results were the inputs for the interaction effect. The interaction effects that variables have on the adsorption processes were studied using RSM (response surface methodology) followed by CCD (central composite design).

Reviewing different articles out there in the literature, four parameters that are considered to affect the adsorption processes mostly were found to beadsorption time, pH, adsorbent dose and initial dye concentration.

3.6.2.1 Preliminary study of individual parameters

The influence of each parameter on the dye adsorption uptake capacity of acid activated banana peel bio-adsorbent was studied based on the one variable at a time approach. Therefore, adsorption time ranging from 20–140 min, pH from 1–7, adsorbent dose from 1.0–4.0 g/L and dye initial concentration from 10–70 mg/L have been considered. In this approach, only the effect of one variable was examined while the others were remained constant. Therefore, adsorption time was varied to 20, 40, 60, 80, 100, 120, 140 min and fixing the pH at 3, adsorbent dose at 2.0g/L and dye concentration at 40 mg/L, and the effect oftime on the adsorption process of dye on the surface of activated banana peel was studied (Huang et al., 2020). Similarly, pH was varied as 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, and 7.0, adsorbent as 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, and 4.0 g/L and dye initial concentration as 10, 20, 30, 40, 50, 50, 60 and 70 mg/L. The parameters considered along the level studied is shown in Table 3.2.

Table 3.2. Parameters and parameter levels for preliminary study

Factors	Unit	Level						
Adsorption time	min	20	40	60	80	100	120	140
pH	–	1.0	2.0	3.0	4.0	5.0	6.0	7
Adsorbent dose	g/L	1.0	1.5	2.0	2.5	3.0	3.5	4.0
Initial concentration	mg/L	20	30	40	50	60	70	80

A 0.1M of NaOH and HCl solutions were used to adjust the pH of adsorption process as was the case required. A cylindrical flask was used to allow the adsorption process at fixed mechanical stirring of 300 rpm. The filtrate was filtered through Whatman filter paper, and analyzed for residual chromium concentration. The response (removal efficiency) was determined using (**Eq**. 3.4). The concentrations of dye after the adsorption process were determined by UV-spectroscopy. Calibration curve of known dye concentration (mg/L) versus absorbance (%) was drawn at concentrations of 0, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mg/L to get the concentration of residual dye in the solution (**Appendix A**). The filtrate from each experiments was analyzed using UV-spectrometer and the residual concentrations were read against calibrated values(Harsha Hebbar et al., 2018).

$$R(\%) = \frac{(C_0 - C_f)}{C_0} * 100 \quad \text{Eq. } 3.4$$

Where, R is the percentage removal (amount adsorbed), %

C_0 is the initial dye concentration, mg/L

C_t is the final dye concentration, mg/L

3.6.2.2 Effects of parameters interaction and model evaluation using RSM-CCD

Preliminary studies give insight about the effect of parameters individually on the adsorption process adsorbates on adsorbents, putting aside the effect they have all together. To investigate the adsorption process yet the more, consideration of interactive effect of parameters on the process makes a logical sense. The preliminary study, however, is useful in terms of level of parameters determination and the ranges are used in the interaction and optimization processes that subsequently followed. The interaction effect and optimization of parameters were performed using response surface methodology (RSM).

Based on the preliminary experiments conducted, the levels of each parameter which this research focused on were set as shown in Table 3.3. The adsorption time, thus, was ranged from

Table 3.3. Factors and corresponding levels for CCD experiments

Factors	Factor symbol	Unit	Level	
			Lower	Upper
Adsorption time	A	min	40	80
pH	B	–	2	4
Adsorbent dose	C	g/L	1.5	2.5
Initial concentration	D	mg/L	30	50

The software design expert produced a total of 30 number of experiments based the empirical equation $2^n + 2n + c$; c is the number of center point experiments and 'n' is number of independent parameters (Guo et al., 2021). Response surface regression for the design response was analyzed by quadratic model **(Eq**. 3.5**)** generated by design expert in the following format.

$$Y = \beta + \alpha_1 X_1 + \alpha_2 X_2 + \alpha_3 X_3 + \alpha_4 X_4 + \mathrm{b}_1 \mathrm{X}_1 X_2 + \mathrm{b}_2 \mathrm{X}_1 X_3 + \mathrm{b}_3 \mathrm{X}_1 X_4 + \mathrm{b}_4 \mathrm{X}_2 X_3 + \mathrm{b}_5 \mathrm{X}_2 X_4 + \mathrm{b}_6 \mathrm{X}_3 X_4 + \mathrm{c}_1 {X_1}^2 + \mathrm{c}_2 {X_2}^2 + \mathrm{c}_3 {X_3}^2 + \mathrm{c}_4 {X_4}^2 + \xi \qquad \text{Eq. 3.5}$$

Where, Y is response variable, β is intercept constant, α_1 - α_4 are main linear effects constant, $\mathrm{b}_1 - \mathrm{b}_4$ are linear-linear coefficients, and $\mathrm{c}_1 - \mathrm{c}_4$ are main quadratic effect coefficients, ξ is error and X_1–X_4 are the independent variables (Behboudi-Jobbehdar et al., 2013).

For a four-factor system, a total of 30 experiments as shown in Table 3.4were generated to determine the optimum conditions for optimum dye removal, taking into consideration the interaction among the factors.

Table 3.4. Experimental design matrix of factors for central composite design

Run	A: Contact time (min)	B: pH (-)	C: Adsorbent dose (g/L)	D: Initial concentration (mg/L)
1	80	4	2.5	50
2	40	4	2.5	50
3	20	3	2	40
4	60	3	2	40
5	60	3	1	40
6	60	3	2	40
7	100	3	2	40
8	80	2	1.5	50
9	60	1	2	40
10	60	3	2	40
11	60	3	2	40
12	80	4	2.5	30
13	40	4	1.5	30
14	60	5	2	40
15	80	2	1.5	30
16	60	3	2	20
17	80	2	2.5	30
18	60	3	2	40
19	40	2	2.5	30
20	80	4	1.5	50
21	40	4	2.5	30
22	80	2	2.5	50
23	80	4	1.5	30
24	40	4	1.5	50
25	60	3	2	60
26	40	2	1.5	30
27	40	2	2.5	50
28	60	3	3	40
29	60	3	2	40
30	40	2	1.5	50

3.6.2.3 Process variables numerical optimization

The model equation and parameters and terms were statistically evaluated using analysis of ariance (ANOVA) and multiple correlation coefficient (R^2). Allthe parameters studied were optimized using numerical optimization (RSM-CCD) to obtain high removal efficiency of activated banana peel adsorbent. The criteria for optimization and to solve the quadratic equation was set as is shown in Table 3.5. The optimum operation conditions obtained from the numerical optimization process was validated using triplicate experimental data as the same conditions.

Table 3.5. Optimization process criteria to solve the quadratic equation

Parameters	Goals	Lower limits	Upper limits	Importance
Adsorption time	In a range	40	80	3
pH	In a range	2	4	3
Adsorbent dose	In a range	1.5	2.5	3
Initial concentration	In a range	30	50	3
Removal efficiency	In a range	40	94	3

3.6.3 Adsorption kinetics and isotherms studies

To understand the effect of adsorption rate and the distribution of adsorbate between the phase, both adsorption kinetics and adsorption isotherms of common models were studied.

3.6.3.1 Kinetics

The rate at which the adsorbate (dye) being adsorbed on the surface of the adsorbent (activated banana peel) was studied using well-known kinetics models, namely pseudo first and second order models. These kinetics models show the efficacy of the adsorbent, indicating how fast or low it adsorbs the adsorbate. Kinetics is the dynamic of the adsorption process that describes the rate at which the adsorbent adsorbs the dye molecules (P. Kumar & Chauhan, 2019; Shobier et al., 2020). To investigate the adsorption of dye on the adsorbent surface, 2 g/L of sample was added to 500 mL of dye solution with initial concentration of 40 mg/L and pH of 3.0 in a flask of 1000 ml. The solution was stirred at 300 rpm using mechanical stirrer at room temperature. The adsorption process was examined at different adsorption time of 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, and160 min. Each filtrate from the adsorption was analyzed for trace concentration of dye. The dye concentration remained after adsorption in the given time interval was determined using spectroscopy at wavelength of 660nm (Bai et al., 2020; Khosravi et al., 2018; Shobier et al., 2020). The amount of dye adsorbed with respect of time (qt) was calculated using **Eq** 3.6 (Zhang et al., 2020). The kinetics of the dye on the surface on the activated banana peel bio-adsorbent samples were fitted to pseudo first-order and pseudo second-order kinetics models and the best fit was selected based on the higher value of R^2(Afolabi et al., 2020; Han et al., 2020).

$$q_t = \frac{(C_0 - C_t)}{m} * V \quad \text{Eq. 3.6}$$

Where, q_t is the amount of adsorbate adsorbed at time t, mg/g

C_0 is the initial concentration of dye, mg/L

C_t is the dye concentration at time t, mg/L

V is the volume of the dye solution, L

m is the mass of the adsorbent, gram

In the same fashion, the amount of adsorbate at equilibrium (q_e) was calculated using **Eq**. 3.7 as follows:

$$q_e = \frac{(C_0 - C_e) * V}{m} \quad \text{Eq. 3.7}$$

Where, q_e is the amount of adsorbate adsorbed at equilibrium, mg/g

C_0 is the initial concentration of dye, mg/L

C_e is the dye concentration at equilibrium, mg/L

V is the volume of the dye solution, L

m is the mass of the adsorbent, gram

For the 2 g/L mass adsorbent used, pH of 3.0 and dye concentration of 40 mg/L, to get equilibrium concentration 4hrswere used to guarantee equilibrium attained where the concentration no longer varies thereafter.

The pseudo first-order kinetics model is given by **Eq**. 3.8.

$$\frac{dq_t}{d_t} = K_1(q_e - q_t) \text{ Eq. 3.8}$$

Where, q_e is the adsorption capacity at equilibrium, mg/L

K_1 is the pseudo first-order rate constant, min^{-1}

t is the adsorpton time, min

Integration of the **Eq**. 3.9 with boundary conditions of t=0 to t=t and qt=0 to qt=qt give rise to **Eq**. 3.6.

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303}t \text{ Eq. 3.9}$$

The plot of $\log(q_e\text{-}q_t)$ versus t is linear correlation and thus K_1 and q_e can be determined from the slope and intercept respectively.

The pseudo second-order kinetics model similarly is expressed as **Eq**. 3.10 and when integrated as **Eq**. 3.11.

$$\frac{dq_t}{d_t} = K_2(q_e - q_t)^2 \text{ Eq. 3.10}$$

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + K_2 t \text{ Eq. 3.11}$$

Where, K_2 is the pseudo second-order adsorption rate constant, $g(mg)^{-1}min^{-1}$

This equation (**Eq**. 3.11) can be linearized by rearranging it to give **Eq**. 3.12.

$$\frac{t}{q_t} = \frac{1}{K_2 {q_e}^2} + \frac{1}{q_e}t \text{ Eq. 3.12}$$

Plotting (t/q_t) versus t, the constant K_2 and q_e were determined from the intercept and slope respectively.

3.6.3.2 Isotherm models

Isotherm models show the equilibrium amount of adsorbateavailable in the solution and the amount of adsorbateavailable on the surface of adsorbent. These models provide basic information to optimize and design adsorption systems, and yet show the distribution of adsorbate molecules in the liquid and solid phase when the system reaches equilibrium. Amongst others isotherm models, Langmuir and Freundlich are the most robust models used to mathematically predict equilibrium adsorption processes. The Langmuir isotherm model predicts the adsorption capacity of the adsorbent when monolayer is completely formed on the surface. It assumes monolayer sorption onto a completely homogenous surface with a finite number of identical sites, and with no interaction between adsorbed molecules. The Freundlich models, on the other hand, assume adsorption takes place on heterogenoussurfacesand multilayer adsorption.

Adsorption isotherm experiments were conducted by adding 2 g/L of adsorbent to 500 ml of different initial concentrations of 25, 45, 65, 85, 105, and 125 mg/L of the adsorbate to be adsorbed, pH of 3.0 and the adsorption process was agitated by a mechanical stirrer for 4hr of time. After each adsorption was finished, the adsorbent was filtered, the equilibrium concentrations were determined using UV-spectroscopy and the corresponding amount of adsorbate at equilibrium (q_e) was calculated.

The linear form of Langmuir isotherm model is given as **Eq**. 3.13.

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \text{ Eq. 3.13}$$

Where, C_e is the adsorbate concentration at equilibrium, ml/L

q_e is the amount of sorbate at equilibrium per unit mass of sorbent, mg/g

q_{max} is the complete monolayer sorption capacity at equilibrium, mg/g

K_L is the Langmuir equilibrium constant, L/mg

The experimental data were linearly regressed as C_e/q_e versus C_e, from which the Langmuir constants q_{max} and K_L were determined from the slope and intercept respectively.

Moreover, the experimental data were also fitted to Freundlich isotherm model which is expressed as **Eq**. 3.1

$$\ln(q_e) = (\frac{1}{n})\ln(C_e) + \ln(K_F) \text{ Eq. 3.14}$$

Where, K_F is the Freundlich constant related to adsorption capacity

n is the Freundlich constant related to adsorption intensity

The Freundlich constants were determined using the straight line plot of $\ln(q_e)$ versus $\ln(C_e)$ from which n was found from the slope and K_F form the intercept.

3.7 Reusability test of activated banana peel bio-adsorbent

Several adsorption and desorption process had been made to test the reusability of the activated banana peel bio-adsorbent over the adsorption of dye molecules. A 2 g/L of the adsorbent was allowed to adsorb 40 mg/L of dye molecules at ambient temperature for 4 hrsand shacked at 500 rpm. The precipitate was added to 500 ml of 0.1 M NaOH solution and shacked for 12 hrs and then washed several times using distilled water until the pH became neutral. The supernatant solution was analyzed and the removal capacity was determined. The adsorption-desorption process was repeated ten times until the capacity of the adsorbent fell below 50%.

CHAPTER FOUR

4 RESULTS AND DISCUSSIONS

4.1 Activated banana peel bio-adsorbent

A two-step (thermal and chemical) activation process produced an activated banana peel bio-adsorbent powder. The bio-adsorbent passed a subsequent physical (under 350 °C temperature and inert environment) and acid activation under different operating conditions; variation of acid concentration, temperature and activation time. The activated banana peel bio-adsorbent so produced was allowed to adsorb a solution of dye.

The recovery efficacy of the bio-adsorbent with respect of sulfuric acid concentration is shown in Figure 4.1. The adsorption process was conducted by varying acid concentration from 0.5 to 2.5 molarity and keeping activation time, pH, and dye dose at 60 min, 3, and 40 mg/Lrespectively. It can be observed from the graph that the removal efficiency increases at fast rate from 65–88%when the acid concentration increases from 0.5–1.5M. A further increment of acid concentration to 2.5M was found to cause the removal efficiency of the activated banana peel bio-adsorbent to decline all the way down to 76%. The result revealed that acid concentration has two-fold implications on efficacy of adsorbent synthesis. At relatively low concentration, the removal efficiency increases that implies the well preparedness of the sample and availability of more surface area for accommodation of dye molecules. It seems that the acid decomposed the amorphous part of the cellulose in the banana peel and causes a porous structure to be developed. The decline of removal efficiency at elevated acid concentration may attribute to the degradation of main structure and loss of porosity for dye molecules to be adsorbed on. A similar result can be seen from the study by Ali et al. (2016)where hydrochloric acid was used to activate banana peelfor removal hexavalent chromium from aqueous solution.

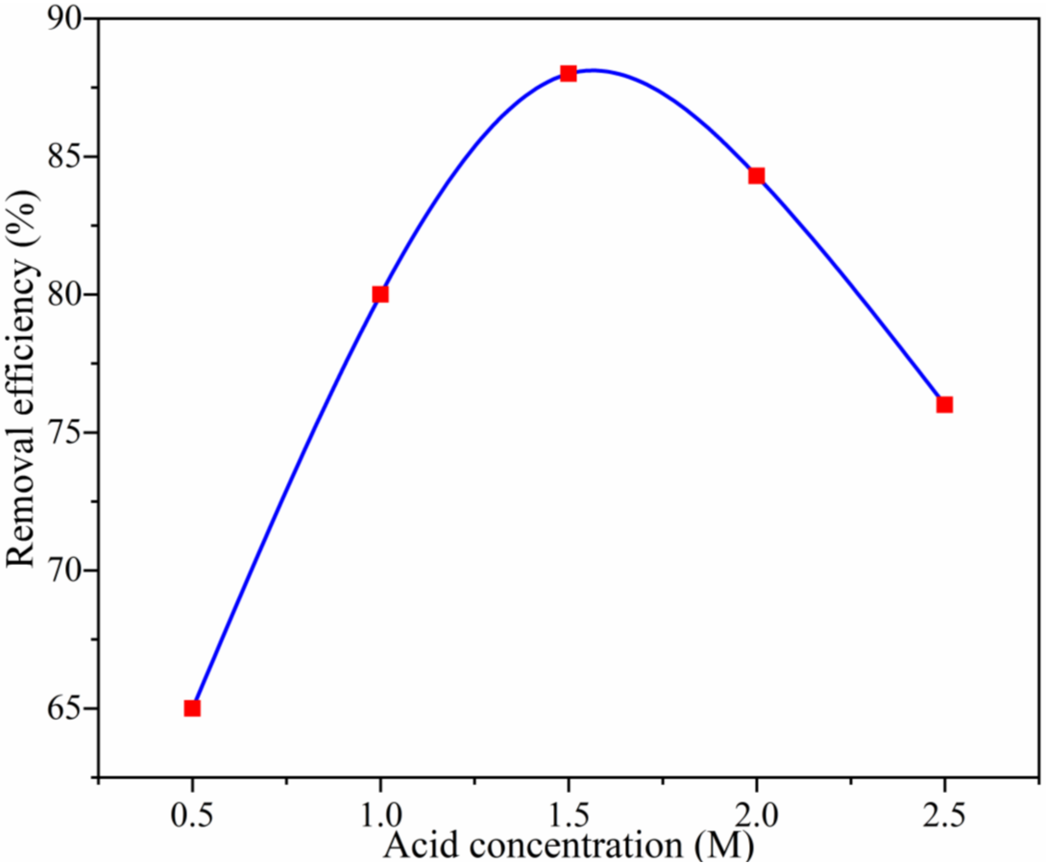

Figure 4.1. Removal efficiency of banana peel bio-adsorbent as function of acid concentration

The result of removal efficiency as function activation temperature and at given activation time of 3 hrs and acid concentration of 1.5M is demonstrated in Figure 4.2. It can clearly be seen from the graph that the removal efficiency increases from 66.3–87.5% as the activation temperature increases from 50–70 °C and remains slightly constant thereafter when the temperature further increases to 90 °C.At the given acid concentration and activation time, it appears that 70 °C (give or take) is favorable condition to synthesis banana peel bio-adsorbent. At these conditions, the activated banana peel bio-adsorbent might assume more room for adsorption of dye molecules on its surface. As is shown in the Figure, there is no significant removal efficiency of the activated banana peel bio-adsorbent when the activation temperature ups to 90 °C.Only 1.4% removal efficiency increment was found when the temperature varies from 70–90 °C. This would be an indication of waste of energy for heating to increase the recovery by factor of small margin. According to Jjagwe et al. (2021), for acid activation process, elevated temperature may lead to pore shrinkage and structural damages that reduces performance of adsorbents.

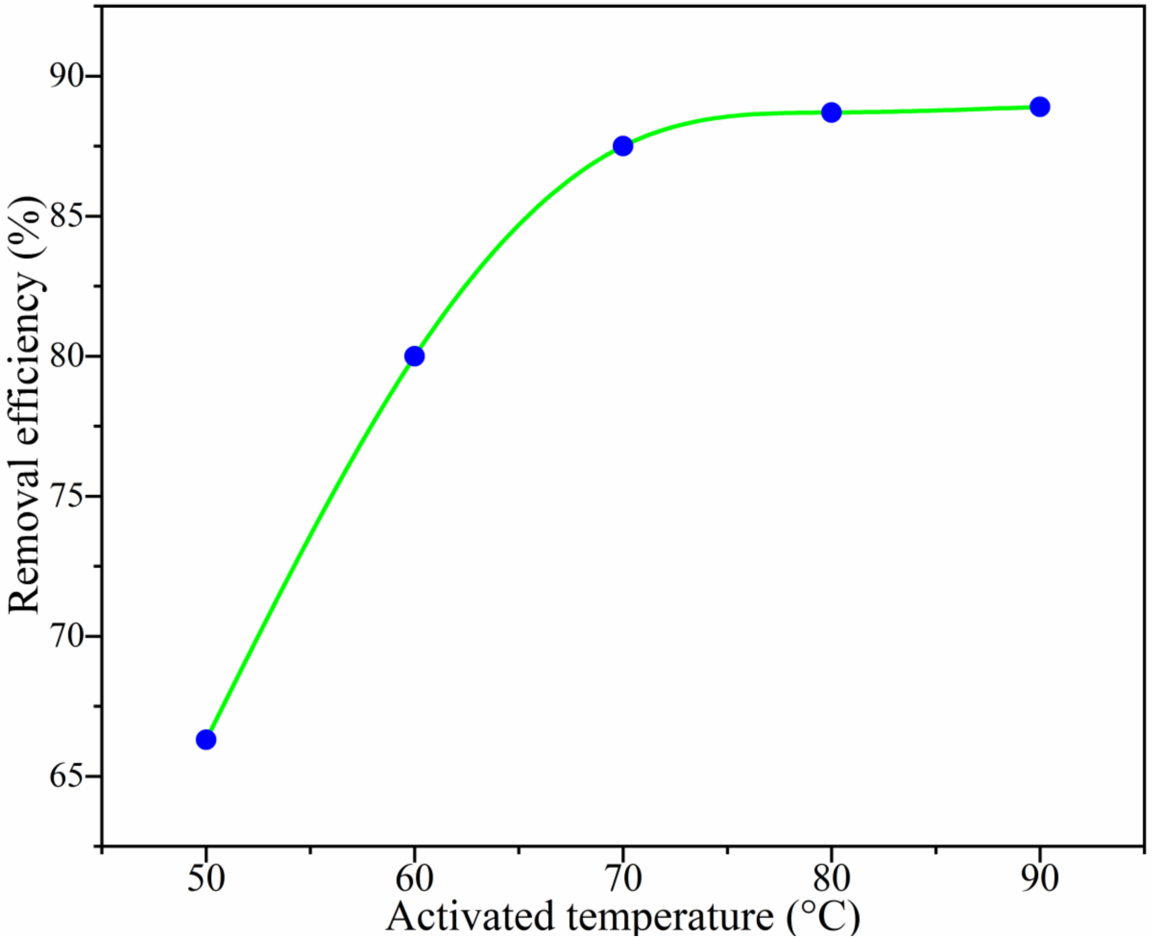

Figure 4.2. Removal efficiency as function banana peel bio-adsorbent of activated temperature

In a similar pattern, the graph of removal efficiency as function of activation time at acid concentration of 1.5M and activation temperature of 70 °C is depicted in Figure 4.3. Removal efficiency of the activated banana peel bio-adsorbent for dye molecules was found to increase rapidly from 56.2% to 89% when the activation time changes from 1 hr to 3 hrs. However, the efficiency does not change substantially despite the time goes to 5 hrs. Activation is a process, it requires time to take place. Hence, increase of efficiency till activation time sounds pretty well. As illustrated in the graph, activation time 3 hrs seems ideal operating condition along the optimum acid concentration and activation temperature.

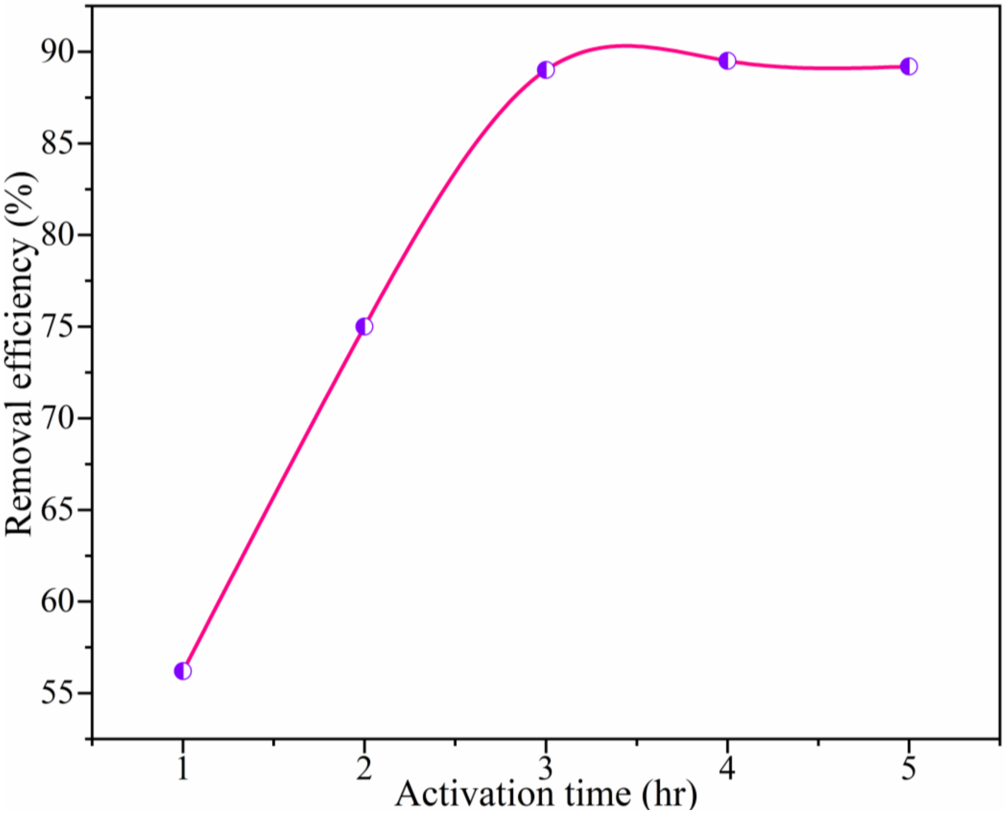

Figure 4.3. Removal efficiency of activated banana peel for dye as function of activated time

All told, it appears on the surface that acid concentration of 1.5M, activation temperature of 70 °C and activation time of 3 hrsare the favorable conditions to get an activated carbon the fulfills requirements of adsorbent. The experiments conducted unfolds the removal efficiency is high, if not, fairly high with other conditions considered, at the aforementioned operating conditions. The activated banana peel bio-adsorbent so produced is shown in Figure 4.4. It was mass produced for further use and characterized using different techniques.

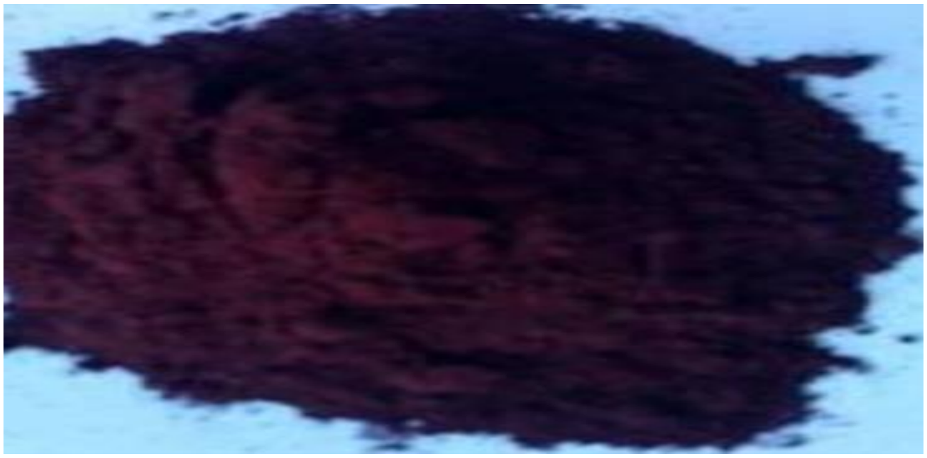

Figure 4.4. Activated banana peel bio-adsorbent

4.2 Characteristics of activated banana peel bio-adsorbent

The raw and physio-chemically activated banana peel bio-adsorbent were characterized using proximate analyses, Brunauer-Emmett-Teller (BET), Fourier-Transform infraredspectroscopy (FTIR), scanning electronmicroscopy (SEM), X-ray diffractive (XRD)and thermal gravimetric analyses. These methods showed that theactivation processes enhanced the surface of the activated banana peel bio-adsorbent. Better yet, thecharacterizations are litmus test that gives insights what happened after the activationprocesses and perhaps substantiate that the banana peel activated fulfills some minimumrequirements for adsorption process.

4.2.1 Proximate analyses of activated banana peel bio-adsorbent

The moisture content, volatile matter, ash and fixed carbon content of the prepared raw and activated banana peel bio-adsorbent are shown in Table 4.1. The parameters of the bio-adsorbent improved owing to the preparation and activation processes as compared to the raw banana peel.According to authors Hammouda&Mihoubi(2014)and Kramarenko et al. (2016) the moisture of content prepared raw banana peel is in between7-10% and that of activated is about 5–7%.

Table 4.1. Proximate analyses result of raw and activated banana peel

S/N	Parameter	Result (%)	
		Raw	Activated
1	Moisture content	9.8	4.5
2	Volatile content	19.1	17.7
3	Ash content	6.4	5.2
4	Fixed carbon	64.7	72.6

4.2.2 Point of zero charge (pHpzc) Analysis

The pH of point zero charge (pHpzc) for a given surface is the pH at which that surface has a net neutral charge (Railsback's, 2006). A plot of final pH values against the initial pH value (pHi) is illustrated in Figure 4.5. The significance of this pH values is that a given adsorbent surface will have positive charge at solution pH values less than the pHpzc and thus can be used to absorb anions adsorbates. On the other hand, the surface has negative charge at solution pH value greater than the pHpzcandis suitable to adsorb cations on its surface. From the Figure, it can be seen that the pHpzc of the banana peelsurface was found to be 4.67. At pH less than 4.67, the bio-sorbent is positively charged because H+ ions reside on surface. At pH greater than 4.67, the bio-sorbent is negatively charged due to the fact that H+ ions enter a high-pH solution, resulting in a negatively charged (H+ poor) surface (Railsback's, 2006).Also some studies reported for the adsorption of ionic reactive dyes over Alfa powder from leaf of StippaTenacissim(AFP)at lower pH value. The AFP was chemically treated to increase the adsorption rate of the powder. Theauthors found that adsorption capacity increased with decreasing pH of the solution.

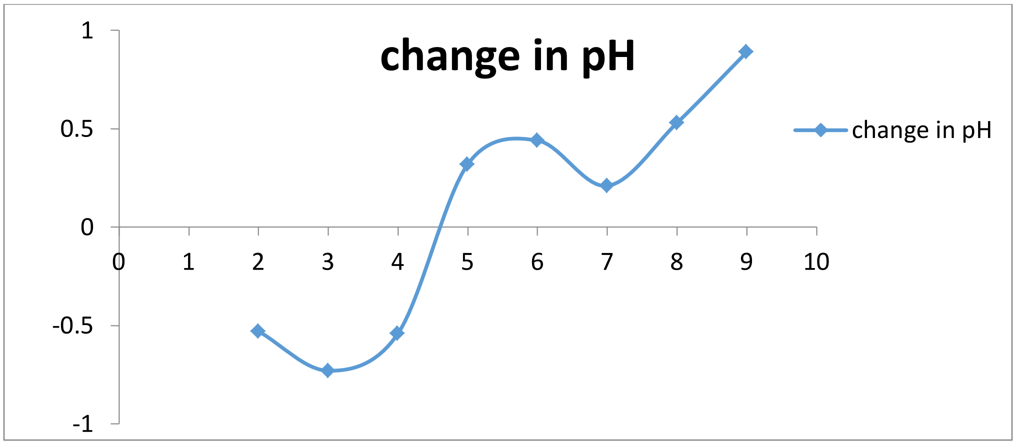

Figure 4.5. Point zero charge (pHpzc) of activated banana peel bio-adsorbent

4.2.3 Scanning electron microscope (SEM) image of activated banana peel bio-adsorbent

The morphology of raw and activated banana peel bio-adsorbent was analyzed with scanning electron microscope and the image is depicted in Figure 4.6 A and B respectively. The SEM images unveiled distinction of the images in terms of porosity and surfaces morphologies. Due to preparations and activation processes, the activated banana peel bio-adsorbent appears to have more surface and porosity. A more or less similar result can be seen from the work of Ramutshatsha-makhwedzha et al.(2022) in which case the activated adsorbent assumed much more surface.

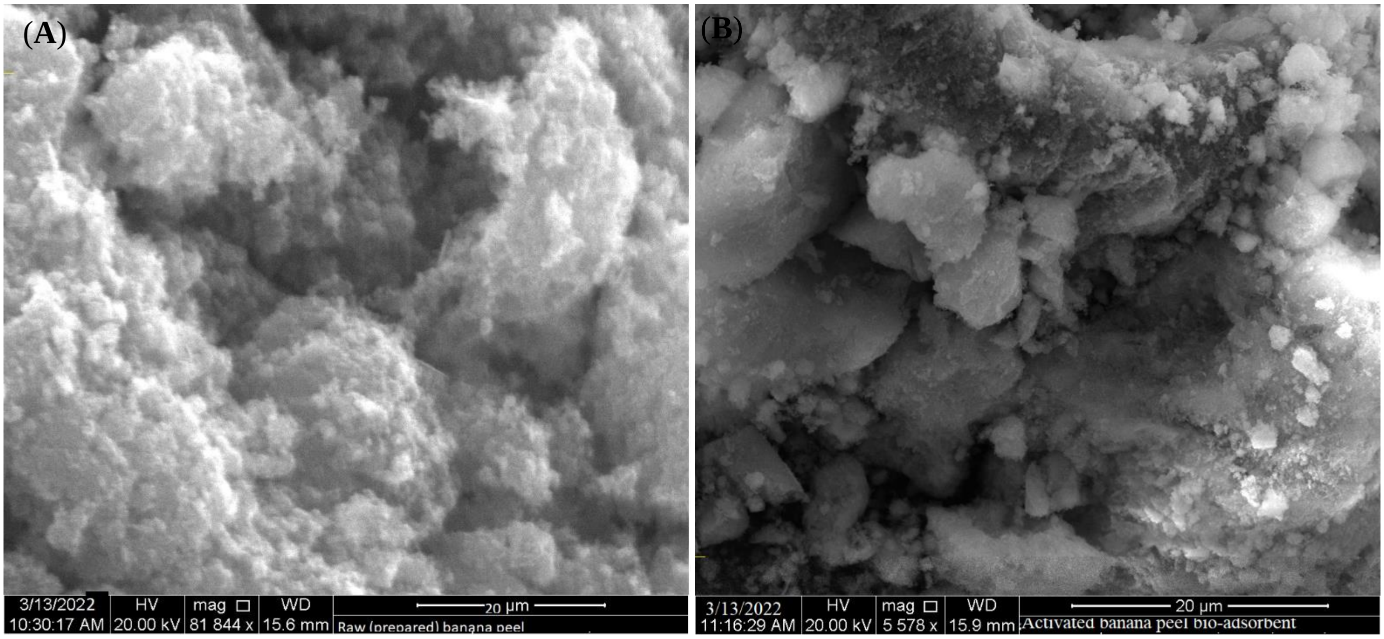

Figure 4.6. SEM results of raw (A) and activated (B) banana peel

4.2.4 BET analyses of raw and activated banana peel bio-adsorbent

Surface area is paramount characteristicsof adsorbents as adsorption process is a surface phenomenon. As is the case with all adsorbents, the activated banana peel produced by physical and chemical process is assumed to have enough surface to qualify for the dye adsorption. The surface areas of the raw and activated banana peel bio-adsorbent are found to be 25 m2/g and 302 m2/g respectively as can be seen on **Appendix B**.Sinto et al.(2018) reported 426 m^2/g surface area of activated banana peel using different techniques.

4.2.5 Fourier transform infrared spectrometry (FTIR) analyses

The FTIR spectra of raw and activated banana peel are shown in Figure 4.7. It can be seen from the spectra that there are some functional groups in both samples at 3684.94, 3619.38, 1117.03, 1005.01, 912.49, 672.95 and 529.33 wavenumbers (cm^{-1}). The weak peak at 3684.94 and 3619.38wavenumbers (cm^{-1}) may show the existence of moisture content, probably OH group. The peak at 1117.03 wavenumber (cm^{-1}) may attribute to the presence of C-O. It can be assumed that there fluoro compound, specifically C-F stretching group at the peak 1005.01. Perhaps, the peaks at 672.95 and 529.33 indicate the presence of halo compounds in the sample (**Appendix C**). Moreover, the change of peak(s) from strongto weak peak patterns might implythat compounds such as water have been removedcompletely or partially during the activationprocess. The two spectra are similar in theirpattern and are different in the quantity of thefunctional groups available. As can be seen from the work of Matei et al. (2021) thespectra of activated banana peel are in line with the spectra of these results.

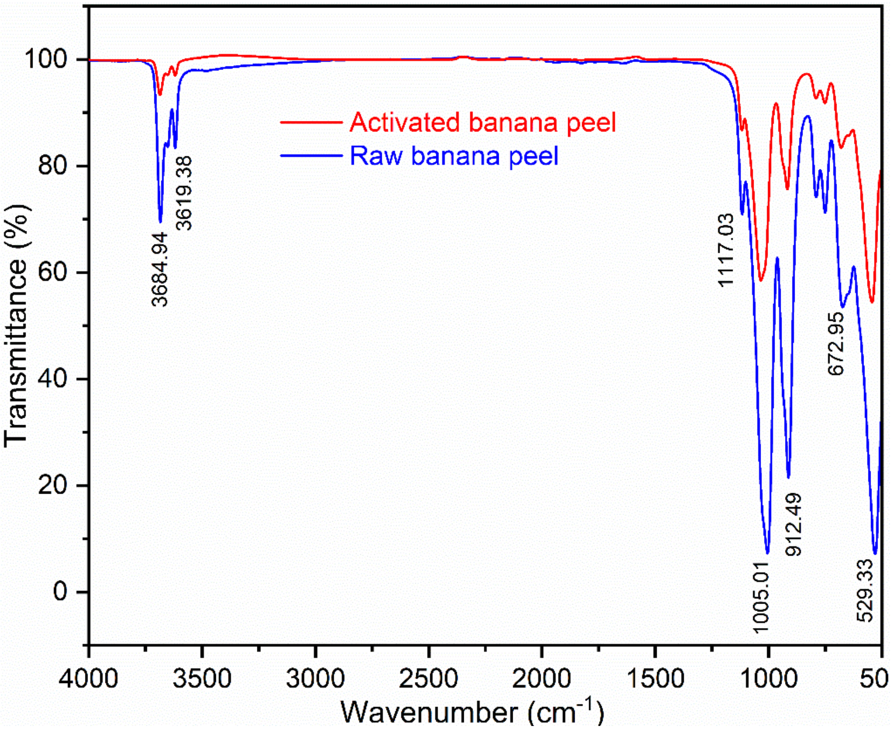

Figure 4.7. FTIR spectra of raw and activated banana peel

4.2.6 TGA of raw and activated banana peel bio-adsorbent

The thermal gravimetric analyses of both raw and activated banana peel has been conducted to analyze the effect of temperature on the sample under oxidized conditions. As shown in Figure 4.8, the activated bananapeel bio-adsorbent started to decompose after 300 °C and the raw sample at 150 °C.The mass loss inbetween 150 and 400 °C might be due to loss of bounded water and some other impurities. The sharp decline of both curve beyond 400 °C may attribute to decomposition of thesample into other smaller components such carbon dioxide.

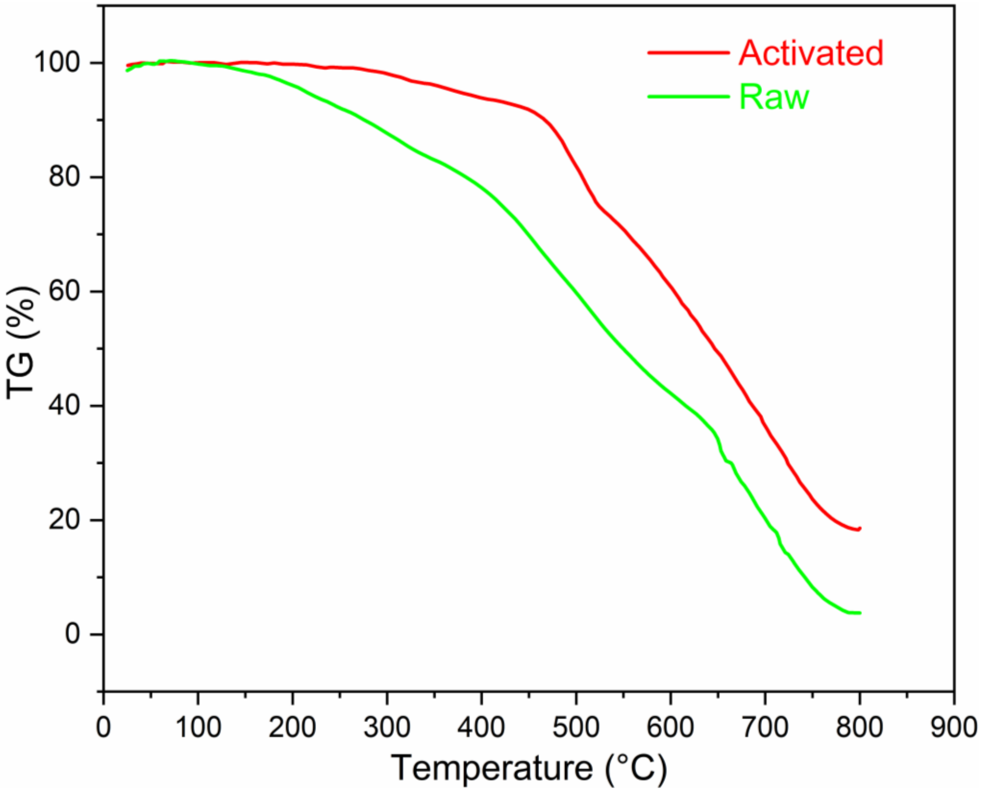

Figure 4.8. Percentage of mass loss of raw and activated banana peel with temperature

4.3 Study of batch adsorption processes

More often than not, it is an important milestone in course of activated carbon adsorbent development to allow the material synthesized to adsorb a pertinent adsorbate. On top of characterization the adsorption experiments give an insight on how appropriate the adsorbent is for a given adsorbate and are a mean to define and limit the range of parameters. Moreover, the adsorption experiments help pinpoint the best, if not optimum, operating conditions when the adsorbent is ever applied in a large scale. In doing so, the levels of the main adsorption parameters such as adsorption time, pH, adsorbent dose and initial dye concentration were scoped based on the effects they have on the adsorption process following the one factor at a time method. Up next, the effect of these operating conditions all at once took place.

4.3.1 Effect parameters one at a time

As preliminary test to scrutinize the adsorption of dye on the surface of the activated banana peel bio-adsorbent, adsorption time in the range of 20–140 min, pH from 1.0–7.0, adsorbent dose from 1–4 g/L and dye initial concentration from 20–80 mg/L were considered. When performing the experiments, adsorption time of 60 min, pH of 3, adsorbent dose 2 g/L and dye concentration of 40 gm/L were kept constant as the parameters varied.

4.3.1.1 Effect of adsorption time

The graph of removal efficiency and adsorption time that varied from 20–140 min, at fixed pH of 3, adsorbent dose of 2 g/L and dye initial concentration of 40 mg/L is depicted in Figure 4.9. The removal efficiency rapidly increases 48.6 to 87.6% as the adsorption time varied from 20 to 60 min. When the adsorption further increases to 140 min with the interval shown, the removal efficiency of the bio-adsorbent for dye adsorbateslightly increase and shortly after that tends to remain almost constant at 92%. The increment of removal efficiency as function of time implies that adsorption requires time to take place. According toZheng et al. (2021) study, adsorption mass transfer phenomenon that involves three main step: external diffusion, internal diffusion and attachment to the active site. As a result, it demands a certain period of time to adsorb a given amount of adsorbate and of course until all the surface available is taken up or equilibrium is attained. When equilibrium is about to attain, the removal efficiency approaches a constant value for the mass transfer between the adsorbent and the solution stops or remains the same with time.As is shown in Figure, it seems that around 60 min of adsorption time would suffice to remove about 88% of the dye adsorbate. Dwivedi et al.(2016)discussed 90 min to remove about 84% of cyanide contaminant. The adsorption time sufficient to removal most the adsorbatemay be short or long depending on the type of adsorbent and adsorbate the behavior of adsorption(Deng et al., 2014).

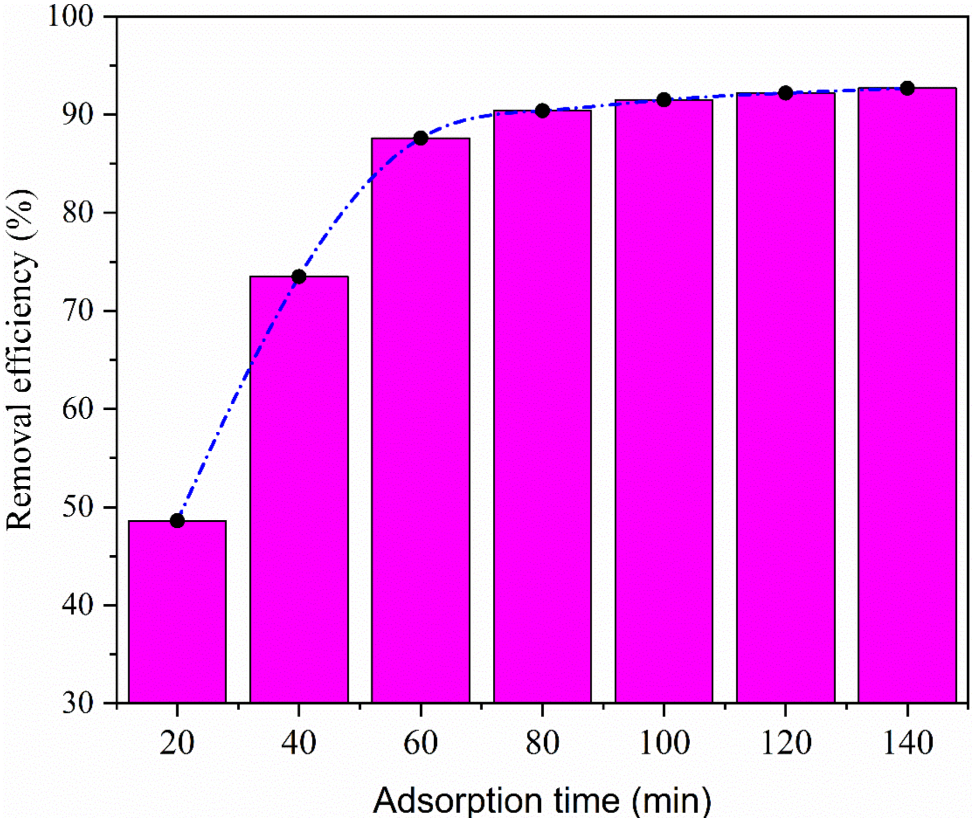

Figure 4.9. Graph of removal efficiency of activated banana peel bio-adsorbent with respect of adsorption time

4.3.1.2 Effect of pH

The pH value of the adsorption process plays an important role as it affects the ionization degree of the dye and thesurface properties of the bio-adsorbent.The interaction between dye and adsorbent depends on thesurface chemistry of the adsorbent and the phase chemistry of the adsorbate. The dyes are complex organic compounds with different functional groups and unsaturated bonds, so they show different levels of ionization at different pHs. In this regard, the biosorption of reactive blue dye solutions was carried out by varying pH of 1 to 7, with bio-adsorbent dose, initial dye concentration and adsorption time kept constantat 2 g/L, 40 mg/L and 60 min respectively.

Figure 4.10 showspercentage of the dye removedby the adsorbent at the aforementioned operating conditions. The removal capacity of the adsorbent below pH of 3 was found to be around 90% and sharply falls all the way down to 40% as the pH increases to 7.It can be deduced that the solution pH was directly related to the availability of positively charged active sites on the surface of the bio-sorbent to bind with the dye molecules. Since the point zero charge of this particular adsorbent surface is 4.7, the it assumes positively charged surface below pH of 4.7. as a consequence, adsorption of the anionic dye molecules becomes more favorable at low pH than high ones. The positive ions (H+) provide an electrostatic attraction between the adsorbent surface and the dye molecules leading to maximum adsorption.

Lima et al. (2008) considered the application of Brazilian pine-fruit shell as a bio-adsorbent to remove reactive red-194 dye from aqueous solution. The authors reported that the amount of dye uptake decreases with increasing the pH solutions from 2.5 up to 6. Elkady et al. (2011) have also investigated the assessment of the adsorption kinetics, equilibrium and thermodynamics for the potential removal of reactive red dye using eggshell bio-composite beads. They reported that the dye removal decreased from 59.3% to 0 after 180 min when pH increased from 1to 10. Gulnazet al. (,2011) showed that a decrease in pH from 5 to 1 caused a significant increase in the amount of reactive red 198 dye adsorbed by Potamogetoncrispus biomass. Rosemal et al. () found that reactive yellow 15 dyes had amaximum adsorption pH 2.

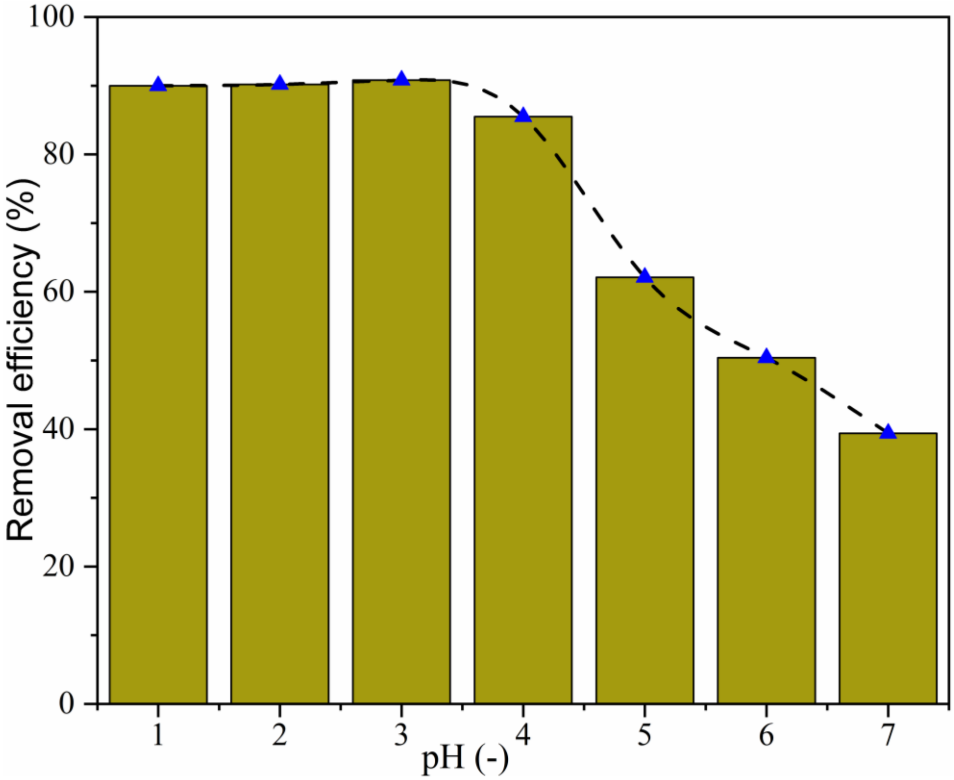

Figure 4.10. Effect of pH on the removal efficiency of activated banana peel bio-adsorbent to anionic dye

4.3.1.3 Effect of adsorbent dose

Adsorbent dose is amongst the essential parameters that strongly affects the adsorption process. The amount of adsorbent is directly related to the availability of room for the adsorbateto reside on. Increasing adsorbent dose implies increasing more surfaces for adsorption to take place and removal efficiency to shoot up. As is illustrated in Figure 4.11, the removal efficiency of the adsorbent increases from 64.4 to 91.5% as the adsorbent dose increases from 1to 2 g/L and appears almost constant thereafter. For a given dye concentration of 40 mg/L, it seems at high dose (say 3g/L and above) the amount of adsorbate molecules available are already taken and the removal efficiency tends to remain constant.

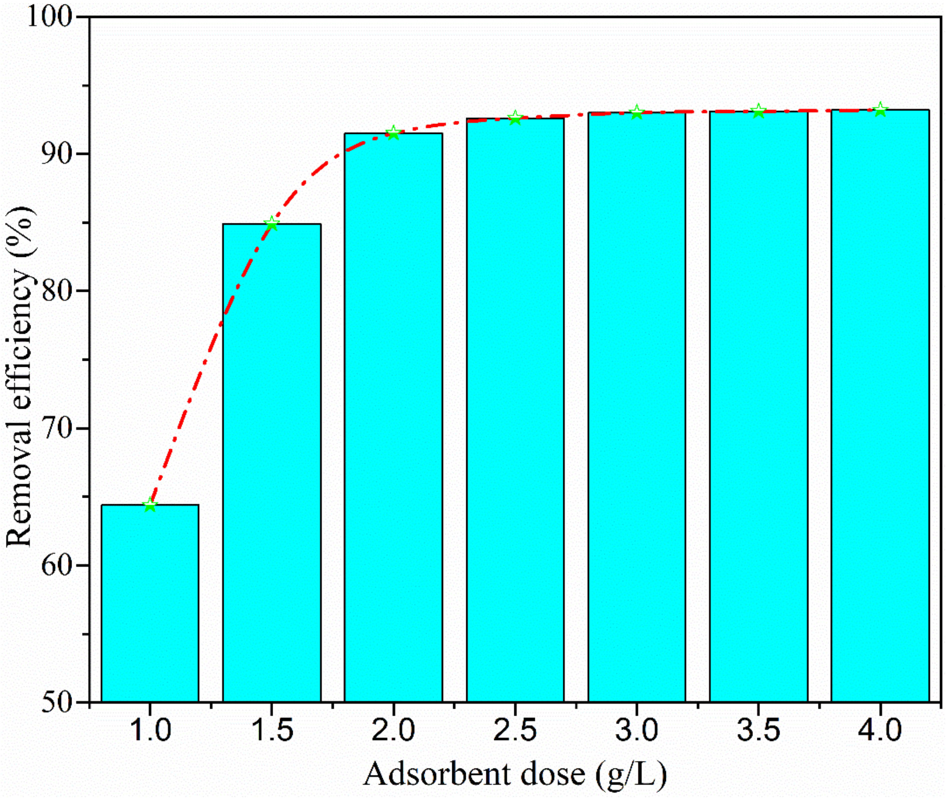

Figure 4.11. The effect of adsorbent dose on the removal efficiency of the activated banana peel bio-adsorbent

4.3.1.4 Effect of dye initial concentration

The removal efficiency of the activated banana peel bio-adsorbent as function of dye initial concentration of 20 to 80 mg/L at fixed adsorption time of 60 min, pH of 3 and adsorbent dose of 2 g/L is demonstrated in Figure 4.12.As can be observed from the graph, the removal efficiency lightly changes from 92.2 to 88.2% as the dye initial concentration varies from 20 to 40 mg/L.

when the dye initial concentration increases to 80 mg/L, however, the removal efficiency sharply declines to 37.4%. It is apparent that the dye initial concentration radically affects the removal efficiency for a given adsorbent of 2 g/L. Increasing the dye concentration (molecules) at this fixed adsorbent amount would mean a small surface area for adsorption. The amount of dye molecules may go out of proportion relative the fixed amount of adsorbent and the removal efficiency falls down.

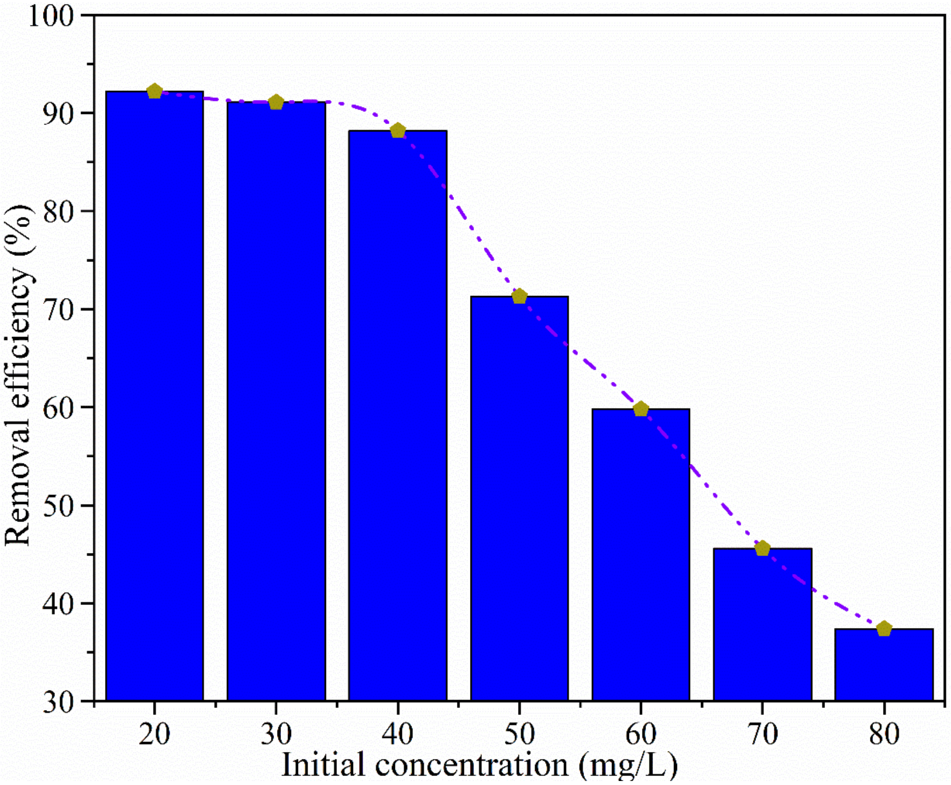

Figure 4.12. Removal efficiency as function of dye initial concentration

4.3.2 Interaction effect of variables and process optimization

As is well known, variables are quantities that used to determine a given physical phenomenon. The effect of these variables is two-fold; they definitely affect the process and one variable affects the others. Parameter interaction is the epicenter of processes that determines the extent to which the processes have a sound result. Processes in this physical world depend on different parameters with different levels of influence, better yet, on range of the parameter considered. Adsorption is a such surface phenomenon that depends on the levels mainly contact time, pH, adsorbent dose, and concentration of adsorbate, and some extent temperature and pressure considered.

In this particular study, based on the individual parameters effect results, the levels of the variables used forthe RSM-CCD study were determined. The range of parameterswere scoped as; adsorption time (40–80 min), pH (2–4), adsorbent dose (1.5–2.5 g/L) and initial concentration (30–50 mg/L).Based on the design expert software, 30 runs were generated, conducted and the effects scrutinized byexamining the significance of the model, parameters, terms and the process was optimized andthe result validated against experimental results at the optimal conditions.

4.3.2.1 Analysis of variance (ANOVA) of model and parameters

Based on the thirty (30) experimental data fed to the software, it developed a generic mathematical model (equation) that is assumed to represent the removal efficiency with respect of the four variables. This model converted the discrete data (30 data points) into continuous form of generic mathematical equation that can predict the removal efficiency of the activated bio-adsorbent for a given operating conditions; particularly, in the range of parameters considered in experiment. The experiment data are reliable but are limited to see too far down the road. Whereas the model produced by vigorous regression can evaluate the performance of the adsorbent for all conditions chosen to examine. However, data generated from model are as good as experimental data if only the model fitted pretty well. Model with p-value of less than 0.05 and R-square value close to unity is believed to fit the experimental data and is acceptable.

In the study, the p- and R-square values are found to be less 0.000 and 0.987 respectively. The quadratic equation that predicts the removal efficiency of the activated bio-adsorbent as function of adsorption time, pH, adsorbent dose and initial dye concentration is given as equation 4.1:

$$
\begin{aligned}
RE(\%) &= 25.1554 + 0.6339 * A + 13.3566 * B + 88.1102 * C + 0.1560 * D \\
&-0.0016 * AB - 0.0277 * AC + 0.0150 * AD + 2.6460 * BC + 0.2230 * BD + 0.0.3822 * CD \\
&-0.0048 * A^2 - 5.3104 * B^2 - 33.1485 * C^2 - 0.0418 * D^2
\end{aligned}
$$

Where,

RE, is removal efficiency of the activated bio-adsorbent, %

A is adsorption time, min

B is pH

C is adsorbent dose, g/L

D is initial dye concentration, mg/L

In addition to the model, the parameters and related interactive terms were evaluated based on p-values and F-values as is summarized in Table 4.2.

Table 4.2. ANOVA analysis of model, main parameters and terms

Source	**Sum of Squares**	**Df**	**Squares Mean**	**F value**	**P-value Prob>F**	
Model	6924.61	14	494.61	82.15	< 0.0001	Significant
A	2527.65	1	2527.65	419.83	< 0.0001	
B	707.42	1	707.42	117.50	< 0.0001	
C	216.60	1	216.60	35.98	< 0.0001	
D	2029.52	1	2029.52	337.10	< 0.0001	
AB	14.63	1	14.63	2.43	0.0139	
AC	52.20	1	52.20	8.67	0.0100	
AD	38.75	1	38.75	6.44	0.0228	
BC	16.20	1	16.20	2.69	0.1217	
BD	11.73	1	11.73	1.95	0.1831	
CD	3.71	1	3.71	0.6155	0.4449	
A^2	842.02	1	842.02	139.86	< 0.0001	
B^2	348.72	1	348.72	57.92	< 0.0001	
C^2	96.75	1	96.75	16.07	0.0011	
D^2	453.38	1	453.38	75.30	< 0.0001	
Residual	90.31	15	6.02			
Lack of Fit	90.24	10	9.02	4.24	0.0532	Not significant
Pure Error	0.0733	5	0.0147			

The statistical analyses are evidence that the actual (experimental) and the model predicted values of the removal efficiencies are alike to acceptable extent in which case the R-square, adjusted R-square and predicted R-square were found to be 0.987, 0.975 and 0.926 respectively.

The predicted and actual values of the removal efficiency along the variable values is shown in Table 4.3.

Table 4.3. Experimental design matrix used in CCD

Run	**A: Adsorption time (min)**	**B: pH**	**C:Adsorbent dose (g/L)**	**D: Initial concentration (mg/L)**	**Removal efficiency (%)**	
					Actual	**Predicted**
1	80	4	2.5	50	71.5	73.3
2	40	4	2.5	50	52.8	51.3
3	20	3	2	40	42.9	45.6
4	60	3	2	40	88.5	88.3
5	60	3	1	40	71.5	74.8
6	60	3	2	40	88.4	88.3
7	100	3	2	40	89.8	86.7
8	80	2	1.5	50	80.7	80.6
9	60	1	2	40	86.7	84.9
10	60	3	2	40	88.2	88.3
11	60	3	2	40	88.3	88.3
12	80	4	2.5	30	86.7	89.3
13	40	4	1.5	30	63.7	62.9
14	60	5	2	40	61.8	63.2
15	80	2	1.5	30	92.5	95.1
16	60	3	2	20	91.2	90.4
17	80	2	2.5	30	94	94.5
18	60	3	2	40	88.4	88.3
19	40	2	2.5	30	80.7	82.6
20	80	4	1.5	50	68.7	67.9
21	40	4	2.5	30	74.2	73.6
22	80	2	2.5	50	80	81.9
23	80	4	1.5	30	87.7	85.8
24	40	4	1.5	50	40	38.7
25	60	3	2	60	53.3	53.7
26	40	2	1.5	30	78.5	75.9
27	40	2	2.5	50	62.7	63.8
28	60	3	3	40	90.5	86.8

29	60	3	2	40	88.2	88.3
30	40	2	1.5	50	56.7	55.2

Moreover, the closeness of the actual values and the model predicted values can be seen from Figure 4.13. It can be seen from the graph that both data are more or less alike.

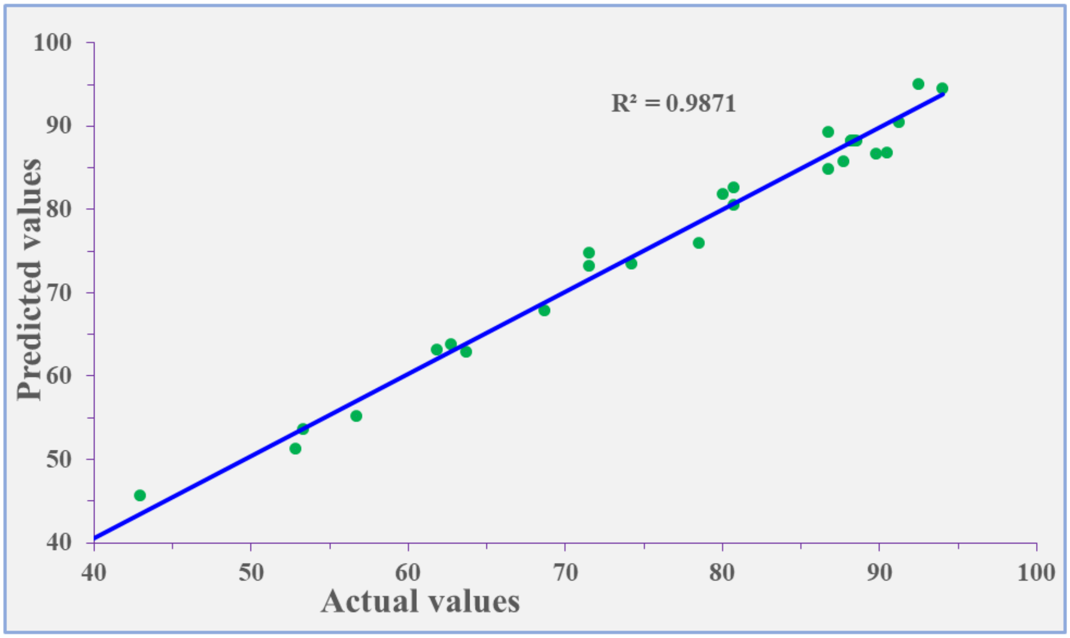

Figure 4.13. Actual vs model predicted values fitting

4.3.2.2 RSM of interactive parameters

More often than not, the parameters that govern physical process, adsorption in this instance, influence the extent and how it goes. Nor is that all, the effect is interactive; it comes from the parameters considered altogether. RSM provides a pair of parameters effect at once in terms of surface plot for easy response visualization.

The interaction of effect of adsorption time and pH on the removal efficiency of the bio-adsorbent at a given adsorbent dose of 2 g/L and initial dye concentration of 40 mg/L is illustrated in Figure 4.14. Figure 4.14 (A) shows the surface plot and Figure (B) is contour plot of removal efficiency with respect of adsorption time and pH variations. It can be seen from graph that the removal efficiency rapidly increases from 62.8% to 91.8% as the adsorption time increases from 40 min to 66 min and pH decreases from 4 to 2.8. Thereafter, the removal efficiency slowly increases as adsorption time ups to 80 min and pH downs to 2.

The increment of removal efficiency at this given operating conditions may attribute to favorable condition that the adsorption time and pH conduce for mass transfer to take place rapidly. Moreover, it seems that the activated bio-adsorbent provided relatively enough surface area to adsorb the dye molecules at first and then tends to approach towards equilibrium where the adsorption process about to stop. The removal efficiency, thus, found to be almost constant.

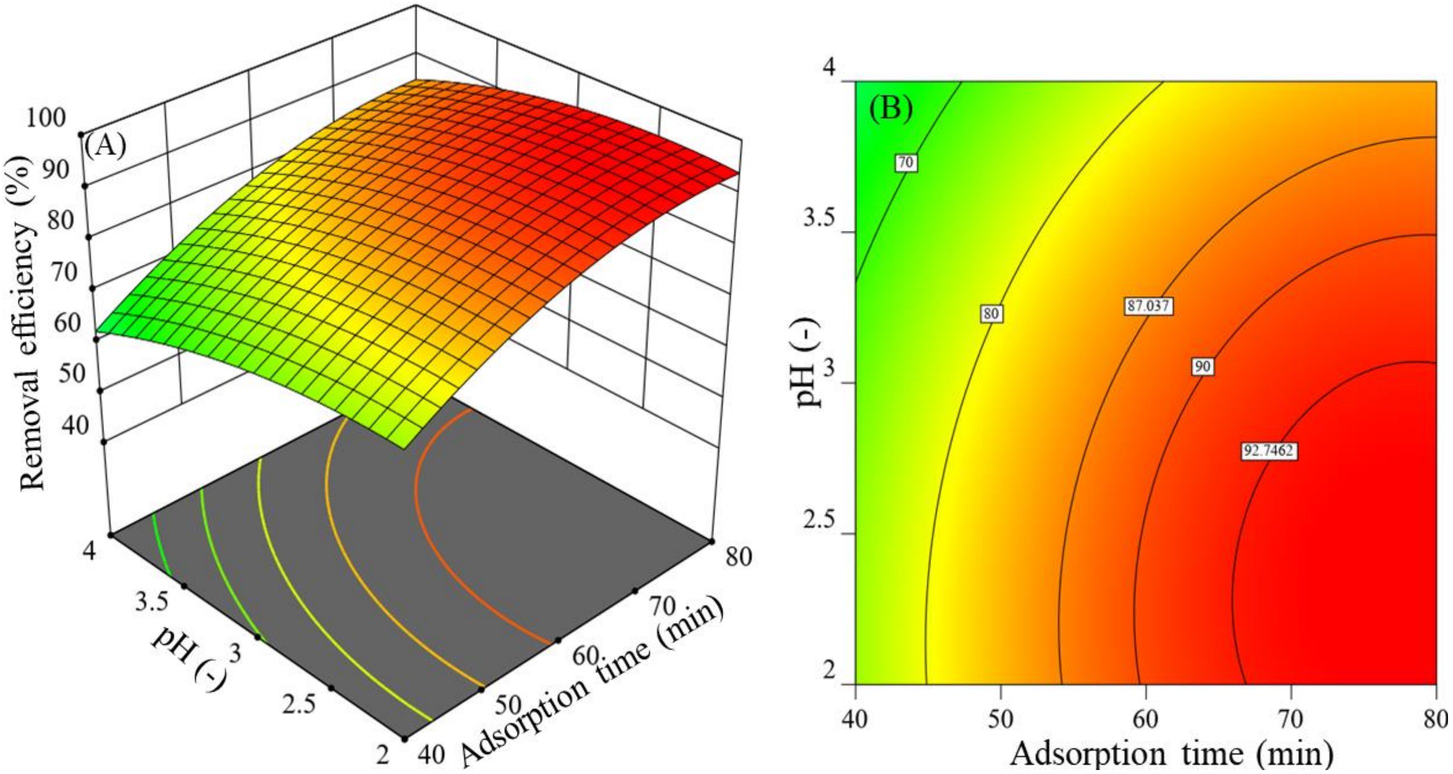

Figure 4.14. Removal efficiency as function of adsorption time and pH; (A) surface plot and (B) contour plot

Likewise, Figure 4.15 demonstrates removal efficiency as function of adsorption time and adsorbent dose at 3 pH and 40 mg/L dye initial concentration, where Figure 4.15 (A) is the surface plot and Figure 4.15 (B) is the contour plot. Figure 4.15 revealsthe increment of the removal efficiency from 64.1% to 90.8% when adsorption time varied from 40 min to 64 min and adsorbent dose varied from 1.5–2.1 g/L. Up next, the removal efficiency slightly increases to 92.5% despite the adsorption time and adsorbent dose increases to 80 min and 2.5 g/L respectively.

The increase of removal efficiency with both adsorbent dose and adsorption time is due to the availability of surface areas adsorbent amount increases and sufficiently enough time for adsorption. Given 40 mg/L dye initial concentration, it apparent that the removal efficiency of the bio-adsorbent increases as the amount increasingly varies.

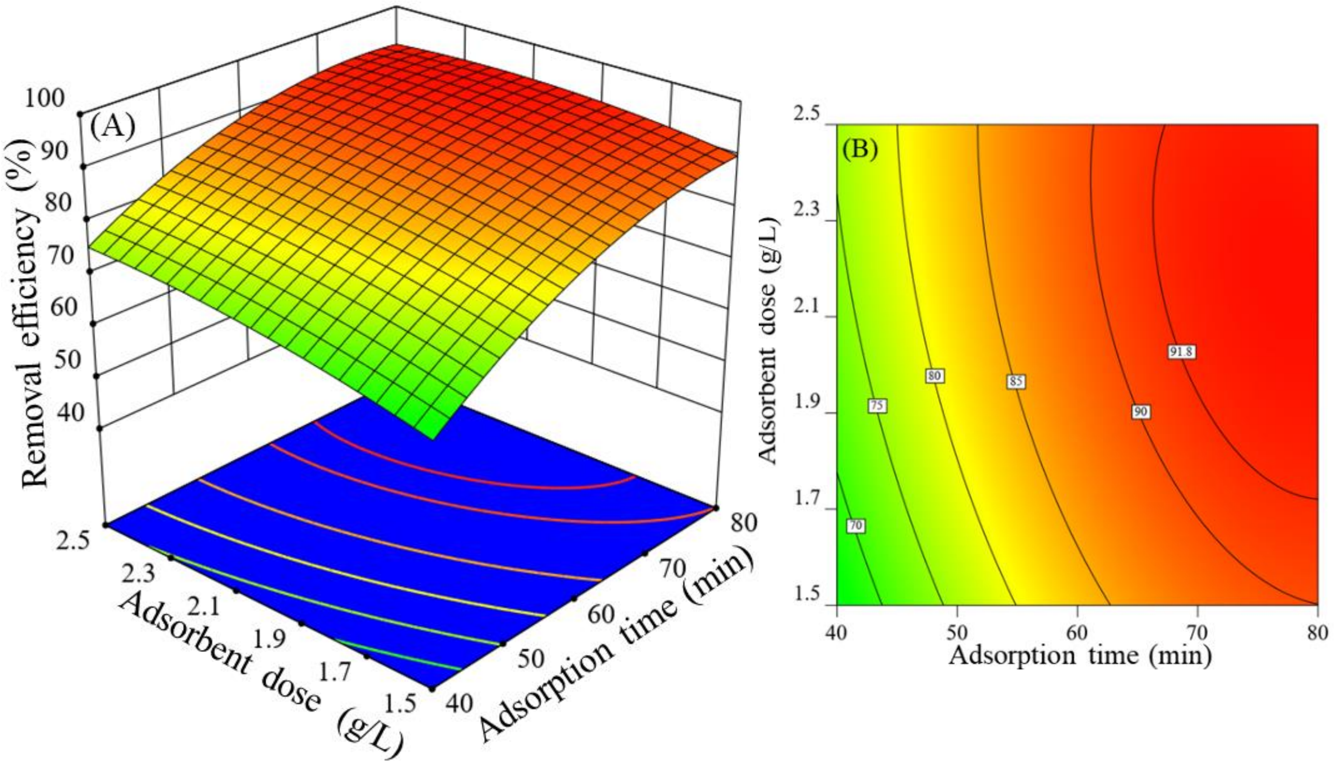

Figure 4.15. Removal efficiency as function of adsorption time and adsorbent dose; (A) surface plot and (B) contour plot

In the similar fashion, how the removal efficiency of the activated bio-adsorbent varies with the variation of adsorption time and dye initial concentration at 3 pH and 2 g/L adsorbent dose is depicted in Figure 4.16. The graph unfolds the increment of the removal efficiency at considerable rate from 58% to 91.8% when the adsorption time increases 40 min to 64 min and the dye initial concentration decreases from 60 mg/L to 38 mg/L. As the model predicted, the removal efficiency shows slow in increase to 96.6% as adsorption time further varied 80 min and initial concentration decreases to 30 mg/L.

It appears that dye initial concentration played significant role in the removal efficiency. High efficiency at low concentration would mean that the activated bio-adsorbent assumed more room for adsorption relative to the molecules of dye. On the other hand, higher dye concentration outnumbers the available surface and causes the removal efficiency to decline sharply.

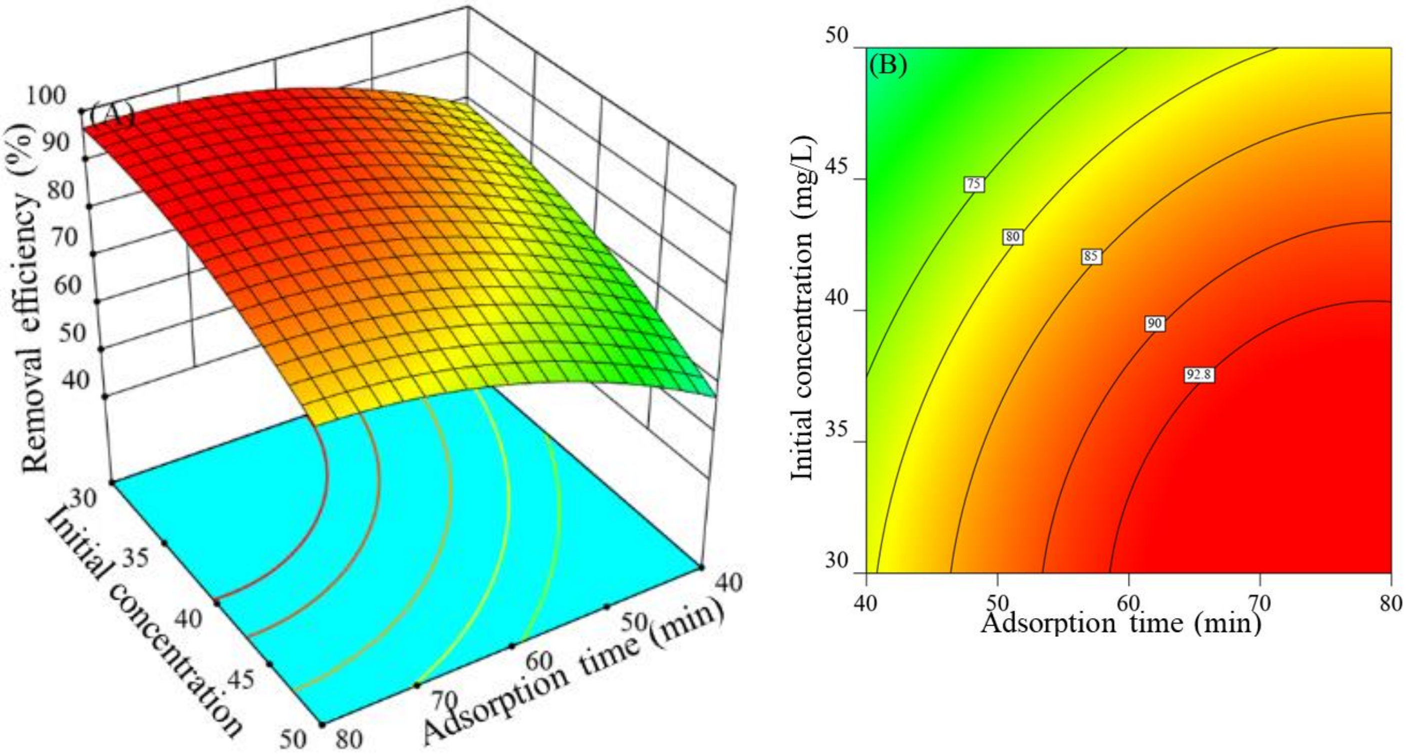

Figure 4.16. Removal efficiency as function of adsorption time and dye initial concentration

The surface and contour plots of the response removal efficiency of dye adsorption process by the activated bio-adsorbent drawn with the variables pH and adsorbent dose at constant adsorption time of 60 min and initial dye concentration of 40 mg/L is shown in Figure 4.17. It can clearly be observed from the Graphs that the removal efficiency of the bio-adsorbent in terms of adsorbing dye molecules has an increment pattern with adsorbent dose and decrement pattern with pH.As such, when the adsorbent amount varied from 1.5–2 g/L and the pH changed from 4–2.8 the efficiency was found to change from 73.8–90% at noticeable rate. It was, however, remains constant, give or take, even though the adsorbent increases to 2.5 and pH further decreases to 2.It can thus be concluded that the cumulative effect of both variables to have a sound removal efficiency is in the vicinity 2 g/L adsorbent dose and 3 pH for the given 40 initial concentration 60 min adsorption time. It also seems that increase of adsorbent amount allows more room for adsorption of dye molecules till the process tends towards equilibrium. At high pH dye solution the adsorption competes with other molecules that causes the efficiency dye removal to decline rapidly.

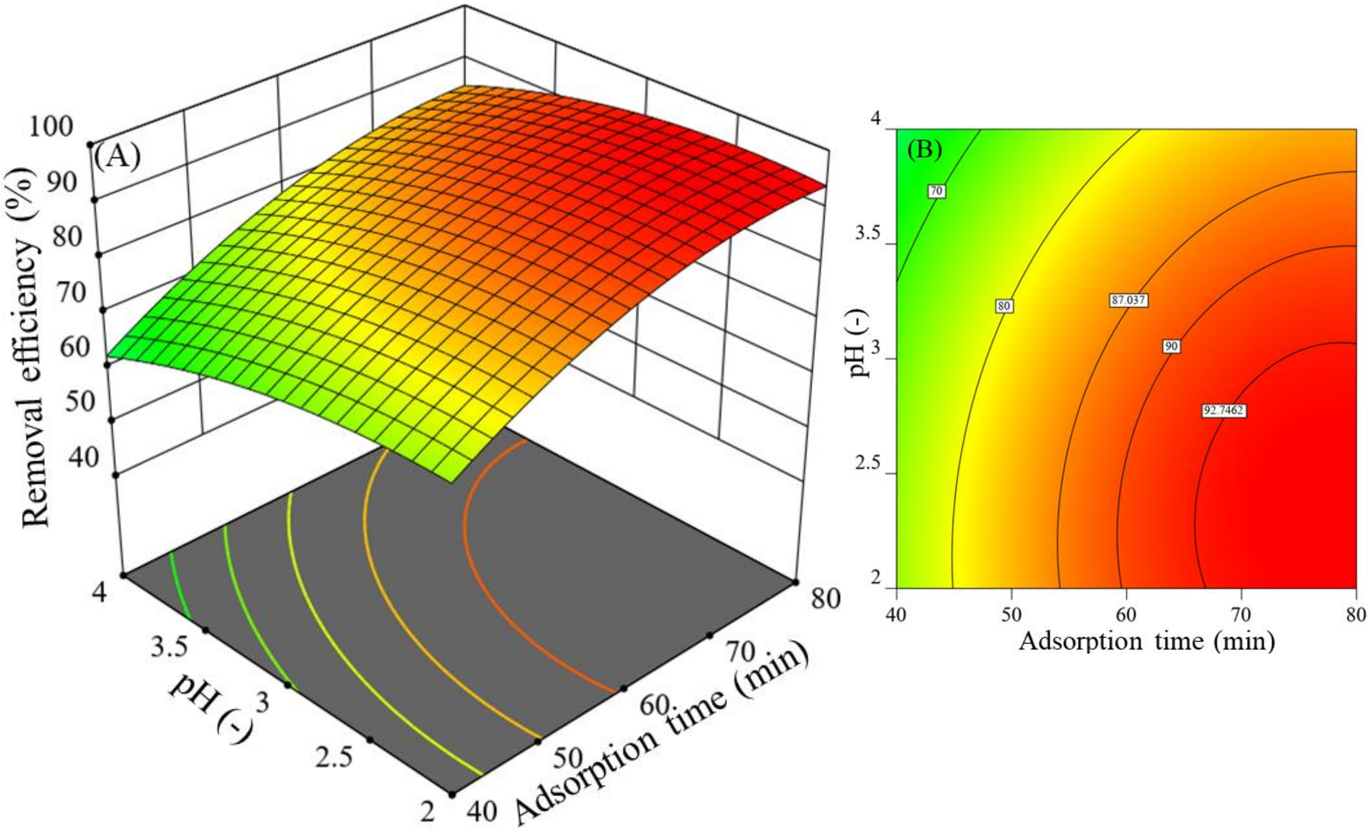

Figure 4.17. Removal efficiency as function of adsorption and pH; (A) surface plot and (B) contour plot

The interaction effect thatboth pH and initial concentration have on the removal efficiency of the activated bio-adsorbent in the event of dye molecules adsorption is given in Figure 4.18 in terms of surface (A) and contour (B) plots. As would be expected, the removal efficiency is more pronouncedly dependent on the dye concentration for constant adsorption time of 60 min and adsorbent dose of 2 g/L. The efficiency found to go up to 94% when the dye concentration was reduced to 30 mg/L.

While the adsorbent amount is kept at 2 g/L, as is the case in this graph, it crystal clear that the removal efficiency declines withconcentration and the reverse holds true. Apparently, since adsorption is surface phenomenon higher dye concentration would outnumber the available surface present in the 2 g/L adsorbent and as consequence some dye molecules remain adsorbed or not removed from the synthetic solution. It is, therefore, imperative that the dye concentration should proportional to the adsorbent dose which in this case is 2 g/L to 40 mg/L to get about 90% of the dye removed, putting other factors aside.

Figure 4.18. Removal efficiency as function of pH and initial dye concentration; (A) 3D surface and (B) contour plot

Figure 4.19 (A) and (B) are 3D and contour plot of removal efficiency of activated bio-adsorbent with respect of adsorbent dose and initial dye concentration at fixed adsorption time of 60 min and pH of 3. The model equation pretty well predicts the removal efficiency to increase from 70–94% based on the variation of adsorbent dose from 1.5–2.0 and initial dye concentration from 50–30 mg/L. As is so often the case, the removal efficiency tends to increase with adsorbent dose and decrease with dye initial concentration.

All told, the removal efficiency of activated bio-adsorbent used to adsorb synthetic dye solution was found to dependent on the four parameters, namely adsorption time, pH, adsorbent dose and initial dye concentration. On top of that, adsorption time and adsorbent dose were found to have a positive effect and pH and initial dye concentration negative effect on the removal efficiency. It appears on the surface that 90% or so of the dye molecules can be removed at favorable operating conditions of the variables without some extended levels considered.

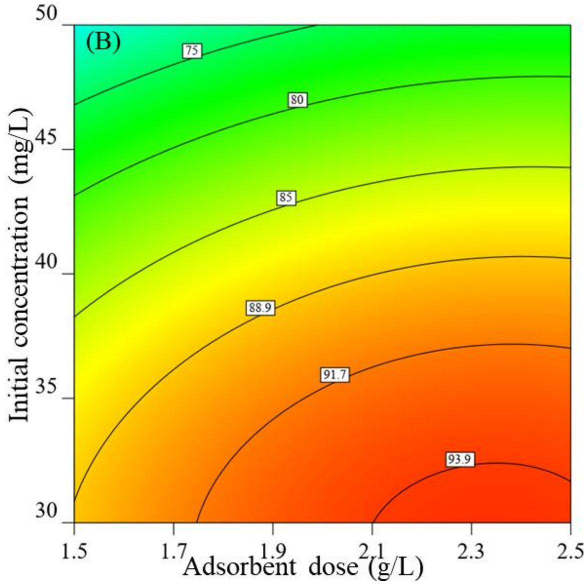

Figure 4.19. Removal efficiency with respect of adsorbent dose and initial dye concentration; (A) 3D surface plot and (B) contour plot

4.3.2.3 Process optimization and variables validation

Some variables affect the removal efficiency positively whereas other negatively, as was seen from experiments and from the quadratic equation predictions.The patterns is then indication of the need of optimization that compromises level parameters and yield an acceptable level of removal efficiency. The optimization gives no lower nor higher but in between values of variables and response based on criteria set. As can be seen in Table 4.4, the optimum operating conditions of dye adsorption process was found to be; adsorption time 60 min, pH 3, adsorbent dose 2 g/L, and initial dye initial concentration 40 mg/L.

The optimum operating condition found was validated with triplicated experimental data and the deviation between the experimental result and that of model predicted was on 1.3%, as shown in Table 4.4.

Table 4.4. Model predicted and experimental response at optimum conditions

	Adsorption time (min)	pH	Adsorbent dose (g/L)	Initial dye concentration (mg/L)	Removal efficiency (%)
Predicted	60	3	2	40	90.5
Actual	60	3	2	40	89.3

4.4 Adsorption kinetics and isotherm models study

Adsorption involves three major mass transfer steps; external diffusion, internal diffusion and deposition on the surfaces of the adsorbent. In external diffusion, the adsorbate diffuses against the thin film in the environs of the adsorbent material. Having passed this barrier, the adsorbateinternally diffusesthrough the pores across the surface of the adsorbent. The adsorbate molecules then find their way to the surface where they are adsorbed. In doing so, the rate at which the adsorbatereaches at the adsorbent surface may be fast or slow based on the physio-chemical interaction between the surface and the molecules of the adsorbate. Besides, the behavior and type of adsorption vary as the case may be.

4.4.1 Kinetics study

To examine the kinetics of dye molecules adsorption on bio-adsorbent, pseudo first order and pseudo second order were studied. To that end, a 2 adsorbent sample was allowed to adsorb 40 mg/L dye solution for different adsorption time (10–160 min). The data so obtained was linearly regressed and fitted to the log (q_e-q_t) versus adsorption time (t) for the pseudo first order model. As is shown inFigure 4.20, the coefficients of determination were found to be 0.739.

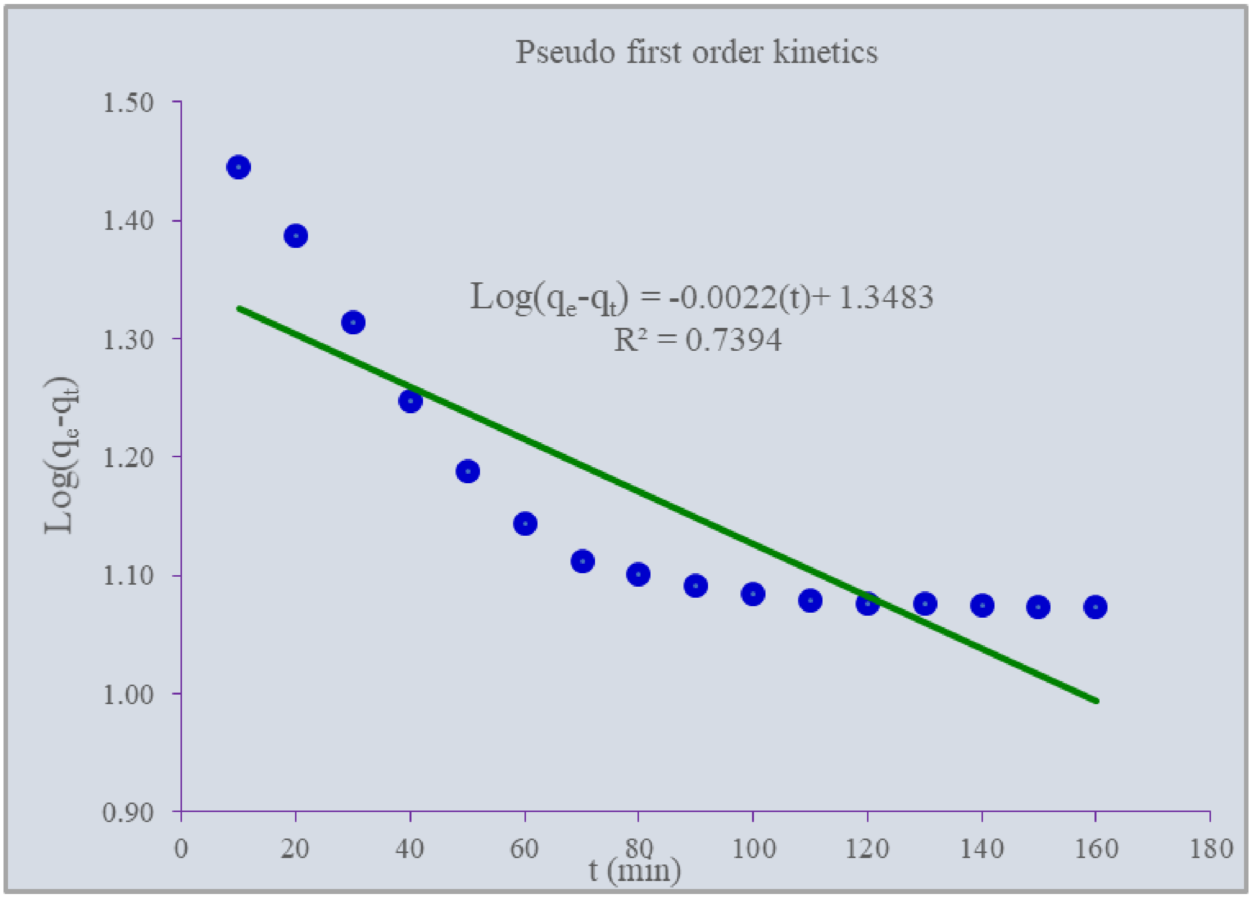

Figure 4.20. Pseudo first order kinetics model fitting

Similarly, the experimental data were fitted to the pseudo second order kinetics which is in the form of t/qt versus adsorption time (t) and the R-square value of the regression come out to be 0.978as is shown in Figure 2.1.Comparing the two regressions, the adsorption of dye molecules on the surface of the activated bio-adsorbent prepared from banana peel seems to follow the pseudo second order kinetics model.

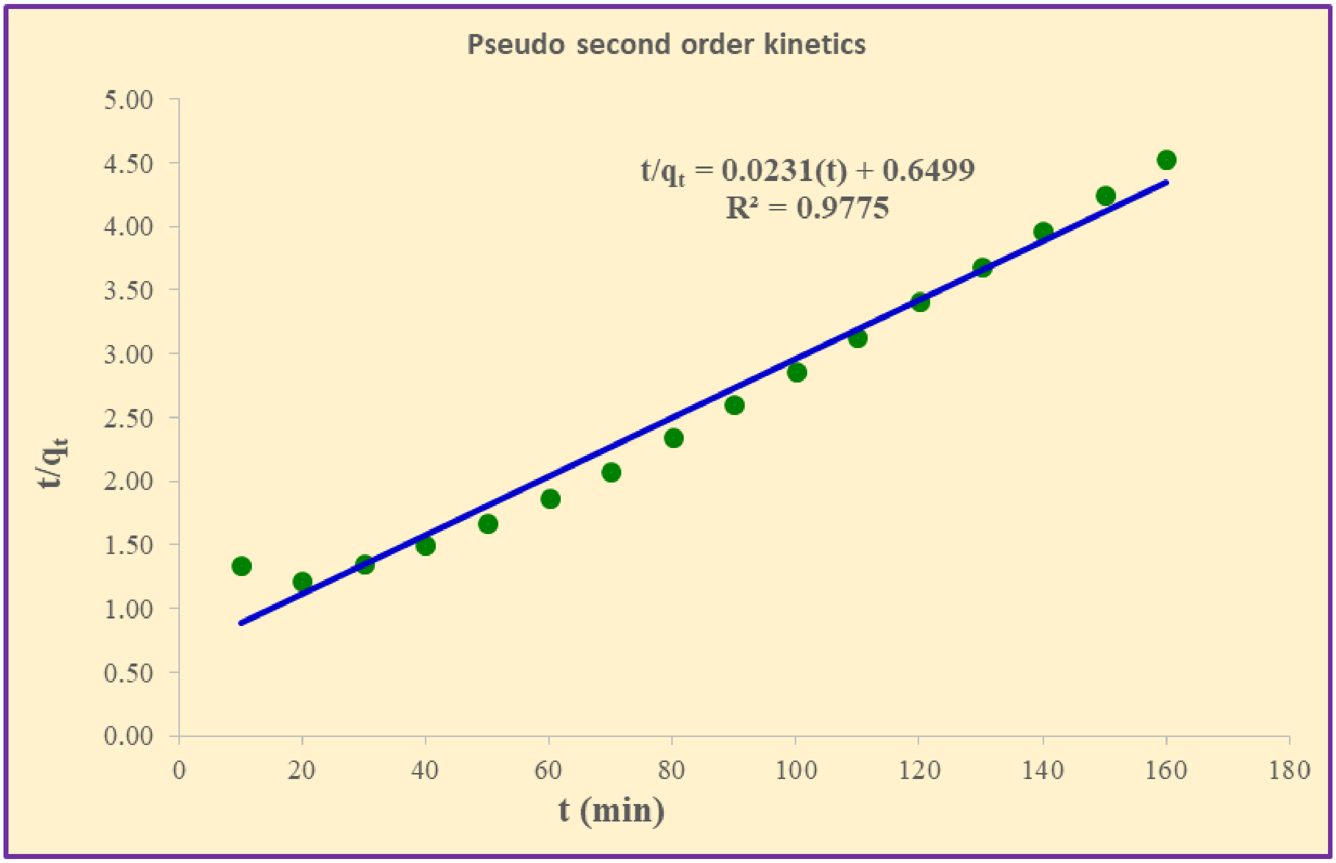

Figure 4.21. Pseudo second order kinetics model fitting

4.4.2 Isotherm study

As an effort to study the behavior of adsorption of dye molecules on the adsorbent surface two well-known adsorption isotherm models, Langmuir and Freundlich, had been regressed. To effect this, different concentration of dye molecules were allowed to be adsorbed on 2 g of sample and the equilibrium concentration and the amount adsorbate being adsorbed at equilibrium were determined. To fit the data to Langmuir isotherm model, a graph of C_e/q_eversus $C_e$was drawn from which R-square, theadsorption capacity at equilibrium (q_e) and the Langmuir equilibrium constant (K_L) were calculated. As can be seen from Figure 4.22, the R-square of the linear regression is 0.9996 for Langmuir isotherm model.

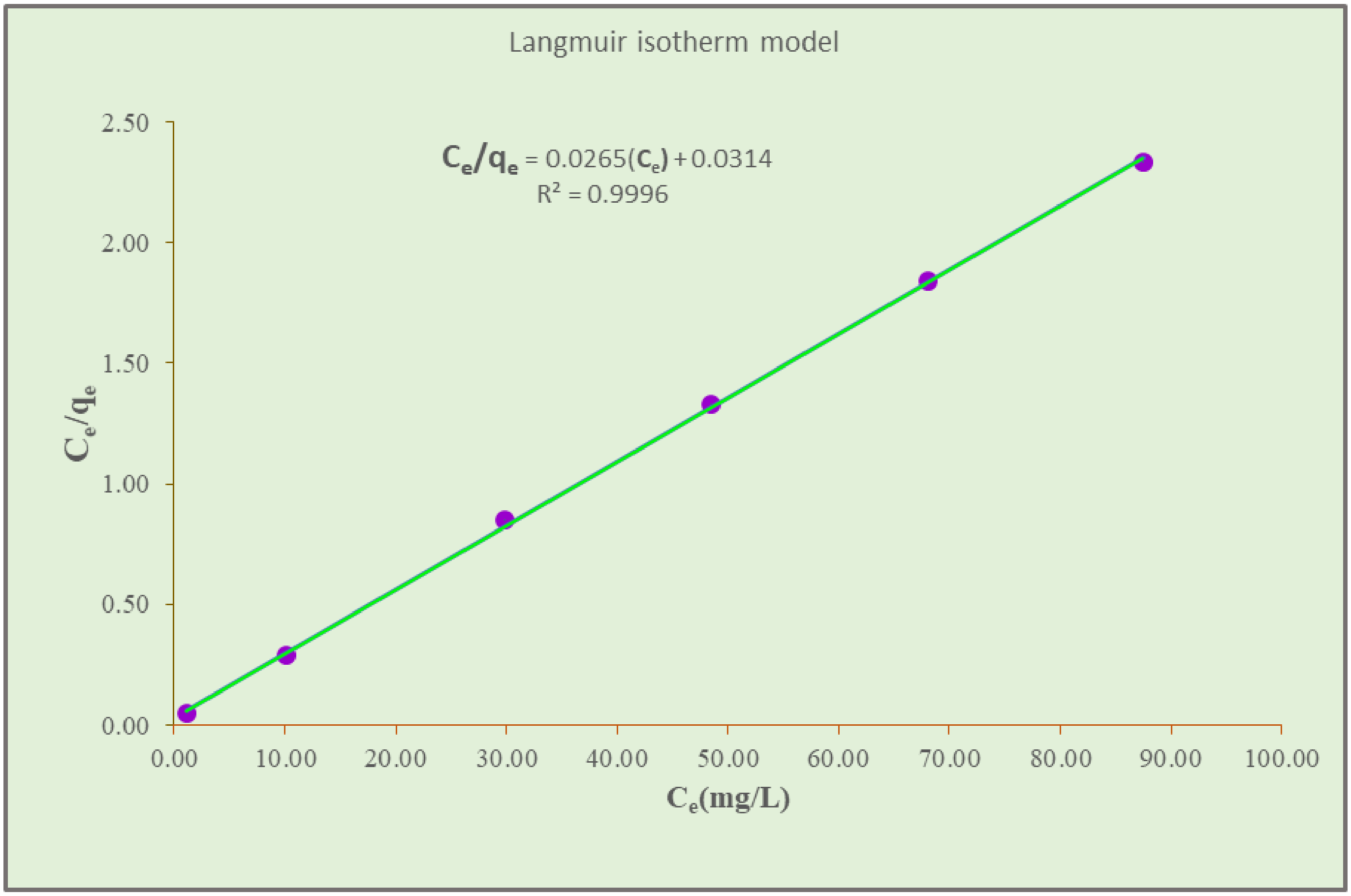

Figure 4.22. Langmuir isotherm model fitting

The coefficient of determination of Freundlich isotherm model, on the other hand, was found to be 0.8916 which way less than the Langmuir isotherm model as shown in Figure 4.23.Therefore, the adsorption behavior of the dye molecules on bio-adsorbent is best described mathematically using Langmuir isotherm model. Furthermore, it can be inferred that the dye molecules formed a monolayer on the surface of the adsorbent.

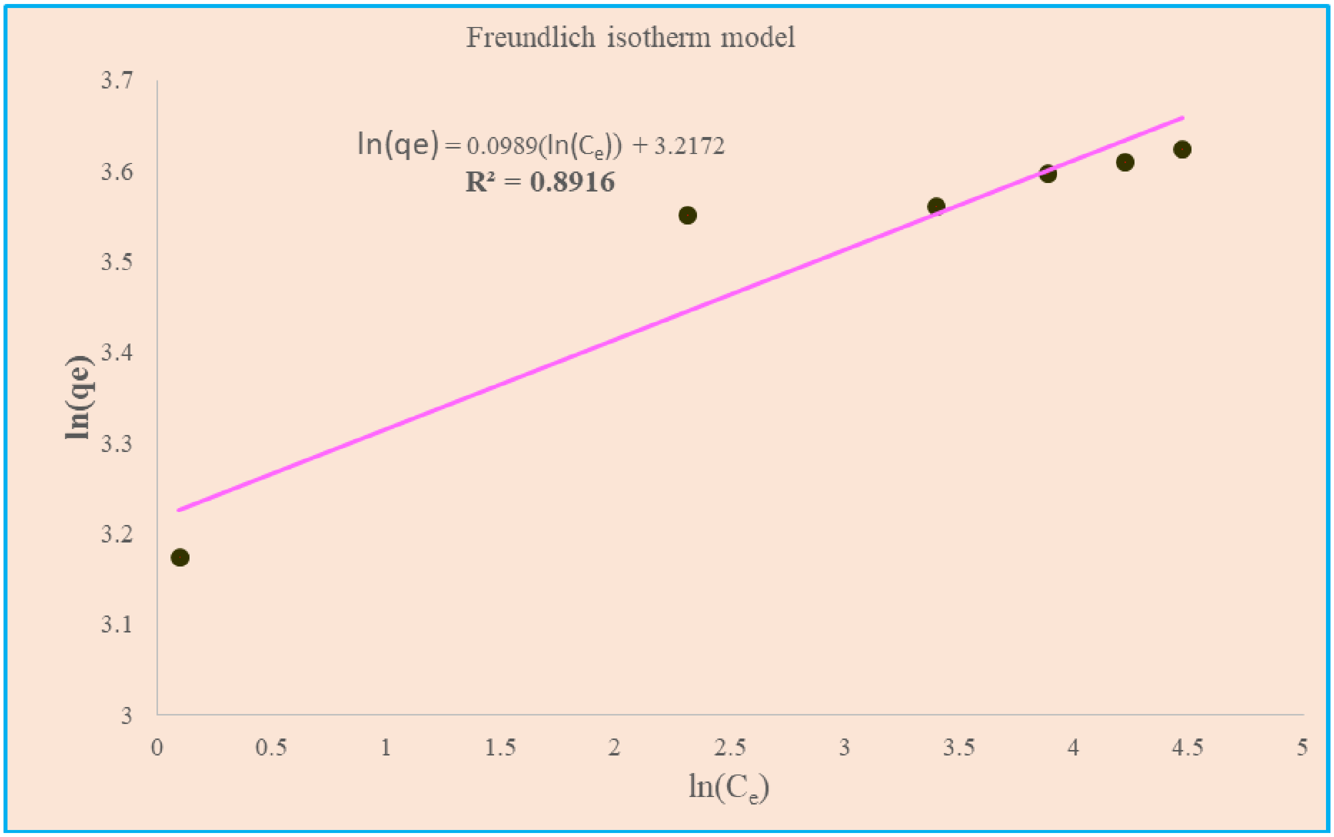

Figure 4.23. Freundlich isotherm model fitting

Summary results of adsorption kinetics and isotherms models and the respective parameters are given in Table 4.5.

Table 4.5. Summary of kinetics and isotherm models

Adsorbent	Pseudo first order kinetics			Pseudo second order kinetics		
	q_e(mg/g)	K_1(min^{-1})	R^2	q_e(mg/g)	K_2(g(mg)$^{-1}$min^{-1})	R^2
Activated banana peel	35.4	0.005	0.7398	35.4	0.0006	0.9775
	Langmuir isotherm parameters			Freundlich isotherm parameters		
	q_m(mg/g)	K_L(L/mg)	R^2	K_F(mg/g)	n	R^2
	38	0.993	0.9996	24.96	10.11	0.8916

4.5 Reusability of activated banana peel bio-adsorbent

The performance of the adsorbent with regard to the number of times it can be used to adsorb dye molecules is shown in Figure 4.24. The removal efficiency of adsorbent declined from 93.5% all the way down to 48% when it was used at first and for 6th time following the adsorption-adsorption processes. It can be concluded that the activated banana peel bio-adsorbent has good regeneration capacity to use it once more.

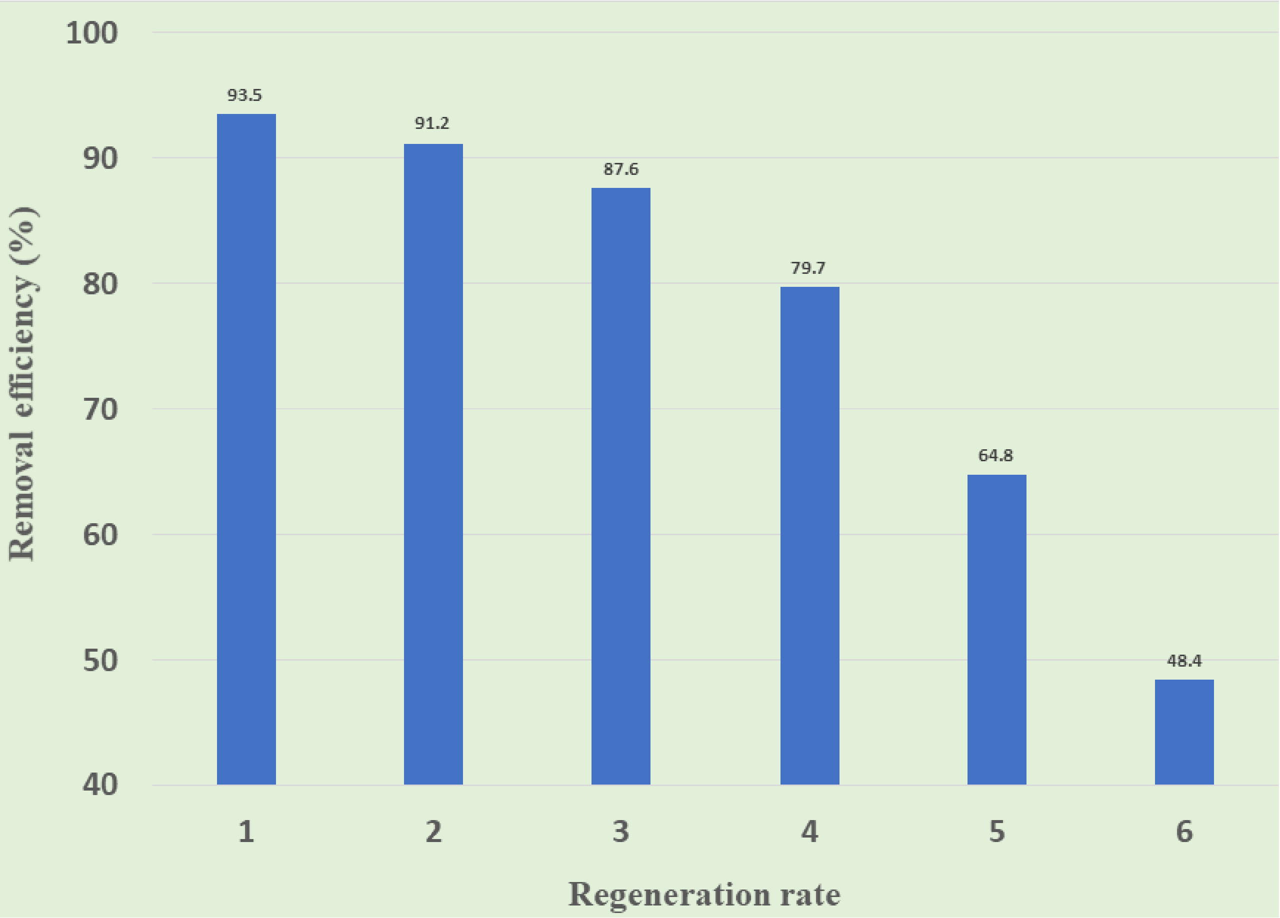

Figure 4.24. Regeneration rate of activated banana peel bio-adsorbent

CHAPETER FIVE

5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

In this study, the adsorption of Reactive Blue dye onto activated banana peel bio-adsorbent was investigated. In order toincrease the adsorption capacities of the bio-adsorbent for the anionic dye Reactive Blue, thermal and chemical surfacemodification was made. With the surface modification, thechange in the surface charges of adsorbent materials was aimed. The activated banana peel bio-adsorbent was allowed to adsorb the dye molecules at different operating conditions. The operating conditions were optimized and this optimum condition can remove most of the dye molecules from the synthetic solution. From the kinetics and isotherm model study, it can be concluded that the rate at which the dye molecules being adsorbed and the behavior of adsorption follow pseudo second order and Langmuir isotherm models.

The regeneration test suggested that the activated banana peel bio-adsorbent can be used four times repeated before its removal performance falls substantially. To sum it up, activated banana peel can be a good candidate of adsorbent material to mitigate wastewater problems to considerable extent. Using banana peel as a means to treat waste water has two-fold advantages: one turning a waste material into useful adsorbent and two it is relatively cheap and easy to prepare.

5.2 Recommendation

- Batch biosorption is economically unattractive in terms of production of sludge. Almost all already existing adsorption techniques are sludge free so sludge removal techniques can be examined or the sludge can be used for other applications or using fixed bed columns may be incorporated for regeneration.
- The use of this banana peel adsorbent can be recommended for the final stage of the wastewater treatment process, where neutralization is required by the environmental legislation, considering that the best performance of the adsorbent occurs in an acid environment.
- More Study and research which can increase the percentage removal of reactive blue dye and the economic feasibility of treated water for removal of the dye need to be considered in the future.
- The capacity of the activated banana peel bio-adsorbent to remove a real wastewater from textile factory can be studied for a range of operating conditions.

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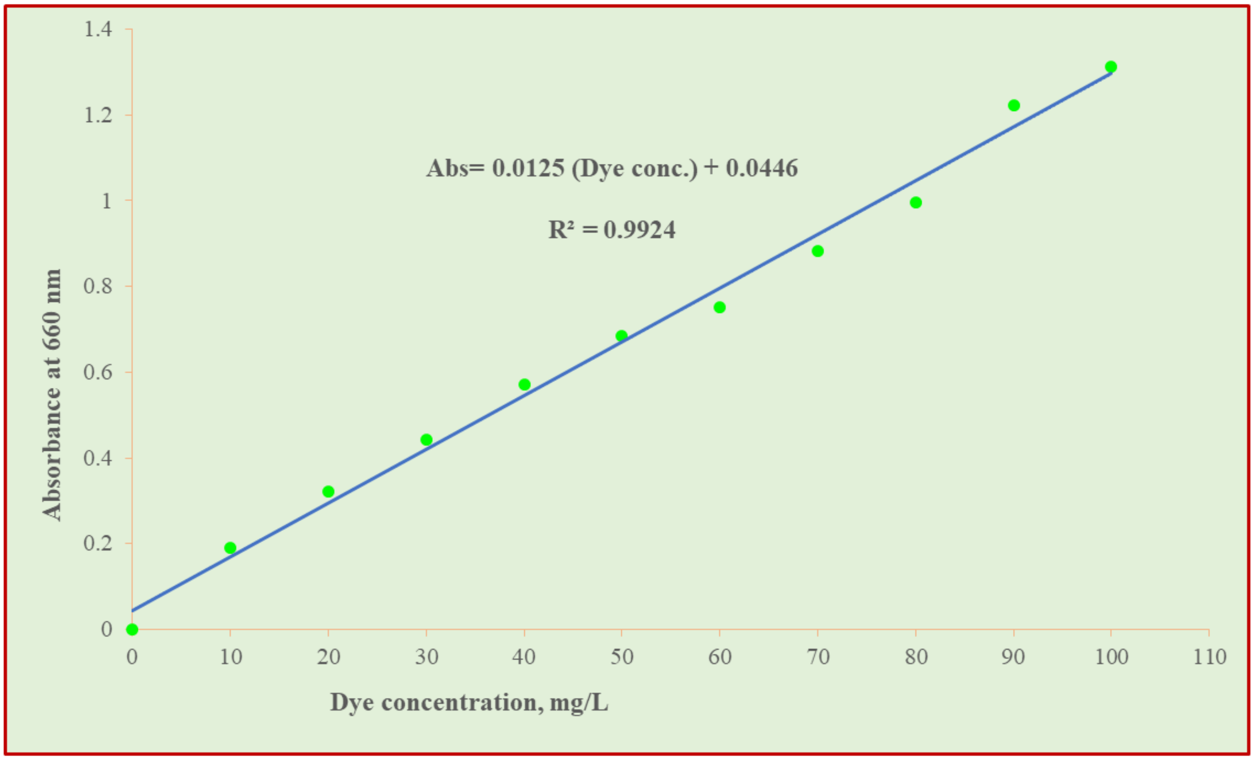
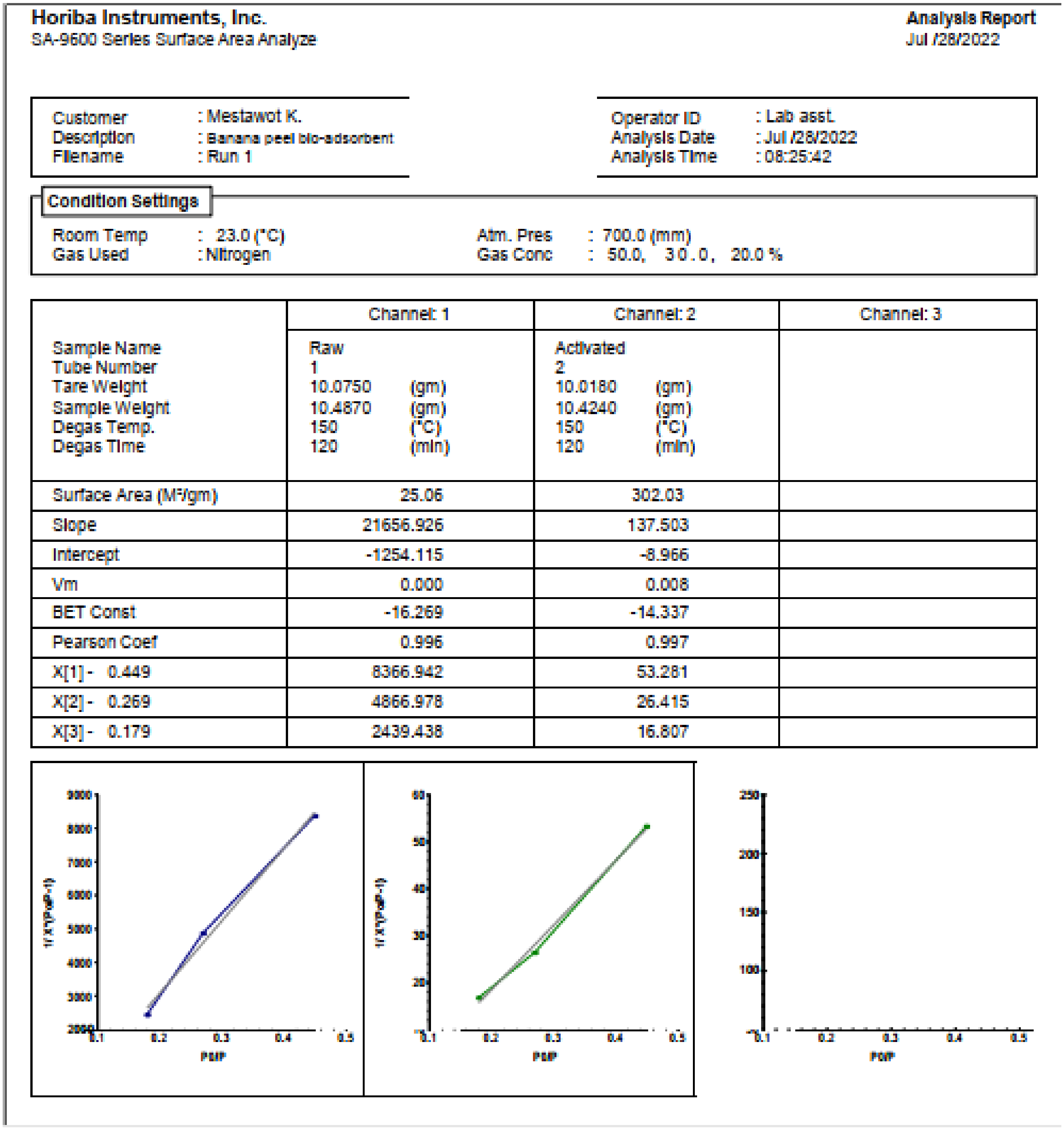
APPENDICES

Appendix A: Calibration curve of dye concentration vs absorbance



Appendix B: BET results



Horiba Instruments, Inc.
SA-9600 Series Surface Area Analyze

Analysis Report
Jul /28/2022

Customer	: Mestawot K.
Description	: Banana peel bio-adsorbent
Filename	: Run 1

Operator ID	: Lab asst.
Analysis Date	: Jul /28/2022
Analysis Time	: 08:25:42

Condition Settings

Room Temp	: 23.0 (°C)	Atm. Pres	: 700.0 (mm)
Gas Used	: Nitrogen	Gas Conc	: 50.0, 30.0, 20.0 %

	Channel: 1	Channel: 2	Channel: 3
Sample Name Tube Number Tare Weight Sample Weight Degas Temp. Degas Time	Raw 1 10.0750 (gm) 10.4870 (gm) 150 (°C) 120 (min)	Activated 2 10.0180 (gm) 10.4240 (gm) 150 (°C) 120 (min)	
Surface Area (M²/gm)	25.06	302.03	
Slope	21656.926	137.503	
Intercept	-1254.115	-8.966	
Vm	0.000	0.008	
BET Const	-16.269	-14.337	
Pearson Coef	0.996	0.997	
X[1] - 0.449	8366.942	53.281	
X[2] - 0.269	4866.978	26.415	
X[3] - 0.179	2439.438	16.807	

Appendix C; IR Spectrum Table by Frequency Range

Absorption (cm-1)	Appearance	Group	Compound Class
3700-3584	medium, sharp	O-H stretching	Alcohol
3550-3200	strong, broad	O-H stretching	Alcohol
3500	Medium	N-H stretching	primary amine
3400-3300	Medium	N-H stretching	aliphatic primary amine
3350-3310	Medium	N-H stretching	secondary amine
3300-2500	strong, broad	O-H stretching	carboxylic acid
3200-2700	weak, broad	O-H stretching	Alcohol
3000-2800	strong, broad	N-H stretching	amine salt
3333-3267	strong, sharp	C-H stretching	Alkyne
3100-3000	Medium	C-H stretching	Alkene
3000-2840	Medium	C-H stretching	Alkane
2830-2695	Medium	C-H stretching	Aldehyde
2600-2550	Weak	S-H stretching	Thiol
2349	Strong	O=C=O stretching	carbon dioxide
2275-2250	strong, broad	N=C=O stretching	Isocyanate
2260-2222	Weak	CΞN stretching	Nitrile
2260-2190	Weak	CΞC stretching	Alkyne
2175-2140	Strong	S-CΞN stretching	Thiocyanate
2160-2120	Strong	N=N=N stretching	Azide
2150	C=C=O stretching	Ketene	
2145-2120	Strong	N=C=N	Carbodiimide

		stretching	
2140-2100	Weak	CΞC stretching	Alkyne
2140-1990	Strong	N=C=S stretching	Isothiocyanate
2000-1900	medium	C=C=C stretching	Allene
2000	C=C=N stretching	Ketenimine	
2000-1650	Weak	C-H bending	aromatic compound
1818	Strong	C=O stretching	Anhydride
1815-1785	Strong	C=O stretching	acid halide
1800-1770	Strong	C=O stretching	conjugated acid halide
1775	Strong	C=O stretching	conjugated anhydride
1770-1780	Strong	C=O stretching	vinyl / phenyl ester
1760	Strong	C=O stretching	carboxylic acid
1750-1735	Strong	C=O stretching	Esters
1750-1735	Strong	C=O stretching	δ-lactone
1745	Strong	C=O stretching	Cyclopentanone
1740-1720	Strong	C=O stretching	Aldehyde