

ADDIS ABABA UNIVERSITY
ADDIS ABABA INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL AND BIO-ENGINEERING
(M.SC. PROGRAM IN ENVIRONMENTAL ENGINEERING)



**UTILIZATION OF CACTUS PEEL AS BIOADSORBENT FOR
THE REMOVAL OF REACTIVE RED DYES FROM TEXTILE
DYE EFFLUENTS**

**A Thesis Submitted to the School of Chemical and Bioengineering
Presented in partial Fulfilment of the Requirements of the Degree of
Masters of Science in Chemical Engineering (Environmental Engineering
Stream)**

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Table of Contents

Acknowledgement	I
List of abbreviations and symbols	IX
<i>Abstract</i>	X
1. Introduction.....	1
1.1 Background	1
1.2 Statement of the problem	3
1.3 Objectives.....	4
1.3.1 General Objective	4
1.3.2 Specific Objectives	4
1.4 Significance of the study	4
1.5 Scope of the research.....	4
2. Literature Review.....	5
2.1 Dyes used in textile manufacturing industries	5
2.2 Textile Dye Operations	5
2.3 Classification of Dyes	6
2.4 Theory of Reactive dyes.....	7
2.5 Environmental problems of textile dye effluents	8
2.6 Dyes used in Ethiopia textile industries	9
2.7 Methods of dye removal from textile wastewater	9
2.7.1 Biological methods	10
2.7.2 Chemical methods	10
2.7.3 Physical methods	10
2.8 Adsorption.....	12
2.8.1 Adsorption Mechanism.....	12
2.8.2 Advantage of adsorption over other conventional methods	13
2.8.3 Adsorbents for dye removal	14

2.9 Factors affecting reactive dye biosorption	16
2.9.1 Effect of pH	17
2.9.2 Effect of initial dye concentration	17
2.9.3 Effect of biosorbent dosage	17
2.9.4 Effect of contact time	18
2.10 Dye Adsorption isotherm model	18
2.10.1. The Langmuir Model.....	18
2.10.2. The Freundlich Model	19
2.11 Dye Adsorption Kinetic Models	19
2.11.1 Pseudo-first-order or Lagergen kinetic model.....	19
2.11.2 Pseudo-second-order kinetic model.....	20
3. Methodology	21
3.1 Materials.....	21
3.1.1 Equipments and apparatus	21
3.1.2 Chemicals and reagents	21
3.2 Experimental Methods and procedures	21
3.2.1 Preparation of cactus peel as biosorbent.....	21
3.2.2 pre-treatment of biosorbent material	21
3.2.3 Characterization of the biosorbent.....	22
3.2.4 FTIR analysis of the material	23
3.2.5 X- ray diffraction (XRD) analysis	24
3.3 Stock solution preparation.....	24
3.4 Experimental Design	24
4. Result and Discussion	27
4.1 Characterization of cactus peel	27
4.1.1 FTIR analysis of biosorbent	27
4.1.2 Powder XRD Analysis.....	29

4.2 Batch Adsorption Studies.....	30
4.2.1 Effect of solution pH	30
4.2.2 Effect of initial dye concentration	31
4.2.3 Effect of biosorbent dose	32
4.2.4 Effect of contact time on the removal efficiency of reactive dye.....	33
4.3 Effects of interaction parameters on percentage dye removal	35
4.3.1 The interaction effect of solution pH and initial dye concentration.....	35
4.3.2 The interaction effect of solution pH and biosorbent dose.....	36
4.3.3 The interaction effect of solution pH and contact time	38
4.3.4 The interaction effect of initial dye concentration and biosorbent dose.....	39
4.3.5 The interaction effect of initial dye concentration and contact time	41
4.3.6 The interaction effect of biosorbent dose and contact time.....	42
4.4 Dye Biosorption Isotherm Models	45
4.4.1 Langmuir isotherm model	45
4.4.2 Freundlich isotherm model.....	46
4.5 Dye Adsorption Kinetic Models	48
4.5.1 Pseudo-first-order or Lagergen kinetic model.....	48
4.5.2 Pseudo second order kinetic model	50
5. Conclusions and Recommendations	53
5.1 Conclusion.....	53
5.2 Recommendations	54
References.....	55
Appendix A: Experimental Data.....	59
Appendix B: Adsorption Isotherms	61
Appendix C: Adsorption Kinetics.....	62
Appendix D: Results from the statically analysis	63

List of Tables

Table 1: Principal existing and emerging processes for dyes removal	11
Table 2: Comparison between physical and chemical adsorption	13
Table 3: proximate analysis of cactus peel	27
Table 4: Analysis of ANOVA for quadratic second order model	44
Table 5: constant parameters of Langmuir and Freundlich isotherm models for biosorption of reactive dye onto cactus peel	48
Table 6: Kinetic parameters for the removal of reactive dye by cactus peel	52
Table 7: Data used for calibration of the UV- Spectrophotometer	59
Table 8: Experimental Data for Effect of solution pH on the removal efficiency of Reactive Dye	60
Table 9: Experimental Data for Effect of initial dye concentration on the removal efficiency of Reactive Dye.....	60
Table 10: Experimental Data for Effect of biosorbent dose on the removal efficiency of Reactive Dye.....	60
Table 11: Experimental Data for Effect of contact time on the removal efficiency of Reactive Dye.....	61
Table 12: Data used for plotting Langmuir and Freundlich models for biosorption of Reactive dye onto cactus peel and their respective constant values	61
Table 13: Data for Pseudo first order kinetics	62
Table 14: Data for Pseudo second order kinetics.....	62
Table 15: adsorption parameters and their constant values of kinetic models	62
Table 16: The experimental design matrix	63
Table 17: Diagnostics case statistics.....	64
Table 18: Characteristic IR absorption frequencies of organic functional groups	66

List of Figures

Figure 1 : preparation of powder cactus peel for biosorption of reactive dye	22
Figure 2: FTIR analysis of acid treated and untreated cactus peel	28
Figure 3 : FTIR analysis of cactus peel after biosorption.....	28
Figure 4 :XRD analysis of cactus peel.....	29
Figure 5: Effect of PH on the removal efficiency of reactive dye	31
Figure 6 : Effect of initial dye concentration on the removal efficiency of reactive dye	32
Figure 7: Effect of biosorbent dose on the removal efficiency of reactive dye	33
Figure 8: Effect of contact time on the removal efficiency of reactive dye	34
Figure 9: The interaction effect of solution pH and initial dye concentration on adsorption of reactive dye (a) contour plot, (b). 3D plot	36
Figure 10: The interaction effect of solution pH and biosorbent dose on adsorption of reactive dye (a) contour plot, (b). 3D plot	37
Figure 11: The interaction effect of solution pH and contact time on adsorption of reactive dye (a) contour plot, (b). 3D plot.....	39
Figure 12: The interaction effect of initial dye concentration and biosorbent dose on adsorption of reactive dye (a) contour plot, (b). 3D plot	40
Figure 13: The interaction effect of initial dye concentration and contact time on adsorption of reactive dye (a) contour plot, (b). 3D plot	42
Figure 14: The interaction effect of biosorbent dose and contact time on adsorption of reactive dye (a) contour plot, (b). 3D plot	43
Figure 15: Langmuir isotherm model plot	46
Figure 16: Freundlich isotherm model plot	47
Figure 17: Pseudo first order for biosorption of reactive dye onto cactus peel	50
Figure 18: Pseudo second order for biosorption of reactive dye onto cactus peel	51
Figure 19: calibration curve to determine final dye concentration	59
Figure 20: Normal plots of residuals	68
Figure 21: Plot of residual Vs. predicted	68

List of abbreviations and symbols

AAIT	Addis Ababa Institute of Technology
ANOVA	Analysis of variance
BG	brilliant green
Ce	Equilibrium concentration in (mg/L)
CCD	Central composite design
FTIR	Fourier transforms infrared spectroscopy
GTP	Growth and Transformation Plan
RSM	Response surface methodology
RD	Reactive dye
UV	Ultraviolet
XRD	X-ray powder diffraction

Abstract

Numerous dye stuffs are used in textile industries to paint their products and produces high discharge rate of wastewater with high load of pollutants. Now the presence of dyes in the aquatic systems has become a serious environmental problem. currently bioadsorbents have become desirable for the removal of dyes from textile dye effluents due to their good performance, low cost, simple design, no sludge generation and their accessibility. In this study, the biosorption characteristics and feasibility of cactus peel have been analyzed to remove reactive dyes from aqueous solutions. Batch biosorption experiments were carried out for the biosorption of reactive dye molecule from aqueous solution onto the cactus peel adsorbent at constant room temperature of 25°C and agitation speed 200rpm. The effects of diverse process parameters like solution pH, biosorbent dosage, contact time and initial concentration were studied in batch adsorption.

For the equilibrium studies, Langmuir and Freundlich isotherm models were applied to identify the relationship between the concentration of dye ions in the solution and the amount of dye ions adsorbed to the cactus peel adsorbent. The interaction effect of process variables was studied using response surface methodology. The results from the experiments showed that, removal efficiency of reactive red dye was found to increase with lower initial dye concentration, lower solution pH, maximum biosorbent dosage and higher contact time. The effective solution pH, initial dye concentration, biosorbent dose and contact time on the reactive red dye removal efficiency of the cactus peel biosorbent was found to be 3.0, 40 mg/l, 6g and 120min respectively for batch biosorption studies. At these experimental conditions the removal efficiency of reactive red dye using cactus peel adsorbent was found to be 99.43%. regression coefficient of the Langmuir isotherm ($R^2=0.9935$) is higher than that of the Freundlich isotherm equation model ($R^2= 0.9722$). Thus, it is a practical and good evidence that the biosorption of the reactive red dye onto the cactus peel biosorbent follows the Langmuir isotherm represents the best fitting of experimental data than the Freundlich isotherm equation. Hence, this is indicative of complete mono-layer coverage of the dye on cactus peel surface and it was found to be 2.1066 mg/g. Biosorption kinetics was determined using pseudo first order and pseudo second order models and it was found that pseudo-second-order model mechanism is the finest model for biosorption of reactive red dye onto powdered cactus peel.

Key Words: - Biosorption, cactus peel, equilibrium, Isotherm models, kinetic models, Reactive dye.

1. Introduction

1.1 Background

World Arithmetic figures show that more than 70 percent of the surface of the Earth is covered by water. But a considerable percentage of this water is not suitable for human consumption and aquatic organisms because of different wastes discharged to it. Water contamination may have occurred due to the growth of industries, increase in population, urbanization, lack of environmental awareness and untreated effluents having different composition discharge from industries and municipalities. Developing nations like Ethiopia hurt more by the scarcity of water as well as water pollution, where already almost 75 percent of health sickness is directly or indirectly related with lack of fresh water. Dyes have numerous applications in industries such as textile, rubber, paper, plastic, leather and cosmetic etc. From these various industries textile levels first in usage of various types of dyes to paint their products. Textile industry is one of the fastest rising industries and expressively helps to the economic growth of a country including our country Ethiopia. This industry also has high water consumption and at the same time produces high discharge rate of wastewater with high load of contaminants. Pollutants that are produced from dyeing industries like that of textile industries are highly poisonous. Wastes from textile industry are one of the major sources of environmental pollution because effluents discharged from dyeing industries are highly colored with a large amount of suspended organic solids. Untreated discharge of the dye effluents into the receiving water body causes harm to aquatic life as well as to human beings by their mutagenic and carcinogenic effects.

The discharge of untreated dye effluents into the environment without any treatment processes during the wet processing of the textile dyeing and finishing processes is the main cause of water pollution that occurs currently. Dyes appear to be colored since they grip some wavelengths of light more than others. Currently textile dyeing industry becomes an alarm in which it releases significant amount of organic matter as well as dyeing agents that produce colors and contributes to water pollution that can disturb human health as well as other aquatic organisms. The availability of little amounts of dyes in water (less than 1 ppm for some dyes) is highly observable and undesirable due to their good solubility [1]. Synthetic dyes are common water pollutants that are typically found in textile wastewater. 10-25% of textile dyes are vanished during the process of dyeing, and 2-20% are directly discharged as aqueous wastes in diverse environmental components [2]. Many of these dyes are toxic and carcinogenic and

this leads to dangerous problem to aquatic living organisms and to the environment as a whole. The availability of untreated dye effluents seriously affects the quality of water that's why the elimination of this pollutant is our prime concern. Because of their complex chemical structures, it is difficult to treat reactive dyes with conventional waste treatment processes [3]. Even if at low concentration reactive dye can cause high prominence and undesirability. Furthermore, the color produced due to dyes in water makes it aesthetically disagreeable [4]. They can have acute or chronic properties on aquatic organisms, which depend on the dye concentration and the exposed time [3]. Textile waste water containing dyes is very problematic to treat, for the reason that dyes are resistant to aerobic digestion and are stable to light, heat and oxidizing agents and can remain in the environment for a long period of time. In unindustrialized countries like Ethiopia wastewaters from textile industries are directly discharged into drains, rivers, stagnant, ponds, or lakes without any treatment or with partial treatment because the existing treatment methods are not cost effective as well as they are ineffective to use them [5]. Many methods have been recommended and applied for removing dyes from textile dye effluents, including chemical Precipitation, ion exchange, filtration, flocculation, membrane separation, etc. These methods have imperfect application because they often involve high capital and operational costs and may have low efficiency that is linked with the generation of secondary wastes such as sludge which needs further treatment or purification. Adsorption method takes an advantage over the other methods, because of its humble design with a sludge free environment and it comprises low investment costs. Now a day adsorption using biomasses, which is named as biosorption become one of the alternate treatment methods for the removal of dyes from textile waste water. In a conceptual manner adsorption is a mass transfer operation in which a substance is transferred from the liquid phase to the surface of a solid and substance becomes adhered by physical and/or chemical interactions. Due to its large surface area, high adsorption capacity and surface reactivity of adsorbents, biosorption can be exploited as low-cost alternative, desirable and super dominant method when it associates with that of conventional Processes [6]. Even if its exact amount is not known numerically, cactus peel is the most abundant solid by-product that is generated in many places of Ethiopia specially in northern Ethiopia, like Amhara and Tigray regions. For example, in Tigray in one woreda named Ganta afeshum different survey result shows that out of the total area of the District more than 1607.05 hectare of the land is covered by cactus crop. Cactus peel fiber is composed of numerous chemical components such as cellulose, hemicelluloses, pectin, lignin and gums [7]. In addition, this material consists of 2.3% nitrogen, 29.4% carbon and 1.7% hydrogen.

1.2 Statement of the problem

In the current situation with increasing demand of the textile products textile industry is used as a bridge development of the second growth and transformation Plan (GTPII) in Ethiopia with the large contribution of foreign and local investors. We know that most of the textile industries are water intensive. As a consequence, polluted waste water is generated which can cause environmental problems except properly treated before it is discharged to the environment. Textile wastewater containing dye wastes is extremely concentrated, so that the existence of small amount of dyes can pollute larger amounts of groundwater which makes domestic water supply unsuitable for use and it causes human health problem as well as environmental pollution specially it affects the aquatic environment.

One difficult task faced by the wastewater treatment plants of textile industries is the removal of the color of these dye compounds, mainly because dyes have resistance to biodegradation and persist in the environment for a long period of time. The presence of dye materials significantly affects the quality of water and the removal of this kind of pollutant is of prime importance. Due to their complicated structure most of dyes are non-biodegradable.

If textile waste water containing dye effluents discharged without treatment it affects the photosynthesis of aquatic plants by preventing the light to penetrate through water. The oxygen levels are also affected and in extreme cases may lead to suffocation of aquatic flora and fauna as reactive red dyes can be degraded to more dangerous substances under anaerobic conditions. Many physical and chemical processes for reactive dye removal have been applied including coagulation and flocculation, photo-decomposition and ultra-filtration, oxidizing agents, membrane and electrochemical methods. Due to relatively high operating costs and low removal efficiencies using the above-mentioned processes, textile, tannery and paper industries rarely apply these to treat their effluents.

Therefore, it is better to develop a low cost and efficient treatment method to remove reactive red dyes from textile dye effluent in order to avoid its adverse influence on environment and human health.

In this research work due to its abundant availability, ease of operation, and low cost, utilization of cactus peel as bioadsorbent for the removal of reactive dyes from textile dye effluents has been used to overcome the above problems. Conversion of this waste to a useful adsorbent contributes not only for the treatment of textile waste water that pollutes the environment but also to minimize the generation of solid wastes. In addition, cactus plant is renewable, abundant, environmentally friendly and adaptable.

1.3 Objectives

1.3.1 General Objective

The general objective of this research study is to utilize cactus peel as bioadsorbent for the removal of reactive red dyes from textile dye effluents.

1.3.2 Specific Objectives

- ✚ Characterizing the cactus peel
- ✚ Investigating the effects of process parameters (like solution pH, adsorbent dosage, initial dye concentration and contact time) on the removal efficiency of reactive dyes.
- ✚ Determining the optimum working conditions as well as kinetic parameters.
- ✚ Investigating adsorption isotherm models for biosorption of reactive red dyes.
- ✚ Analyzing the biosorption capacity of cactus peel for the removal of reactive dye from textile dye effluents.

1.4 Significance of the study

This research study can have an advantage to protect the environment particularly the aquatic environment and avoid human diseases that results due to the depletion of the aquatic environment by providing cactus peel as biosorbent for removing dyes from textile dye effluents.

Commonly, this research work has the following significances

- ✚ Produce environmentally competitive and low-cost adsorbent for the removal of reactive dyes from textile dye effluents using locally available cactus peel.
- ✚ It helps to strengthen the knowledge in the area of biosorption using cactus peel.
- ✚ Offers baseline information for treatment of textile dye wastewater for Ethiopia textile industries.
- ✚ It helps as a reference for additional researches to be conducted in the removal of dyes from textile industries.

1.5 Scope of the research

The scope of this research has been covered modifying and characterizing of cactus peel as bioadsorbent for removal reactive dyes from textile dye effluents, characterization of reactive dyes before and after we use bioadsorbent using standard procedures and laboratory test methods. In addition to this the removal efficiency of reactive dye on the cactus peel biosorbent was investigated. At the last optimization and designing of experiments were achieved by the help of Design expert software. All experimentations were done on a laboratory scale.

2. Literature Review

2.1 Dyes used in textile manufacturing industries

There are many classes of dyes used in textile dyeing and printing operations. The most commonly used dyes are reactive and direct dyes for coloring cotton and disperse dyes for dyeing polyester [8]. Reactive dyes are extensively used in textiles industries because of favorable features, bright color, water-fast, simple application techniques with low energy consumption [9]. Reactive dyes are the major class of dyes used in textiles industry and it is the azo dyes based on the azo chromogen (-N=N-) and the existence of bright color due to these azo bonds and associated chromophore.

Direct dyes can be added to fibers directly without the encouragement of affixing agents. Whereas reactive and direct dyes are water soluble, the low water solubility of disperse dyes requires them to be functional as a distribution of finely ground powders in a dye bath. A dye molecule involves two key components: the chromophores, responsible for making the color, and the Auxochromes, which in addition to support the chromophore, also to cause the molecule soluble in water and give greater affinity toward the fibers [10]. Dyes have high structural diversity and can be categorized in many ways [11].

All dyes are organic aromatic compounds having conjugated double bond system, to which chromophores and Auxochromes are attached. These functional groups decrease the number of conjugated double bonds wanted for light absorption and result in molecules that are small enough to diffuse into fibers. Chromophores are unsaturated functional groups alone; they can absorb visible or near ultraviolet radiation. In a dye molecule, they used as electron acceptors. Auxochromes are saturated functional groups. Auxochromes used as electron donors because the atom attached to the conjugated system has nonbonding electrons.

2.2 Textile Dye Operations

The textile industry comprises a number of processes that are used to change fibers of natural origin such as cotton, silk and wool, and of synthetic origin such as nylon; first into fabrics by weaving and knitting and then into the final products by applying wet processes such as dyeing, printing, and finishing. These phases involve treating the fabric with chemical baths including dispersing agents, salts, emulsifiers, leveling agents, and often need additional washing, rinsing, and drying steps, and hence they also consume a large amount of fresh water, chemicals and a large production of wastewater streams. In terms of waste generation and environmental

problems, wet processing is the most important textile process. The majority of wastewater containing dye wastes is generated after dyeing and printing operations. For a dye house to turn grey goods into a finished product, numerous consecutive steps must occur, including fabric preparation, scouring, bleaching and finishing (dyeing, printing etc...). Among these fabrics finishing unit processes, scouring, bleaching, dyeing and finishing are the most water intensive textile processes. Though many of these steps are done at specialized fabric preparation or finishing facilities, some of these operations are employed by dye houses in most industries.

2.3 Classification of Dyes

One of the difficult problems that challenged in the waste water treatment of textile industries is the removal of dye from textile dye effluents that originates from many types of dyes used in the textile dyeing and printing operations. Commonly Textile dyes can be classified under the categories of anionic, cationic and nonionic types [12]. Anionic dyes contains the direct, acid and reactive dyes. Basic dyes are the only class of cationic dyes used in the textile industry operations. Nonionic dyes raise to disperse dyes , which do not ionize in an aqueous medium. Further dyes may be grouped based on two main classifications. These are based on their chemical structure and dyeing applications or practice. The easier way of dye classification for textile industries is by dyeing application. Under this classification dyes can be grouped as: acid dyes, disperse dyes, basic dyes, direct dyes, reactive dyes, chrome dyes, vat dyes, and sulphur dyes. Let's see the classification of dyes based on their usage or applications one by one.

i) Direct Dyes

Direct dyes are water soluble anionic dyes that are functional on cotton, cellulose, paper, leather, and nylon. Direct or substantive dyeing is usually carried out in a neutral or somewhat alkaline dye bath, at or near boiling point, with the accumulation of either sodium chloride (NaCl) or sodium sulfate (Na₂SO₄). Examples of direct dyes are azo, phthalocyanines, stilbene, and oxazine.

ii) Acid Dyes

These are water soluble anionic dyes and are being convened according to the lines of being colored and also the aromatic compounds contain in the structure that can be ionize. Acid dyes are useful to fibers such as silk, wool, nylon and modified acrylic fibers using neutral to acid dye baths. Attachment to the fiber is attributed, at least partially, to salt formation between anionic groups in the dyes and cationic groups in the fiber. They are continually used in an acidic solution. Some of the examples for acid dyes include picric acid and martius yellow.

iii) Reactive Dyes

Reactive dyes employ a chromophore attached to a substituent that is capable of directly reacting with the fiber substrate. These dyes form a covalent chemical bond with fiber is ether or ester linkage under appropriate conditions. The main chemical classes of reactive dyes are azo dyes. Typically, these chemical classes are used for dyeing and printing of cotton and wool.

iv) Basic Dyes

These dyes are cationic dyes and water soluble. Frequently acetic acid is added to the dye bath to help the uptake of the dye onto the fiber. They are functional on paper, polyacrylonitrile, modified nylons, and modified polyesters. In addition, they are used to apply with silk, wool, and tannin–mordant cotton when brightness shade was more required than fastness to light and washing. Generally, the chemical classes are diazahemicyanine, triarylmethane, cyanine, hemicyanine, thiazine, oxazine and acridine.

v) Disperse Dye

These are significantly water insoluble nonionic dyes for application to hydrophobic fibers from microfine aqueous dispersion. They are used mainly on polyester, polyamide, polyacrylonitrile, polypropylene fibers and a lesser on nylon, cellulose acetate, and acrylic fibers. Chemical classes of dyes mostly belong to azo and anthraquinonoid.

vi) Mordant dyes

These dyes have mordant dyeing property that simplifies the fixing of dye to a fiber by good quality of the presence certain groupings in the dye molecule which are capable to hold metal residuals by formation of covalent and coordinate bonds involving a chelate compound. Most natural dyes are mordant dyes and there is therefore a large literature base telling dyeing techniques. The most significant mordant dyes are the synthetic mordant dyes, or chrome dyes, used for wool. The mordant, potassium dichromate is used after-treatment.

vii) Vat dyes

Vat dyes are insoluble in water that can apply mainly for dyeing fiber by changing them to their leuco compounds by reduction and solubilization with sodium hydrosulphite and sodium hydroxide solution that is called as vatting process. The main chemical classes of vat dyes are anthraquinone and indigoid.

2.4 Theory of Reactive dyes

Reactive dyes are water soluble, anionic dyes that involve relatively simple dyeing methods; they are usually used for dyeing cellulosic fibres, such as cotton and rayon. Reactive dyes are

colored organic compounds that are capable of making a covalent bond between reactive groups of the dye molecule and nucleophilic groups on the polymer chains within the fiber. It was estimated that the covalent attachment of the dye molecules to the fiber would produce very high wash fastness because covalent bonds were the strongest known binding forces between molecules. The energy required to breakdown this bond would be of similar order as that required to break covalent bonds in the fiber itself. Reactive dyes were primarily familiarized commercially for application to cellulosic fibers, and this is still their most important use. The growth rate of reactive dyes for cellulosic fibers is anticipated to continue increasing because reactive dyes stay to gain market share at the expense of other dye types such as azoic dyes. Reactive dyes have also been developed for application on protein and polyamide fibers. In addition, researches into the development of reactive dyes for polyester and polypropylene fibers have been demonstrated to the level of technical opportunity but such dyes are not yet of commercial interest.

2.5 Environmental problems of textile dye effluents

Waste water containing dye effluents represents enormous water pollution which is damaging for humans, for fish and aquatic plants [13, 14]. Dyes in water give out a bad colour and can cause diseases like haemorrhage, ulceration of skin, nausea, severe irritation of skin and dermatitis [15]. They can block the penetration of sunlight from water surface stopping photosynthesis [16]. Dyes also enhance the biochemical oxygen demand of the receiving water and decrease the re-oxygenation process and hence hinder the growth of photoautotrophic organisms. Discharging of wastewater containing dye compounds into water sources has significantly reduced the quality of water. Since they have a synthetic origin and complex aromatic molecular structures, azo dyes are usually inert and problematic to biodegrade in waste streams [17]. They also affect photosynthetic activities of aquatic lives because dyeing effluents will deplete the dissolved oxygen contents in water and prevent sunlight from reaching to the water sources [18]. In addition to this dye wastewater and their degradation products are usually toxic, mutagenic, teratogenic and carcinogenic, which are undoubtedly harmful to aquatic organisms and human beings.

Therefore, appropriate techniques and processes must apply in industries for efficient removal of these toxic chemicals from water bodies. Many Physico-chemical processes have been projected and applied for treatment of textile wastewater [5]. Among the different recent dye removal methods, Adsorption, ion exchange, membrane filtration, ozonation, elctrokinetic coagulation, Fenton reagent and photo catalyst are the most commonly used.

Adsorption technologies for wastewater treatment are becoming more common in recent years due to flexibility and simplicity of design, ease of operation, insensitivity to toxic pollutants and the harmless nature of involved substances [19, 20].

2.6 Dyes used in Ethiopia textile industries

In Ethiopia textile industry is among the major manufacturing industries, in which the government has given special care to make good for the growth and transformation plan(GTPII). Most of them are involved in processing natural fibers, particularly cotton. There are diverse classes of dyes used in Ethiopia textile dyeing and printing operations. The most commonly used dyes are reactive and direct dyes for coloring cotton. Worldwide Synthetic textile dyes used each year are gone during manufacture and processing operation and 20% of these dyes discharge to the environment through effluents that result from the treatment of residual industrial waters [21]. Among the various classes of dyes, Reactive dyes are the brightest class of soluble dyes used by the Ethiopia textile industry as their pigment value is very high. However, Ethiopia does not have the industries that flourished in the developed countries, textile and leather industries are given more attention due to the accessibility of raw materials and further development of such industries is expected for the coming years. Reactive dyes are used commonly in textiles industries regarding favorable characteristics of bright color, water-fast, simple application techniques with low energy consumption [2].

2.7 Methods of dye removal from textile wastewater

Currently numerous methods are developing for removing dyes from textile waste water containing dye effluents. Generally, the technology can be divided into three main classes: biological, chemical and physical methods [22]. All of them have their own advantages and drawbacks. Because of high cost and final disposal problems, many of these conventional methods for treating textile wastewater containing dye effluents have not been usually applied on a large scale in the textile and paper Industries [23].

The methods applied for removal of dyes from textile waste water containing dye effluents includes Adsorption, membrane filtration, ozonation, chemical Precipitation, ion exchange, flocculation, membrane separation, etc. Among that Adsorption method is an advantageous over the other methods, because of its simple design with a sludge free environment, with regard to their efficiency in the removal of contaminants and it involves low investment costs. Adsorption does not have an adverse environmental effect for treatment of textile wastewater containing dye that's why in developing countries like Ethiopia it is a good study area where it becomes interest.

2.7.1 Biological methods

Biological treatment method is occasionally an economical alternative when compared with Physical and chemical processes. Textile dye effluents have high resistant to biodegradation and they are hard to treat by conventional biological treatments. Biodegradation methods such as adsorption by (living or dead) microbial biomass, fungal decolorization, bioremediation systems and microbial degradation are commonly used in the treatment of industrial wastes. Biological treatment requires large land area and is inhibited by sensitivity toward diurnal variation as well as toxicity of some chemicals, and has less flexibility in design and operation [24].

Biological treatment is not capable of acceptable colour removal with existing conventional biodegradation processes. Though many organic molecules are degraded, many others are intractable due to their complex chemical structure and synthetic organic origin [25].

2.7.2 Chemical methods

Chemical methods consist of coagulation or flocculation combined with floatation and filtration, precipitation-flocculation with Fe^{2+} / $\text{Ca}(\text{OH})_2$, electro floatation, electro kinetic Coagulation, conventional oxidation methods by oxidizing agents (ozone), electrochemical processes. These chemical techniques are often expensive, since chemical methods involves the usage of extreme chemicals further treatment may be needed because there is the possibility that some secondary pollution problems like sludge will generate after the removal of dyes from textile dye effluents which needs further treatment to remove this sludge.

2.7.3 Physical methods

Physical methods of dye removal from textile waste water containing dye effluents include membrane-filtration processes (Nano filtration, reverse osmosis, electrodialysis, etc.) and adsorption techniques. Membrane filtration has a potential to clarify concentrate and to separate dye continuously from different textile effluents [26]. The concentrated sludge left after adsorption leads into final disposal problems, high capital cost and the formation of blockage, and membrane replacement is its main disadvantages. This method of filtration is appropriate for water recycling purpose from the textile dye plant if the effluent contains low concentration of dyes, but it is incapable to reduce the dissolved solid content, which makes water re-use a difficult task. The major drawback of the membrane processes is that they have a short life time before membrane fouling occurs and their cost of periodic replacement of the membrane.

Table 1: Principal existing and emerging processes for dyes removal [23]

	Technology	Advantages	Disadvantages
Conventional treatment processes	Coagulation Flocculation	Simple, economically viable	High sludge production, handling and disposal problems
	Biodegradation	Economically attractive, publicly satisfactory treatment	Slow process, necessary to create an optimal favorable environment, maintenance and nutrition requirements
	Adsorption on activated carbons	The most effective adsorbent, high capacity, produce a high-quality treated effluent	Unsuccessful against disperse and vat dyes, the regeneration is expensive and results in loss of the adsorbent, non-destructive process
Established Recovery processes	Membrane separations	Removes all dye types, produce a high-quality treated effluent	High pressures, expensive, incapable of treating large volumes
	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
Emerging removal processes	Advanced oxidation process	No sludge production, little or no consumption of chemicals, efficiency for recalcitrant dyes	Economically unfeasible, formation of by-products, technical constraints
	Selective bioadsorbents	Economically attractive, regeneration is not necessary, high selectivity	Requires chemical modification, nondestructive process
	Biomass	Low operating cost, good efficiency and no toxic effect on microorganisms	Slow process, performance depends on some external factors (pH, salts)

2.8 Adsorption

Dye removal from textile wastewater containing dye effluents by adsorption techniques has become common from time to time. Adsorption is a mass transfer process which comprises the accumulation or concentration of a substance at the surface of another (solid surface). we can employ adsorption processes if we need to remove soluble material from the solution phase when the material is neither volatile nor biodegradable. It is the process that takes place when a liquid or a gas known as the adsorbate accumulates on the surface of a solid adsorbent and forming a molecular film. The substance being adsorbed is the adsorbate and the adsorbing material is named the adsorbent. In the bulk material, all the bonding requirements such as ionic, covalent or metallic of the constituent atoms of the material are occupied.

2.8.1 Adsorption Mechanism

Micro-porous cactus has a unique structure which essentially is a three-dimensional network, or labyrinth of carbon atoms some in hexagonal arrangements and some as individual carbon atoms bonded together extremely close but not closely packed. This bonding arrangement results in space existing between the atoms to create an interconnecting three-dimensional passageway in which every space unit has a connection to all others within the cactus surface. The site, place or space where a molecule can be trapped (adsorbed) is called an adsorption site. These adsorption sites can be modified in terms of their size (widened or narrowed) and in terms of their chemical composition. The surface can be bonded to hydrogen, oxygen, chlorine, nitrogen, *etc.* to alter the polarity of the surface. Changing this polarity can enhance the adsorption process for polar molecules. The porosity can be widened by gasification with water vapor, oxygen or carbon dioxide. The parent materials may also be impregnated with zinc chloride, potassium hydroxide or hydrochloric acid, these treatments improving adsorption characteristics, a process known as activation.

Generally speaking, Adsorption involves three basic steps.

i) Bulk solution transport

In this step the adsorbents travel from the bulk solution to the boundary layer of a fixed film liquid neighbouring the adsorbent. The dynamic force for this step is advection and dispersion in adsorbent contactors.

ii) Film diffusion transport

In this step adsorbates transfer from inert liquid film to the entry openings of the adsorbent.

iii) Pore transport and adsorption

In this step, adsorbate will be attached to the adsorbent by distribution along the active surface of the adsorbent.

Generally speaking adsorption is a removal process where certain molecules are bound to an adsorbent particle surface by either chemical or physical attraction.

Physisorption and Chemisorption

Physisorption or physical adsorption is a kind of adsorption in which the adsorbate adheres to the surface only through weak intermolecular interactions. In this case, the attraction interactions are van der Waals forces and, as they are weak the process results are reversible. It is characterized by:

- ✓ Low temperature, always under the critical temperature of the adsorbate
- ✓ Type of interaction: Intermolecular forces (van der Waals forces)
- ✓ Adsorption taking place in multilayer
- ✓ Low activation energy

Chemisorption or chemical adsorption is a type of adsorption where a molecule (the adsorbate) adheres to a surface of solid material (to the adsorbent) through the creation of a chemical bond. Unlike to physisorption, chemisorption occurs only as a monolayer and, moreover, substances chemisorbed on solid surface are hard to remove because of stronger forces at stake. It is characterized by:

- ✓ High temperatures.
- ✓ Type of interaction: strong; covalent bond between adsorbate and surface.
- ✓ Adsorption takes place only in a monolayer.
- ✓ High activation energy

Table 2: Comparison between physical and chemical adsorption

Physisorption	Chemisorption
Without chemical bonding.	With chemical bonding.
Reversible can be desorption.	Non – reversible.
Nonselective surface attachment.	Selective surface attachment.

2.8.2 Advantage of adsorption over other conventional methods

Adsorption is a suitable separation process when it compares with other conventional methods due to its high efficiency, fast and easy operation and simple and flexible design. In addition to this the adsorbent can be easily recovered and reused for additional purposes. Adsorption is commonly used for the removal of dye from textile wastewater containing dye effluents due to its low capital costs and the abundance of low cost adsorbents. The adsorption process may

generate insignificant contaminated pollutants and has low initial capital and operating costs [27]. Adsorption is nearly free from the environmental effects because no sludge is produced during the treatment process. Main drawback that related with most Physico-chemical methods is that they need secondary treatment to treat and dispose the sludge generated during the removal of dyes from textile waste waters.

2.8.3 Adsorbents for dye removal

The advantage of an adsorption process principally depends upon the nature of the adsorbents and their Physico-chemical properties. The adsorbent should have high selectivity, high adsorption capacity, long life time and should be accessible in abundance at relatively low cost. Today a large number of commercially available and low-cost adsorbents are used for removal of dyes from textile dye effluents.

Commercial Adsorbents

A number of commercially available adsorbents have been studied for textile wastewater treatment. Some of the important ones include silica gel, activated alumina and activated carbon, etc. The efficiency of these solid adsorbents in the textile wastewater treatment process depends on its structure, porosity and specific surface area.

Silica Gel

Silica gel is a non-hazardous, inert and efficient support and is generated by decreasing the pH value of the alkali silicate solution to less than ten. The adsorption of some anionic dyes, D&C Red 6, Acid Yellow 1, Acid Blue 25, Guinea Green B, on nanosized alumina-modified silica particles of different compositions and modal sizes was studied. They stated that the negatively charged dyes were electrostatically attracted positively charged cores and chemisorbed by forming a surface. The advantage of the adsorbent was its small size (<20 nm) and the capacity of the dyes to form chemical bonds with surface groups of the core particles [30].

Activated Alumina

The activated alumina includes a series of non-equilibrium forms of partially hydroxylated alumina oxide, Al_2O_3 . Activated alumina is a filter media made by treating aluminium ore so that it becomes porous and extremely adsorptive. The main disadvantage of activated alumina is that the adsorption efficiency is highest only at low pH. The ability of locally available industrial by-product to remove textile dyes from aqueous solutions was examined. The results show that the low cost locally available industrial waste material generated from aluminium

sulphate manufacturing process have significant practical applications for removal of dyes from textile wastewater containing dye effluents. The waste deposit contains different oxides, hydroxides and sulphates with a heterogeneous surface [29].

Activated Carbon

Activated carbon has been the most common and broadly used adsorbent in treatment of wastewater throughout the world. Today researchers are looking for low cost adsorbents for water contamination control, where cost factors play a major role. Low cost adsorbents can be prepared from a wide variety of raw materials which are abundant and cheap, having high organic content and low inorganic content that can be easily activated [30]. The preparation of low cost adsorbents from waste materials has numerous advantages, mainly of economic and environmental nature.

Low Cost Adsorbents

Materials which are locally and abundantly existing such as agricultural wastes, natural minerals and industrial by-products can be exploited as low-cost adsorbents. Conversion of these materials into adsorbents not only used for textile wastewater treatment but also it helps to decrease the amount of waste disposal to the environment and provide an alternative to commercial activated carbon.

Agricultural Wastes

Raw agricultural wastes and waste materials from forest industries such as rice and wheat wastes, Seeds of agricultural products, sawdust and bark have been used as adsorbents that have an implication in treating textile waste water containing dye wastes. These materials are best possibilities for textile wastewater treatment because of their eco-friendly and low cost, availability in large amount and renewable in nature. Most of the time agricultural wastes have large weight due to the existence of lignin, cellulose and hemicelluloses components [24]. It is highly suggested that using agricultural wastes as adsorbent for removal of different pollutants from industrial wastewater avoid the environmental nuisance. These comprises Adsorbents from rice and wheat wastes, Seeds of agricultural products, Stalks of agricultural wastes and Peels of different agricultural waste etc.

In previous study the effect of pre-treatment of three agricultural residues, wheat straw, corncob, and barley husk, on adsorption process in textile waste water was examined. It is investigated that a higher percentage of dye removal was achieved at a faster rate by the milled samples proving milling to be a better and more cost-effective treatment, except for barley husk which had a higher percentage removal for the control [6].

Eucalyptus bark

Eucalyptus bark that is a very abundant, low-cost, forest residue was used, as an adsorbent to remove Remazol BB which is a reactive dyestuff from aqueous solutions. The effects of different variables that were temperature, initial pH, sodium chloride concentration and initial dye concentration/bark concentration ratio on adsorption of the dye examined. The experiments performed under the same conditions with an activated carbon and reported that adsorption capacity of eucalyptus bark obtained as about one half of the activated carbon.

Cactus peel

Cactus is a member of the plant family Cactaceae, within the order Caryophyllales. Cactus show various adaptations to preserve water. Cactus have special adaptations to encourage efficient water use where they survive in hot and dry environments. The cactus crop residues after harvesting which are considered as solid waste such as peels of cactus plant can be used as an alternative low-cost adsorbent which can further help in reducing the cost of waste disposal and lowering wastewater pollution. Cactus peel powder has been tested for their potential to adsorb brilliant green (BG) dye from synthetic wastewater by adsorption [31]. In this study, cactus peels were used as an adsorbent for its potential for removal of reactive dye from textile wastewater containing dye effluents. The cactus plant peels from stem section were collected and process through a series of process to change it in to biosorbent.

Industrial and Municipal Wastes

Industrial operations produce large amount of solid waste materials as by-products. These industrial by-products are available in large amount, have low cost and causes disposal problem. If we use these industrial wastes as adsorbent for treatment of waste water the quantity of waste materials disposed to the environment reduced and at the same time contamination of wastewater can be reduced at reasonable cost. Thus, a number of industrial wastes with or without treatment have been examined as adsorbents for the removal of pollutants from wastewaters. Some of them includes Fly Ash, Steel industry waste and Aluminium industry waste (red mud).

2.9 Factors affecting reactive dye biosorption

The removal efficiency of reactive dyes from textile dye effluents mainly depends on several environmental parameters including solution pH, contact time, initial dye concentration, surface of biosorbent, and biosorbent dosage.

2.9.1 Effect of pH

pH is a measure the degree of acidity or basicity of an aqueous solution. We know that the degree of ionization of a species is principally affected by pH. The pH value of the dye solution is an important factor in adsorption process which determine the surface charge of the adsorbent which will affect the interaction between the adsorbate (dye solution) and biosorbent (cactus). The Effect of change in pH of dye solution on the removal efficiency of reactive dyes using cactus peel was studied by keeping the other variables (initial dye concentration, contact time, and biosorbent dosage) constant. At high pH of the dye solution, the removal efficiency of dye will increase for adsorption of cationic dye and decrease for adsorption of anionic dye [24].

2.9.2 Effect of initial dye concentration

To predict the final concentration the initial dye concentration of textile dye effluent is important since a given amount of biosorbent material can only adsorb a fixed volume of dye [32]. The effect of the initial of dye concentration depends on the relation between the initial concentration of the dye solution and the available active sites of the adsorbent surface.

In this experiment, the effect of change in initial concentration of dye solution on adsorption of reactive dye using cactus peel was studied by keeping the other variables (pH of solution, contact time, and biosorbent dosage) constant. Generally the dye removal efficiency will decrease with increasing initial dye concentration, because at a low concentration there will be unoccupied active sites on the adsorbent surface, and when the initial dye concentration increases, the active sites required for adsorption of the dye molecules will be lacking [33]. Therefore, the higher the concentration of the dye, the smaller the volume it can remove.

2.9.3 Effect of biosorbent dosage

In this research, the effect of change in biosorbent dose on adsorption of reactive dye was studied by keeping the other variables (pH of solution, initial concentration of dye solution, and shaking time) constant. Calibration curve was used to estimate the dye concentration present in the solution at any time from its corresponding value of absorbance. Normally, dye removal efficiency increases with increasing adsorbent dosage. Initially the rate of increase in the percent dye removal has been found to be fast which slowed down as the dose increased. With rise in adsorbent dose, there is less proportionate increase in adsorption, resulting from many sites remaining unsaturated during the adsorption [34]. But after a certain dosage the increase in removal efficiency is insignificant with respect to increase in dose because the active sites will be occupied by the adsorbate solution.

2.9.4 Effect of contact time

The effect of contact time on adsorption of dye was studied by preparing dye solution with fixed adsorbent dose, PH of solution and initial dye concentration for different time intervals and shaken until it reaches equilibrium. In this experiment, the effect of contact time on adsorption of reactive dye using cactus peel was studied by keeping the other variables (pH of solution, initial dye concentration, and biosorbent dosage) constant. Generally, percentage removal of dye increases with an increase in contact time to a certain level. Further increase in contact time does not increase the removal efficiency of dye due to the deposition of dyes on the available active sites of the adsorbent surface [35]. The time required to reach this state of equilibrium is called the equilibrium time, and the amount of dye adsorbed at the equilibrium time illustrates the maximum adsorption capacity of the biosorbent material.

2.10 Dye Adsorption isotherm model

Adsorption isotherm models are vital models that are relevant when we want to design the adsorption systems. The isotherms specify how the adsorbed molecules distribute themselves between the liquid phase and the solid phase when the adsorption process reaches equilibrium. The data found from these isotherm models gives us valuable information about the capacity of the biosorbent material under different operating conditions. In this research study adsorption isotherm model was used to characterize the interaction of the dye ions with the cactus peel biosorbent. This will be used to know the amount of dye adsorbed by a given mass of the cactus peel adsorbent. Langmuir and Freundlich isotherms are the most commonly used linear isotherm models. Regression methods will be used to determine the coefficients of the isotherm equations.

2.10.1. The Langmuir Model

The Langmuir model shows quantitatively the formation of a monolayer adsorbate (reactive dye solution) on the surface of the adsorbent (powder cactus peel), and after that no further adsorption takes place. In addition to that, the Langmuir represents the equilibrium distribution of reactive dye ions between the solid and liquid phases.

The Langmuir isotherm works based on the assumption that all binding sites have equivalent affinity ensuing in the formation of monolayer of adsorbed molecules [36].

The adsorption takes place at specific sites of the adsorbent. Each site retains one molecule of the dye compound. saturation point is reached, where no additional adsorption can occur.

All sites are approximately identical and energetically equivalent.

This can be expressed by the formula:

$$\frac{C_e}{q_e} = \frac{1}{qmKL} + \frac{1}{qm} C_e \quad (2.1)$$

Where: qm is the amount of dye adsorbed per unit mass of the adsorbent

equivalent to formation of complete monolayer

kL is the Langmuir constant related to the equilibrium constant of the adsorption process

$C_e \left(\frac{mg}{L}\right)$ and $q_e \left(\frac{mg}{g}\right)$ are the equilibrium liquid phase concentrations

and amount of solute adsorbed at equilibrium, respectively.

2.10.2. The Freundlich Model

The Freundlich isotherm was used to describe adsorption to heterogeneous surfaces having adsorption sites of varying affinities [37]. Freundlich isotherm is the most recognised model for multilayer adsorption process.

This model is applied to adsorption process on heterogeneous surfaces of the biosorbent with an interaction between dye molecules. The Freundlich isotherm equation is given as:

$$\text{Log } q_e = \log K_f + \frac{1}{n} \log C_e \quad (2.2)$$

Where K_f and n are Freundlich adsorption constants, related to adsorption capacity and sorption intensity respectively which obtained from the linear plot of $\log(q_e)$ against $\log(C_e)$ which gives a straight-line graph with $1/n$ as slope and $\log(K_f)$ as intercept.

2.11 Dye Adsorption Kinetic Models

In order to efficiently use cactus peel as potential biosorbent, contact time is fundamental importance parameter. Therefore, the efficiency of the adsorbent was examined by studying its adsorption kinetics. The kinetic properties of adsorbate uptake have been used to know the adsorption capacity of the adsorbent at a given time(t) for the batch adsorption process. Pseudo first order and pseudo second order models are the most commonly used kinetic models that are used to examine the mechanism of sorption to fit the biosorption data of different dyes onto various biosorbents.

2.11.1 Pseudo-first-order or Lagergen kinetic model

The Pseudo-first-order or Lagergen rate equation is the first equation for sorption of liquid/solid system based on solid capacity.

The Pseudo-first-order equation is given by the equation written below.

$$\log(q_e - qt) = \log q_e - \left(\frac{k_1}{2.303}\right)t \quad (2.3)$$

Where: q_e is the adsorption capacity at equilibrium

qt is the adsorption capacity at time t and

k_1 is the rate constant of pseudo first – order adsorption (min^{-1})

The value of adsorption rate constant (K_1) for the adsorption of dyes from textile dye effluents on cactus peel was determined from the slope of the linear plot of $\log (q_e - q_t)$ against t .

2.11.2 Pseudo-second-order kinetic model

The pseudo-second-order kinetic model is based on the assumption that the adsorption might be second-order, and the rate limiting step may involve some forces through sharing or the exchange of electrons between biosorbent and adsorbate [48].

The pseudo-second-order model is expressed by the formula:

$$\frac{dq}{dt} = K_2(q_e - q_t)^2 \quad (2.4)$$

Integrating for the boundary condition $t = 0$ to $t = t$, and $q_t = 0$ to $q_t = q_t$, the equation is given as follow:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + K_2 t \quad (2.5)$$

rearranging equation (2.5) into its linear form becomes:

$$\frac{t}{q_t} = \frac{1}{(K_2 q_e^2)} + \frac{t}{q_e} \quad (2.6)$$

Where K_2 is the rate constant of sorption, q_e is the amount of dye adsorbed at Equilibrium, (mg/g), q_t is amount of dye sorbed on the surface of the adsorbent at any time, t . The value of adsorption rate constant (K_2) and the amount of dye adsorbed at Equilibrium (q_e) for the adsorption of dyes from textile dye effluents on cactus peel was determined from the slope of the linear plot of $\frac{t}{q_t}$ against t .

3. Materials and Methods

3.1 Materials

3.1.1 Equipments and apparatus

The major equipments and apparatus that were used during this thesis work includes Analytical balance (Ohaus, EP 214C Switzerland), grinder, 250ml plastic bottles, Orbital shaker (GFL 3074 Model), Sieves (200-250mm size) , pH meter (model: JENWAY; 3505 pH meter), magnetic stirrer, U.V- spectrophotometer (Jenway 6300 England), FTIR (model: Perkin Elmer Spectrum 65), XRD, drying oven (model: Memmert,100- 800 Germany), Furnace (Nebetherm LHT 02/16 Germany), Micro pipette (10-25ml), crucible, volumetric flasks (50-250 ml), pipettes, desiccators, test tubes, glove and whats man filter paper etc.

3.1.2 Chemicals and reagents

The major raw material used as biosorbent during this experimental works was cactus peel. Most of the chemicals used in this thesis study were of analytical-laboratory grade obtained from different chemical supplies of Addis Ababa city. Powder reactive dye was obtained from Ayka Addis textile industry. The reactive dye was used without extra purification as adsorbate. The chemicals that were used during this research work includes 0.1M HCl, and 0.1M NaOH solution, KBr, distilled water and tap water.

3.2 Experimental Methods and procedures

3.2.1 Preparation of cactus peel as biosorbent

Fresh cactus peel sample used for this research study was collected from agricultural farm lands of Adigrat city in which it is abundantly available and have low cost. Then the peels of cactus sample collected was first washed by tap water and further cleaned by distilled water to remove impurities. The peels have been Filtered to get rid of water and the cleaned biomass was dried in oven at 90 °C for 24 hours until all the moisture content was removed from it. Then the dried cactus was ground into fine powders using grinder and sieved through a screen.

3.2.2 pre-treatment of biosorbent material

The ground and sieved cactus peel was soaked and agitated at 200 rpm for 24 hours with HCl to wash out the impurities on the surface and to improve the adsorptive capacity of the biosorbent. In addition to this in the presence of HCl, soluble components of cactus peel dissolved in acidic solution and the adsorbent surface get oxidized in order to have high absorption capacity. The adsorbent was washed by distilled water until the outlet pH reached near to neutral. Then the biomass dried at 105 °C for 24 hours in oven and used as biosorbent for further batch adsorption studies [31].



Figure 1 : powder cactus peel for biosorption of reactive dye

3.2.3 Characterization of the biosorbent

i) Moisture Content Determination

The moisture content of cactus peel was determined by oven drying method that has been carried out according to the procedure listed below:

- First the cactus peel was collected from agricultural lands of Adigrat city.
- Second the mass of the cactus powder was measured using analytical balance.
- Third the powder of cactus peel was putted into oven at 105°C for 3 hrs.
- finally, the mass of the dry content was measured and its moisture content was calculated using the following formula written as

$$\text{moisture content} = \frac{W_1 - W_2}{W_1} * 100 \quad (3.1)$$

Where: W_1 is original weight of the powder cactus peel before drying and

W_2 is weight of the powder cactus peel after drying in oven .

ii) Ash content determination

The ash content of the cactus powder sample was determined using muffle furnace. A ceramic crucible was washed and dried in an oven for 35 minutes at a Temperature of 105°C and it has been cooled in desiccators for a certain minute. The crucible was weighed using analytical

balance. Then it has been transferred to a muffle furnace at a temperature of 500°C for one hour, for complete de-carbonization to get white ash. The crucible and ash were cooled and the weight has been recorded. The result was expressed as follow:

$$\text{Ash content (\%)} = \frac{W_f}{W_i - x} * 100 \quad (3.2)$$

Where: W_f weight of the ash and
 W_i is original weight of the powder cactus peel sample
 x is percentage of moisture content taken for test.

iii) Volatile matter determination

To determine the volatile matter, 3g of sample was added in the crucible and weighed. It was kept in the muffle furnace at a temperature of 600 °C for 15 minutes. Then it was taken out and kept in the desiccators for 10 minutes to cool down and measured.

$$\text{VM} = \frac{(M_i - M_f) * 100}{M_i} \quad (3.3)$$

Where: VM = Volatile matter
 M_f is mass of the ash
 M_m is moisture mass and M_i is initial mass of the sample

iv) Fixed Carbon

The carbon content was calculated by sum up the moisture content, volatile matter and ash content reduce from 100 as follows:

$$\text{FC} = 100 - (\text{moisture content} + \text{volatile matter} + \text{ash content}) \quad (3.4)$$

Where FC = fixed carbon

3.2.4 FTIR analysis of the material

FTIR characterization was performed in order to identify the functional groups existing on the biosorbent that might be involved in the reactive dye uptake process. FTIR analysis was conducted on cactus peel powder before and after adsorption using Perkin Elmer spectrum 65 model FTIR spectrometer in average wave length from 4000 to 400cm⁻¹ to observe the changes in functional groups. The prepared cactus peel samples for the analyses were first milled in a ceramic pestle to powdery conditions and the powder was mixed with KBr particles to make it suitable to infrared analysis. The mixture was then press to a small thickness to make the sample a pellet that required for FTIR study. Then the adsorbent was scanned in the spectrum range of 4000-400 cm⁻¹. This spectrum is a graph which comprises percentage of transmittance along Y- axis and wavelength along X- axis. The type of the functional group present with in the adsorbent can be predicted by the help of available table by studying the peak between a particular wave length.

3.2.5 X- ray diffraction (XRD) analysis

XRD spectra of powdered cactus peel was characterized by using X-Ray Diffractometer at Addis Ababa university arat kilo campus of chemistry department. XRD analysis is made to identify the crystallographic structure of the sample (cactus peel). The x-ray powder diffraction method is used to characterize specific crystals using specific characteristic diffraction peak patterns and it involves of three basic elements X-ray tube, sample holder and the X- ray detector that takes the diffracted X-rays. The powder cactus peel was packed and loaded into the diffractometer. The powder was packed into the holder then pressed down and flattened in order to present a smooth diffraction surface. Then, the diffractometer was run over a 2θ range of 3° to 90° .

3.3 Stock solution preparation

Reactive dyes are water soluble anionic dyes that requires simple dyeing methods and they are usually used for dyeing cellulosic fibres, such as cotton and rayon. For this research work Reactive dye powder was taken from Ayka Addis textile industry and it was used as adsorbate molecule in conducting batch adsorption experiments. A stock solution of dye (1000 ppm of reactive dye solution) was prepared by dissolving 1 g of powder dye in 1000ml distilled water. It was then kept in a volumetric glass to make further dilute dye solutions. Samples of different dye concentrations were prepared by dilution from the prepared stock solution. Typically, initial dye concentrations of 40 ppm, 60 ppm and 80 ppm were prepared that are used in conducting batch adsorption experiments.

3.4 Experimental Design

The experimental runs were conducted randomly and suitable analysis technique has been ensured by the help of Design – Expert[®] version 7. software. In addition, the central composite design (CCD) is used for fitting a quadratic surface, which usually works well for the process optimization and it reduces the number of experiments to be carried out [2]. pH of the solution, initial dye concentration, biosorbent dose and contact time were the set of four independent process factors to investigate their effect on the output variable (response), which is the removal efficiency of the reactive dye from aqueous solution by using powder cactus peel biosorbent. Results from these analyses were used as input to conclude about the research outputs. For the experimental design of four independent variables ($n = 4$) and two center points ($n_c = 2$) using central composite design (CCD) each with two different levels, the total number of experiments (N_t) was calculated using the following formula:

$$N_t = 2^n + 2n + n_c = 2^4 + 2(4) + 2 = 26 \quad (3.5)$$

3.4.1 Batch Adsorption Studies

Effect of solution pH

pH is a measure the degree of acidity or basicity of an aqueous solution. We know that the degree of ionization of a species is principally affected by pH. The pH value of the dye solution is an important factor in adsorption process which determine the surface charge of the adsorbent which will affect the interaction between the adsorbate (dye solution) and biosorbent (cactus). The Effect of change in pH of dye solution on the removal efficiency of reactive dyes using cactus peel was studied by keeping the other variables (initial dye concentration, contact time, and biosorbent dosage) constant. The effects of initial pH on reactive dye solution of was investigated by varying the pH from 3 to 9.

Effect of initial dye concentration

The initial dye concentration of the dye solution is important since a given mass of biosorbent material can only adsorb a fixed volume of dye [32]. In this research study, the effect of change in initial concentration of dye solution on adsorption of reactive dye using cactus peel was studied by keeping the other variables (pH of solution, contact time, and biosorbent dosage) constant.

Effect of biosorbent dose

The effect of biosorbent dose is a significant factor that affects the biosorption process which gives us relevant information about the effectiveness of the biosorbent and used to know the relationship between the concentration of dye ions in the solution and the amount of dye ions adsorbed to the cactus peel adsorbent. In this experiment, the effect of variation in biosorbent dose on adsorption of reactive dye was studied by keeping the other variables (pH of solution, initial concentration of dye solution, and contact time) constant.

Effect of contact time on the removal efficiency of reactive dye

In this experiment, the effect of contact time on adsorption of reactive dye using cactus peel was studied by keeping the other variables (pH of solution, initial dye concentration and biosorbent dosage) constant. Generally, the rate of removal of dye increases with an increase in contact time to some extent. Further increase in contact time does not increase the percentage removal efficiency due to deposition of dye molecules on the available active sites of the adsorbent material [35].

3.4.2 Dye Biosorption Isotherm Models

Adsorption isotherms are vital models that are applicable when the design of adsorption system is mandatory. The isotherm models designate how the adsorbed molecules dispense themselves between the liquid phase and the solid phase when the adsorption process reaches equilibrium. The data found from these models gives us appropriate information about the capacity of the biosorbent under different conditions. In this research study adsorption isotherm model was used to characterize the interaction of the dye ions with the cactus peel biosorbent. Adsorption isotherms have many important practical implications, for example; it gives as an evident information on how the biosorption process proceeds, and used to observe how efficiently a given adsorbent interacts with adsorbate. The most widely known surface biosorption models for single-solute systems are the Langmuir and Freundlich isotherm [39].

Langmuir isotherm model

The Langmuir model illustrates quantitatively the formation of a monolayer adsorbate (reactive dye solution) on the outer surface of the adsorbent (powder cactus peel), and after that extra adsorption doesn't takes place. By that, the Langmuir signifies the equilibrium distribution of reactive dye ions between the solid and liquid phases. The Langmuir isotherm is based on the assumption that all binding sites have equivalent affinity resulting in the formation of monolayer of adsorbed molecules [14].

Freundlich isotherm model

The Freundlich isotherm was used to define adsorption to heterogeneous surfaces having adsorption sites of varying affinities. Typical property of heterogenic surface is that the areas where adsorption happens vary in terms of adsorption energy. Freundlich isotherm is the most basic known model for multilayer adsorption process. This model is applied to adsorption on heterogeneous surfaces with an interaction between dye molecules.

3.4.3 Dye Adsorption Kinetic Models

The sorption mechanism and the rate of the adsorption process are crucial for assessing the biosorption process. To use cactus peel efficiently as a potential biosorbent, contact time is of fundamental importance process parameter. Therefore, the efficiency of the adsorbent will be investigated by studying adsorption kinetics carefully. The kinetics of biosorption designates the solute uptake rate in a given residence time of sorption process. The most common kinetic models that are used to evaluate the performance of the biosorbent for dye removal to fit the biosorption data are the pseudo first order and pseudo second order models.

4. Result and Discussion

4.1 Characterization of cactus peel

The proximate analysis of powdered cactus peel was summarized in table below as follows:

Table 3: proximate analysis of cactus peel

contents	Value (%)
Moisture content	2.63
Ash content	1.56
Volatile matter	7.22
Fixed carbon	88.59

4.1.1 FTIR analysis of biosorbent

FTIR characterization was performed in order to investigate the functional groups that exists on the biosorbent that might be involved in the reactive dye biosorption process. The spectrum of the adsorption peak at the range $3420-3440\text{cm}^{-1}$ may represent the existence of O–H stretching vibrations of cellulose, pectin and lignin and –NH groups on the adsorbent surface. The spectrum also shows the adsorption peaks around 1382 cm^{-1} and 1050 cm^{-1} which shows the presence of -C-H bending vibration of alkane and C-O stretching vibration respectively [36]. The wave length of the peaks around 2921cm^{-1} might assigned to –CH stretching vibration functional groups. After HCl treatment, more functional groups were presented to the surface. From the Peaks of FTIR spectrum, it could be evidently investigated that the major involvement of functional groups like –NH, –OH, C-O, C-H, –CH, and –COOH present on the biosorbent surface in reactive dye biosorption process.

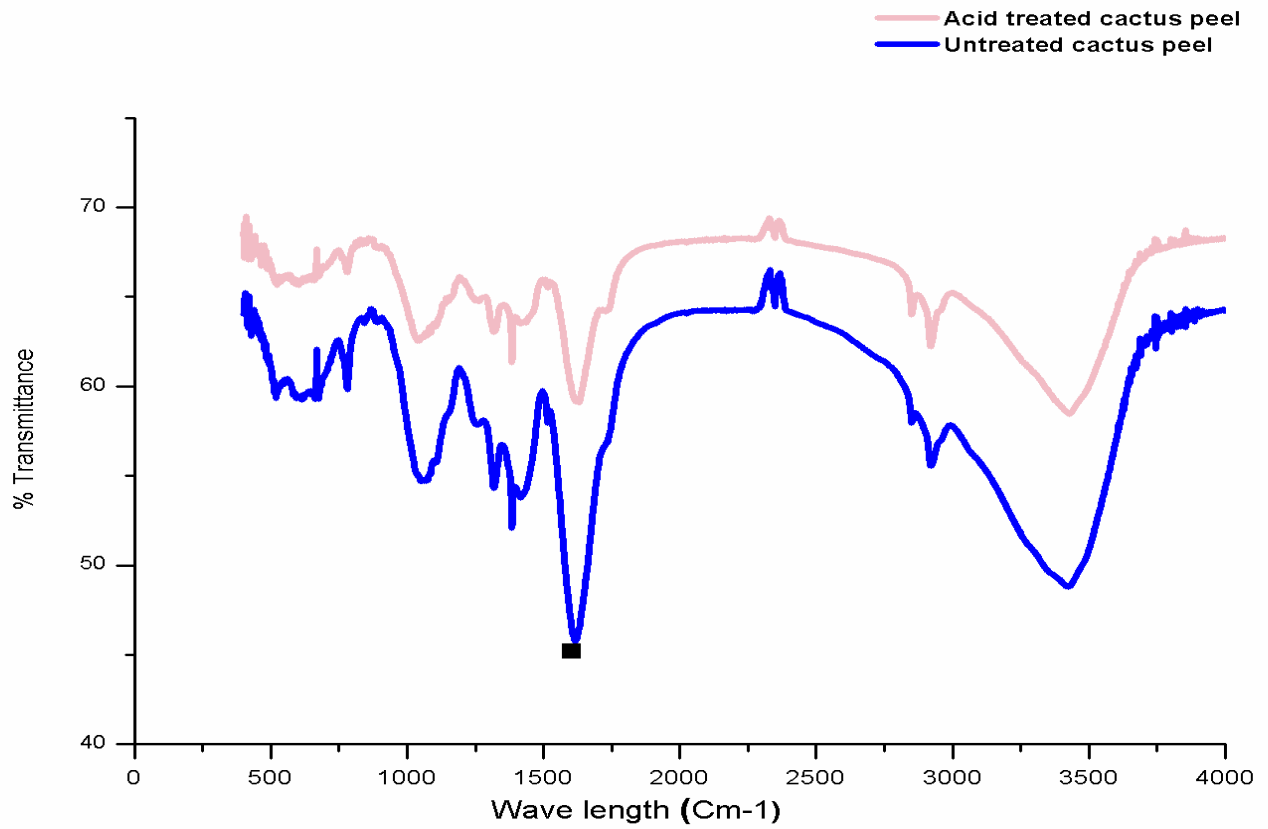


Figure 2: FTIR analysis of acid treated and untreated cactus peel

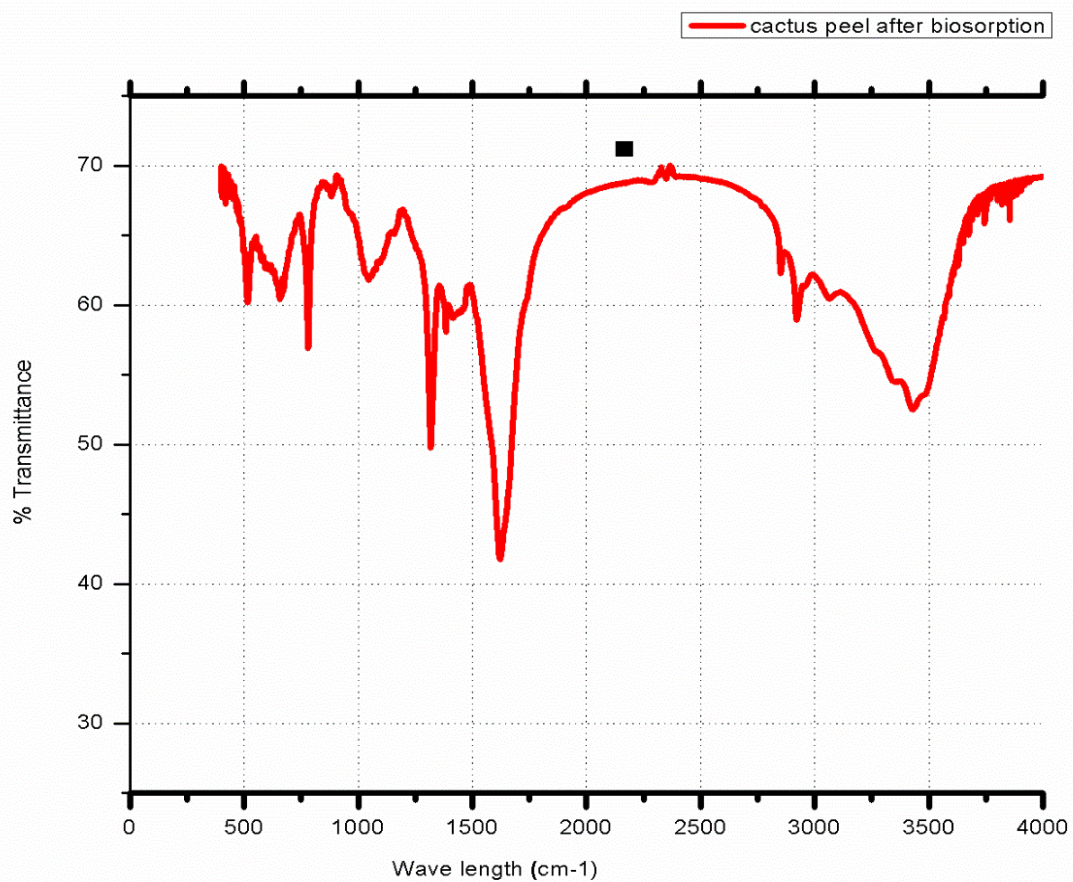


Figure 3 : FTIR analysis of cactus peel after biosorption

Figure 3 above displays FTIR analysis of cactus peel biosorbent after biosorption with many adsorption peaks which shows the functional properties of the biosorbent. From this graph stretching vibration absorption band at 1616.35 cm^{-1} is assigned to carboxylic groups. A wave length of 3415.38 shows the presence of O-H stretch hydroxide group. As seen in figure.3 broad peak representing hydroxyl and amine groups shifts from 3424.02 to 3415.38 cm^{-1} after adsorption of reactive dye. This is due to the attachment of reactive dye molecules on the available functional groups of the cactus peel biosorbent surface.

4.1.2 Powder XRD Analysis

Figure 4 below shows the characteristic peaks on the powder XRD pattern of cactus peel biosorbent. Most of the diffraction peaks for cactus peel biosorbent are located around scattering angle (2θ) of $15\text{-}35^\circ$. This might be due to the reason that as the 2θ becomes lower the biosorbent material could have further porous character and the more it has adsorption capacity. Thus, the diffraction peaks of the adsorbent appeared at scattering angles (2θ) of $15.36, 24.93, 28.75, 30.58, 36.35$ and 38.56° . The sharp peaks demonstrate the crystalline nature of the biosorbent material. Product synthesized of cactus peel is also assumed to be impure due to the availability of additional peaks far away from the most probable 2θ values which may account for the existence of their corresponding oxides or unreacted acid molecules.

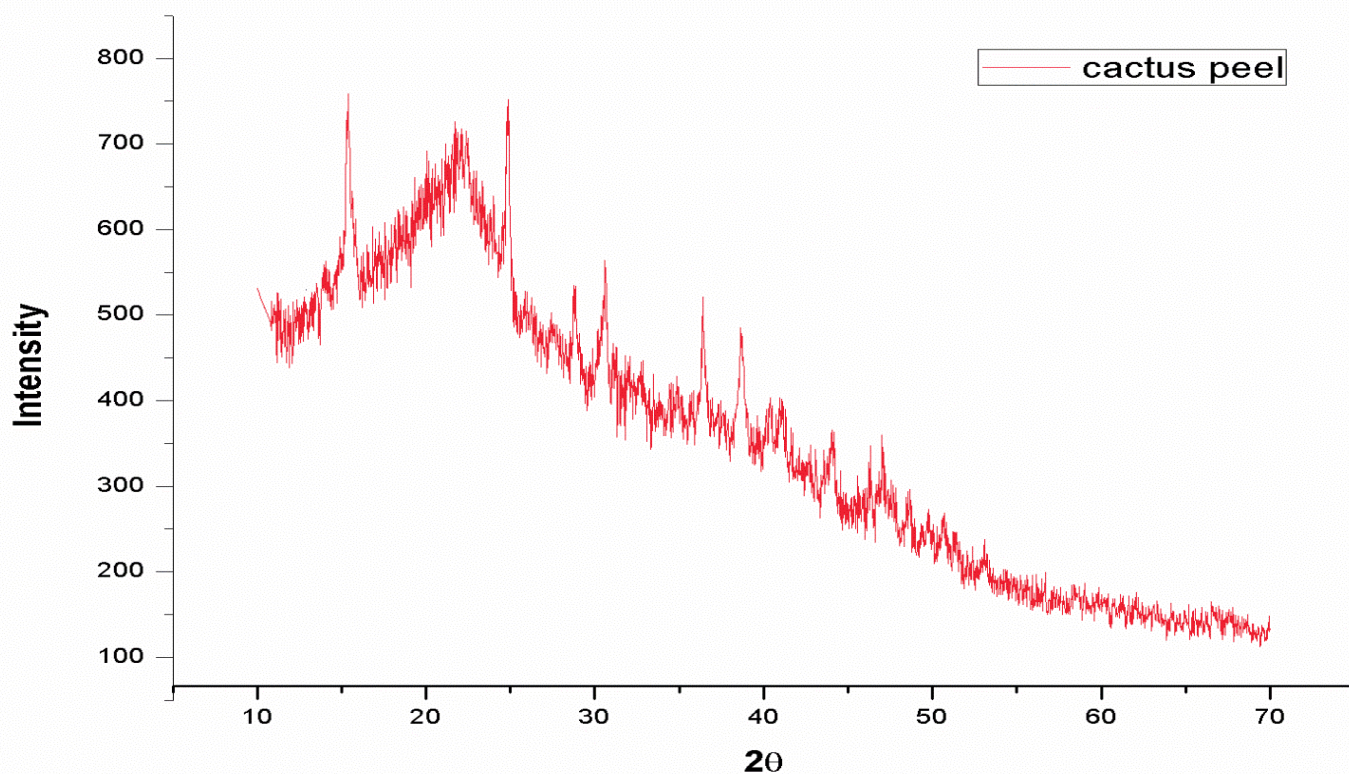


Figure 4 :XRD analysis of cactus peel

4.2 Batch Adsorption Studies

4.2.1 Effect of solution pH

pH is a measure the degree of acidity or basicity of an aqueous solution. We know that the degree of ionization of a species is principally affected by pH. The pH value of the dye solution is an important factor in adsorption process which determine the surface charge of the adsorbent which will affect the interaction between the adsorbate (dye solution) and biosorbent (cactus). The Effect of change in pH of dye solution on the removal efficiency of reactive dyes using cactus peel was studied by keeping the other variables (initial dye concentration, contact time, and biosorbent dosage) constant. The effects of initial pH on reactive dye solution of was investigated by varying the pH from 3 to 9. An increase in pH beyond 9, the amount of hydroxyl ions increased in the solution and dye ions react and precipitate with OH⁻ ions which results impossible the biosorption process [49]. Lowering the pH below 3 of the solution probably results in decreasing of biosorption levels and this can be explained due to competition between protons and dye ions for the capturing same sites of the adsorbent [51].

Figure 5 below shows the removal efficiency of reactive dye by cactus peel at different pH values of the dye solution. Therefore, from this graph we can observe that as pH decrease removal efficiency of the adsorption process goes up. This shows the fact that to remove reactive dye from textile dye effluents using cactus peel biosorbent an acidic pH is suitable condition. This is because low pH value leads to an increase in concentration of hydronium [H⁺] ion in the system and the surface of cactus peel may gain positive charge by absorbing H⁺ ions. As the cactus peel is positively charged at low pH value, a strong electrostatic attraction appears between the negatively charged anionic dye and the cactus peel leads to maximum adsorption of the dye. On the other hand, increase in pH value of the dye solution lead to increase in the number of negatively charged sites on the adsorbent. The maximum removal efficiency of reactive dye ions was found to be at pH 3.0. Thus pH 3.0 was considered as optimum pH value for the removal of reactive dyes by using cactus peel as biosorbent.

Removal eff.

● Design Points

X1 = A: pH

Actual Factors
 B: Con = 60.00
 C: Dose = 4.00
 D: Time = 80.00

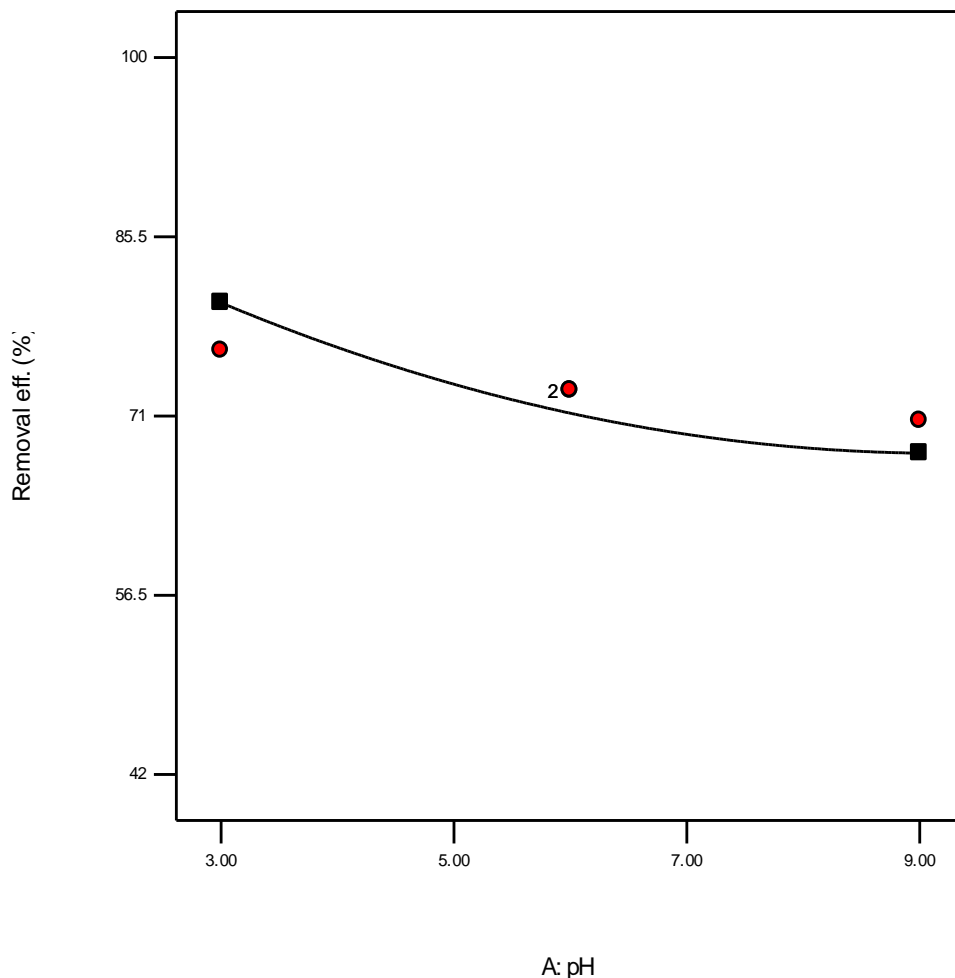


Figure 5: Effect of PH on the removal efficiency of reactive dye

4.2.2 Effect of initial dye concentration

The initial dye concentration of the dye solution is important since a given mass of biosorbent material can only adsorb a fixed volume of dye [32]. In this research study, the effect of change in initial concentration of dye solution on adsorption of reactive dye using cactus peel was studied by keeping the other variables (pH of solution, contact time, and biosorbent dosage) constant. The effect of initial dye concentration on the adsorption of reactive dye was examined as shown in (Figure 6) below. The experiments are carried out at constant initial pH of 6, biosorbent dose 4gm and contact time of 80 minute. At lower dye concentrations active sites of biosorbent to solute concentrations ratio is higher, which cause an increase in color removal [38]. The result from the graph below indicated that removal efficiency of reactive dye decreases with an increase in the initial dye concentration. This is due to the fact that at higher dye concentrations the active sites of the adsorbent were occupied by the dye ions and become saturated.

Removal eff.

X1 = B: Con

Actual Factors

A: pH = 6.00

C: Dose = 4.00

D: Time = 80.00

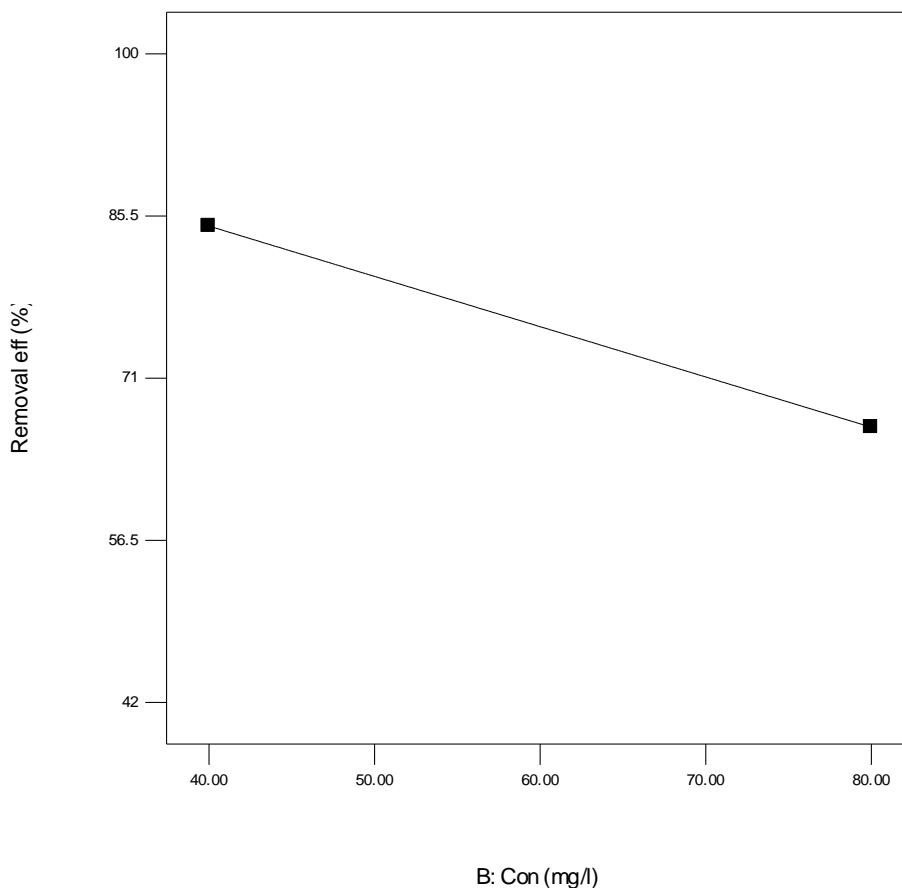


Figure 6 : Effect of initial dye concentration on the removal efficiency of reactive dye

4.2.3 Effect of biosorbent dose

The effect of biosorbent dose is a significant factor that affects the biosorption process which gives us relevant information about the effectiveness of the biosorbent and used to know the relationship between the concentration of dye ions in the solution and the amount of dye ions adsorbed to the cactus peel adsorbent.

In this experiment, the effect of variation in biosorbent dose on adsorption of reactive dye was studied by keeping the other variables (pH of solution, initial concentration of dye solution, and contact time) constant. Figure 7 below explains the effect of adsorbent dosage on the removal efficiency of reactive dye from textile dye effluents by using cactus peel. The percentage of reactive dye removed increased with increase in biosorbent dosage due to increased adsorption surface area of the active sites of the adsorbent. But further increase in the adsorbent dosage did not show an increased removal of reactive dye concentration because the active sites of the biosorbent will be occupied by the reactive dye solution

Removal eff.

- Design Points

X1 = C: Dose

Actual Factors

A: pH = 6.00

B: Con = 60.00

D: Time = 80.00

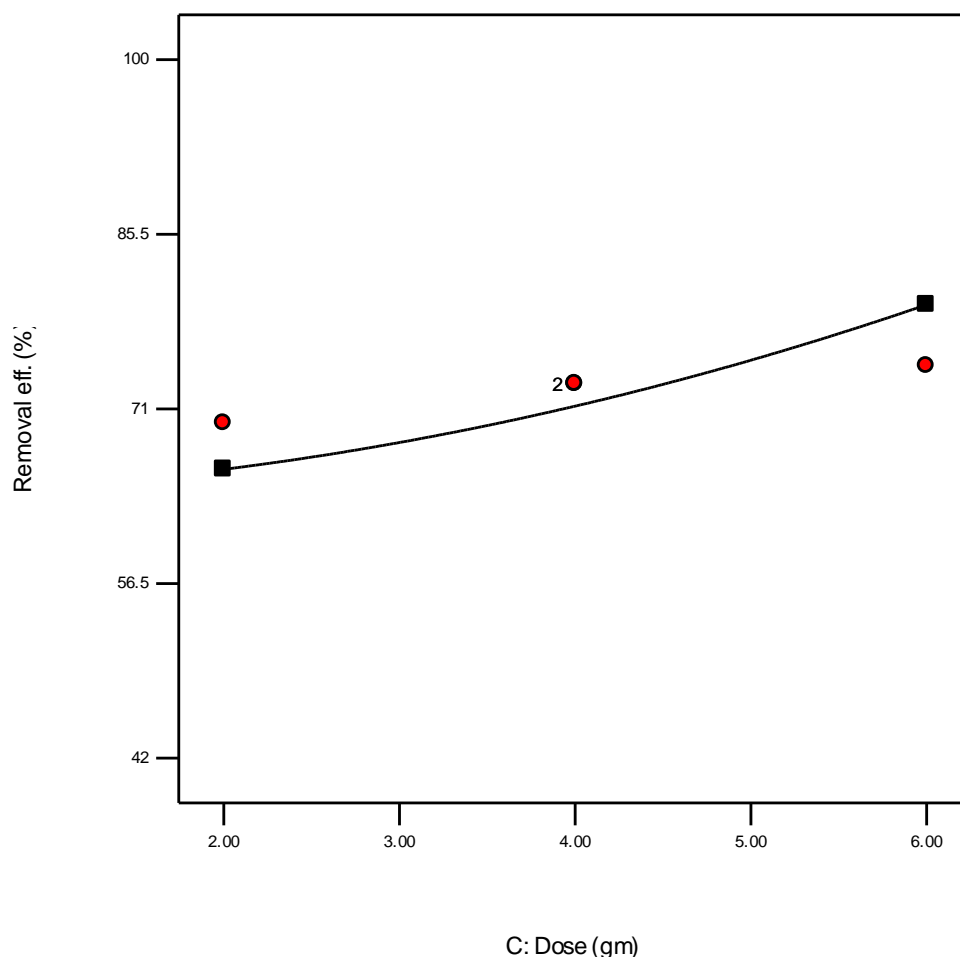


Figure 7: Effect of biosorbent dose on the removal efficiency of reactive dye

4.2.4 Effect of contact time on the removal efficiency of reactive dye

In this experiment, the effect of contact time on adsorption of reactive dye using cactus peel was studied by keeping the other variables (pH of solution, initial dye concentration and biosorbent dosage) constant. Generally, the rate of removal of dye increases with an increase in contact time to some extent. Further increase in contact time does not increase the percentage removal efficiency due to deposition of dye molecules on the available active sites of the adsorbent material [35]. Figure 8 below illustrates the relationship between the shaking time and the removal efficiency of reactive dye by using cactus peel biosorbent. As can be seen from the figure 8 shown below the removal efficiency of reactive dye increases with increasing in shaking time period and reached equilibrium typically after 120 minutes as the final dye concentration does not seem to increase much after this limit. The reason might be the overload of the active sites of the biosorbent by the dye ions so that further adsorption process doesn't takes place. Therefore, we can conclude that reactive dye and cactus peels should be in contact for 120 minutes in order to get maximum removal efficiency.

Removal eff.

X1 = D: Time

Actual Factors
A: pH = 6.00
B: Con = 60.00
C: Dose = 4.00

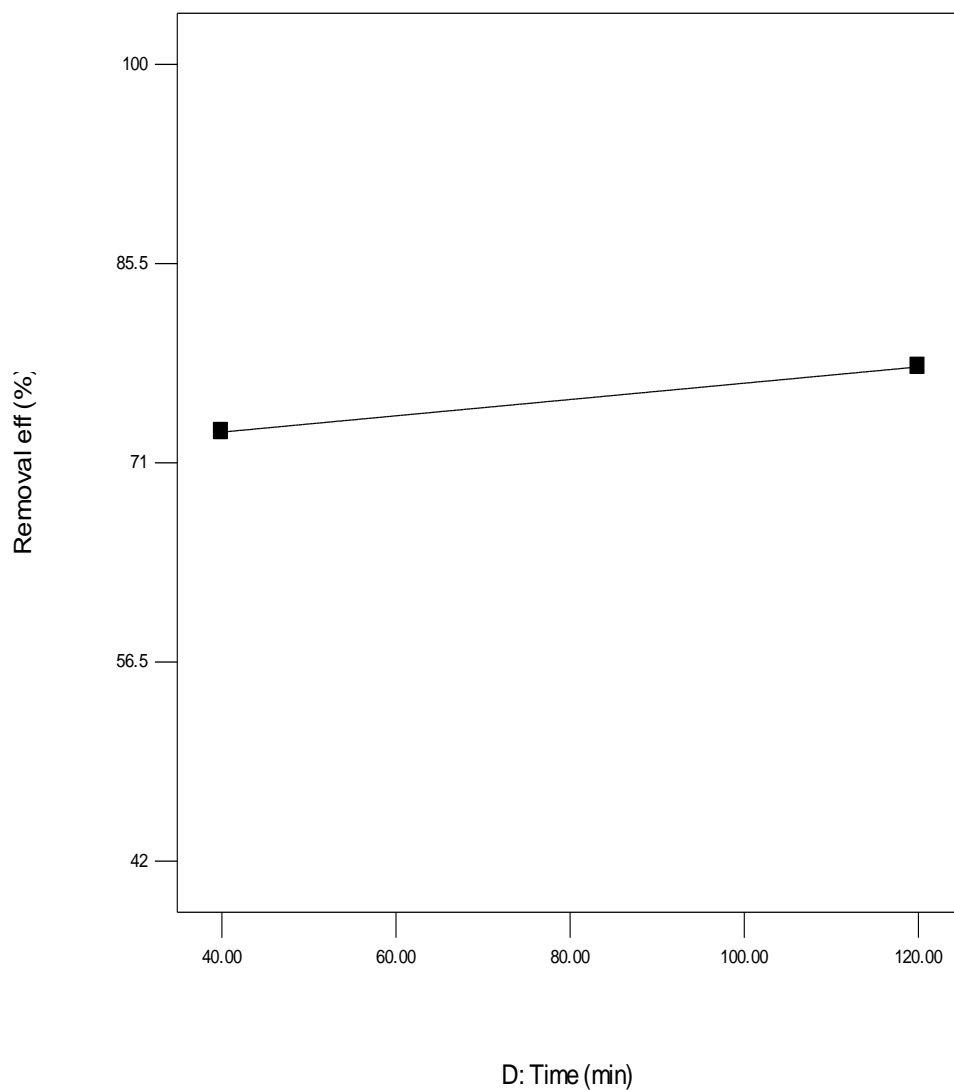


Figure 8: Effect of contact time on the removal efficiency of reactive dye

4.3 Effects of interaction parameters on percentage dye removal

4.3.1 The interaction effect of solution pH and initial dye concentration

As we can observe from the contour plot of figure 9 a and 3D plot of figure 9 b below as solution pH and initial dye concentration increases removal efficiency of reactive dye decreases. At low solution pH value and at low initial dye concentration there is high removal efficiency of reactive dye. Therefore this is a good evident that the interaction effect of solution pH and initial dye concentration affects the removal efficiency of reactive dye using cactus peel powder as biosorbent. The graph shown below indicates that maximum reactive dye removal occurred at pH value of 4.5 and initial dye concentration of 45mg/l with fixed adsorbent dose of 4gm and fixed shaking time of 80 min.

Design-Expert® Software

Removal eff.

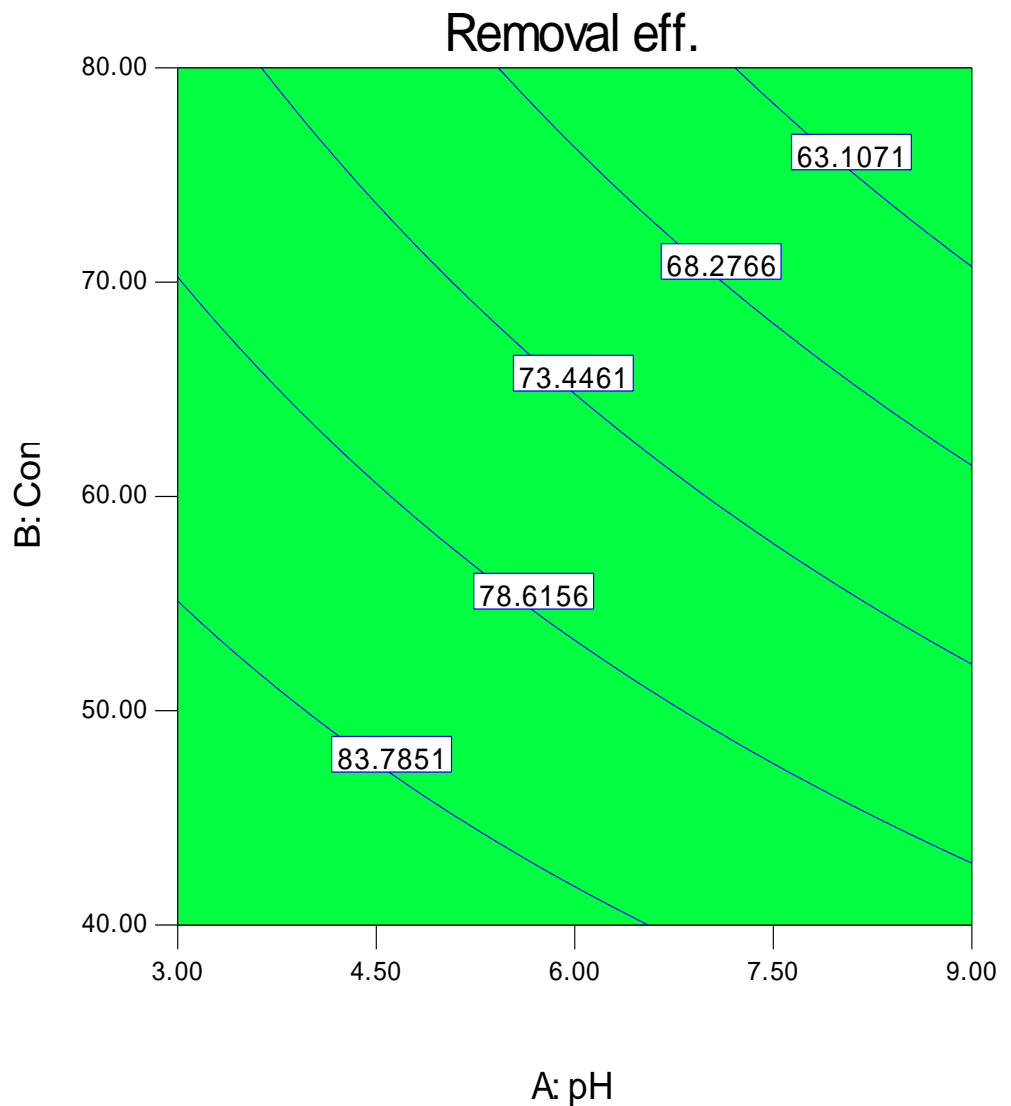
X1 = A: pH

X2 = B: Con

Actual Factors

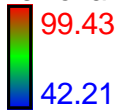
C: Dose = 4.00

D: Time = 80.00



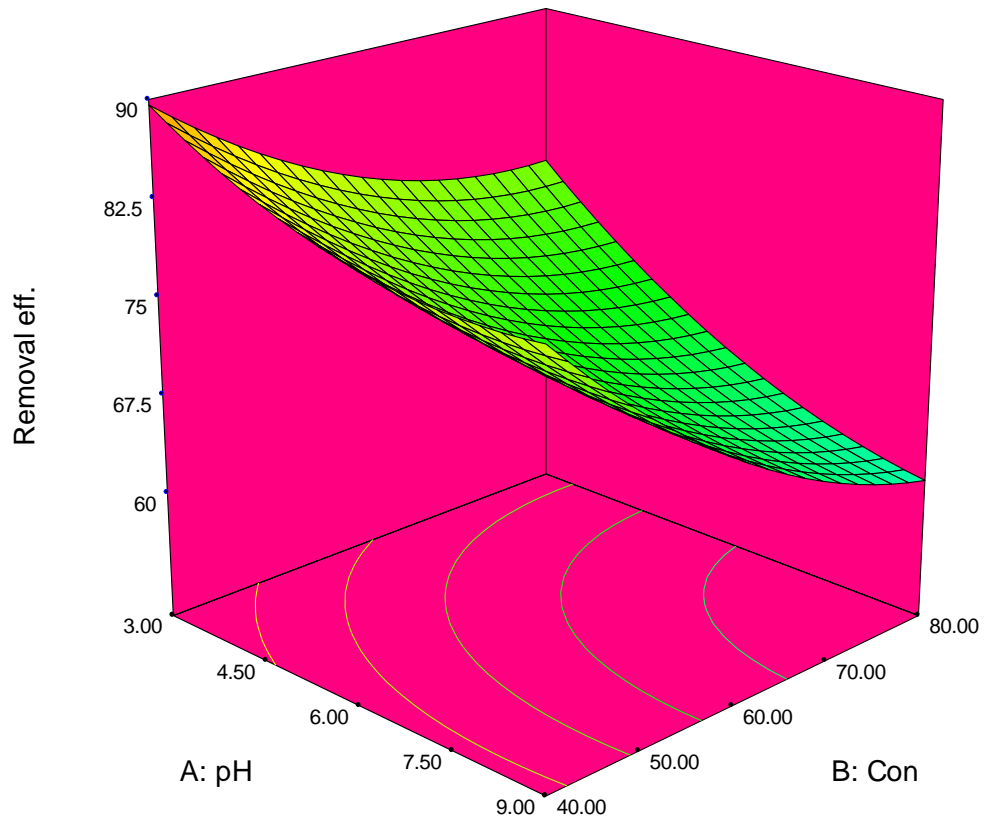
(a)

Removal eff.



X1 = A: pH
X2 = B: Con

Actual Factors
C: Dose = 4.00
D: Time = 80.00



(b)

Figure 9: The interaction effect of solution pH and initial dye concentration on adsorption of reactive dye (a) contour plot, (b). 3D plot

4.3.2 The interaction effect of solution pH and biosorbent dose

As we can observe from figure 10a (contour plot) and figure 10b (3D plot) shown below the percentage removal of reactive dye increases as pH of the dye solution decreases and the percentage removal of reactive dye increases as biosorbent dosage (powder cactus peel) increases. This is due to the reason that the dye is anionic dye with higher pH value that can easily remove at lower solution pH and large amount of biosorbent dose. At low solution pH and at high biosorbent dosage maximum removal efficiency of reactive dye occurs.

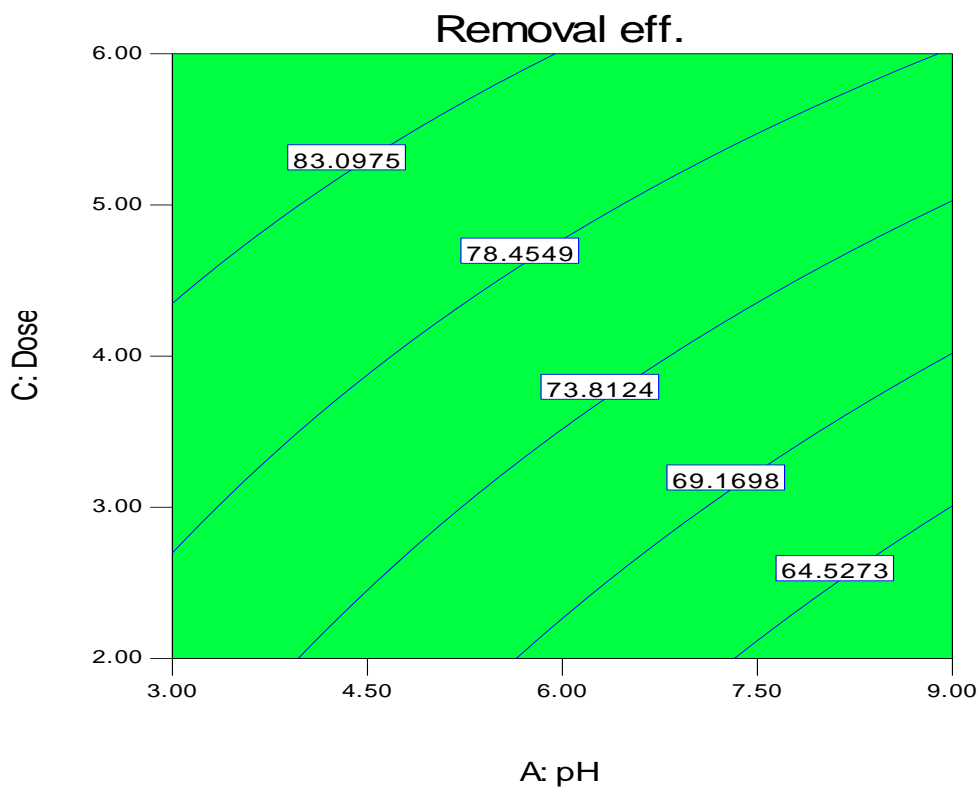
Therefore, it is a practical evidence that their interactions affect the biosorption process.

Design-Expert® Software

Removal eff.

X1 = A: pH
X2 = C: Dose

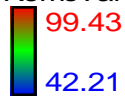
Actual Factors
B: Con = 60.00
D: Time = 80.00



(a)

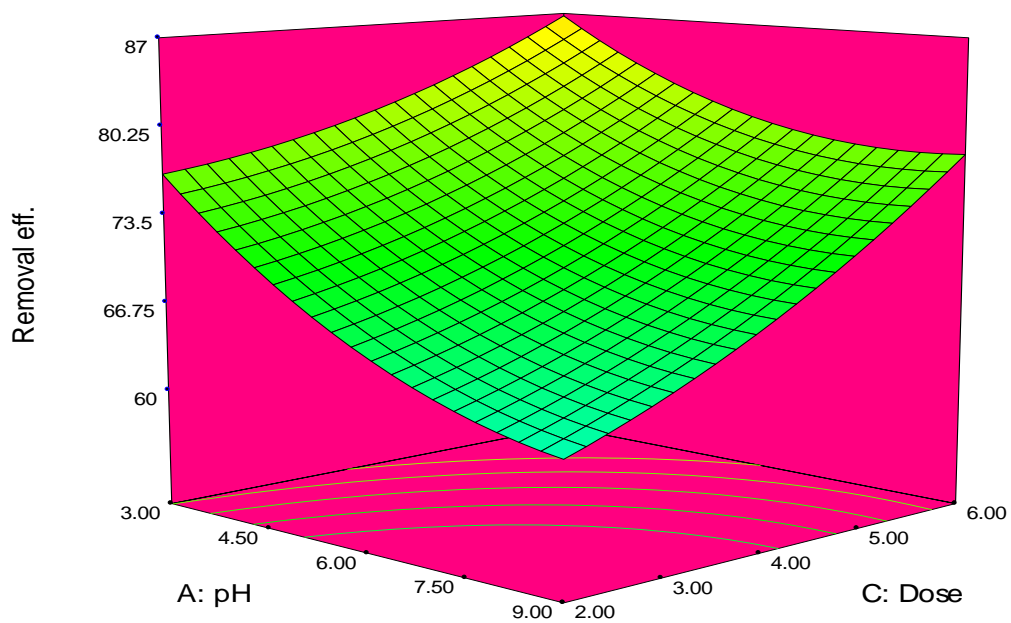
Design-Expert® Software

Removal eff.



X1 = A: pH
X2 = C: Dose

Actual Factors
B: Con = 60.00
D: Time = 80.00



(b)

Figure 10: The interaction effect of solution pH and biosorbent dose on adsorption of reactive dye (a) contour plot, (b). 3D plot

4.3.3 The interaction effect of solution pH and contact time

As we can see from the contour plot of figure 11 a and 3D plot of figure 11 b below as the pH of the dye solution increases removal efficiency of reactive dye decreases and the percentage removal of reactive dye using cactus peel powder as biosorbent increases as contact time of the adsorption process increases. At low solution pH and at maximum shaking time percentage removal of reactive dye was found to be high. Thus, this is a good evidence that the interaction of solution pH and contact time affects the removal efficiency of reactive dye.

Design-Expert® Software

Removal eff.

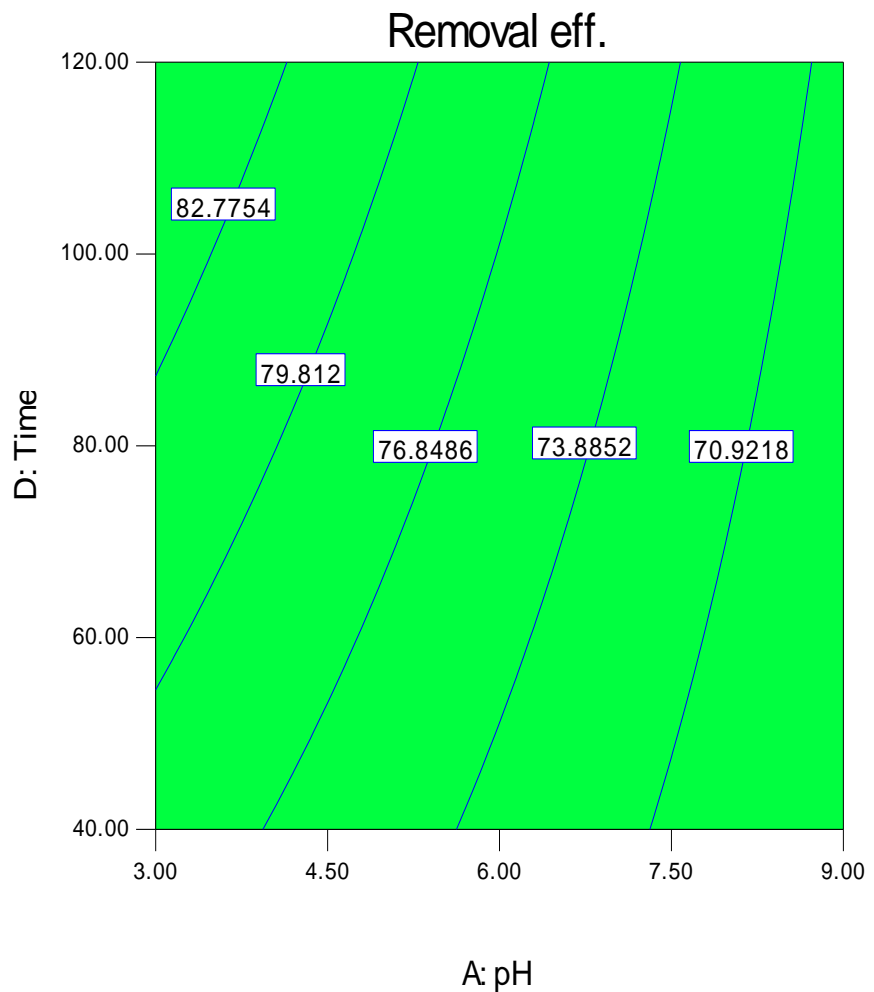
X1 = A: pH

X2 = D: Time

Actual Factors

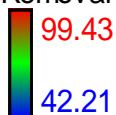
B: Con = 60.00

C: Dose = 4.00



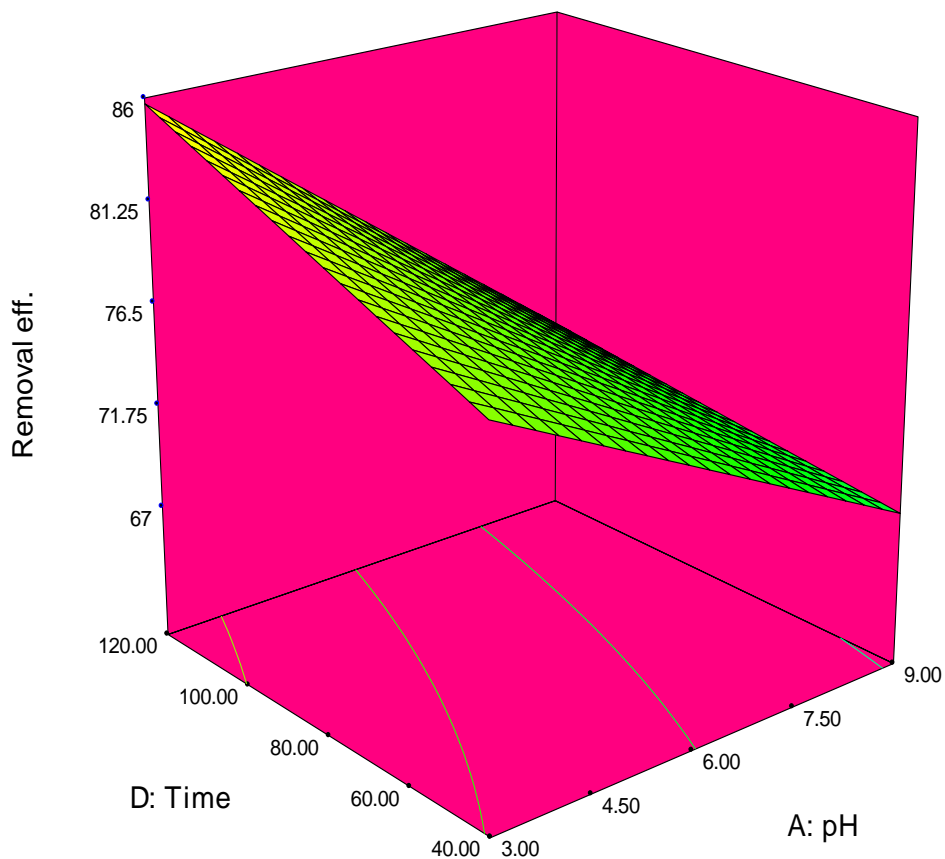
(a)

Removal eff.



X1 = A: pH
X2 = D: Time

Actual Factors
B: Con = 60.00
C: Dose = 4.00



(b)

Figure 11: The interaction effect of solution pH and contact time on adsorption of reactive dye (a) contour plot, (b). 3D plot

4.3.4 The interaction effect of initial dye concentration and biosorbent dose

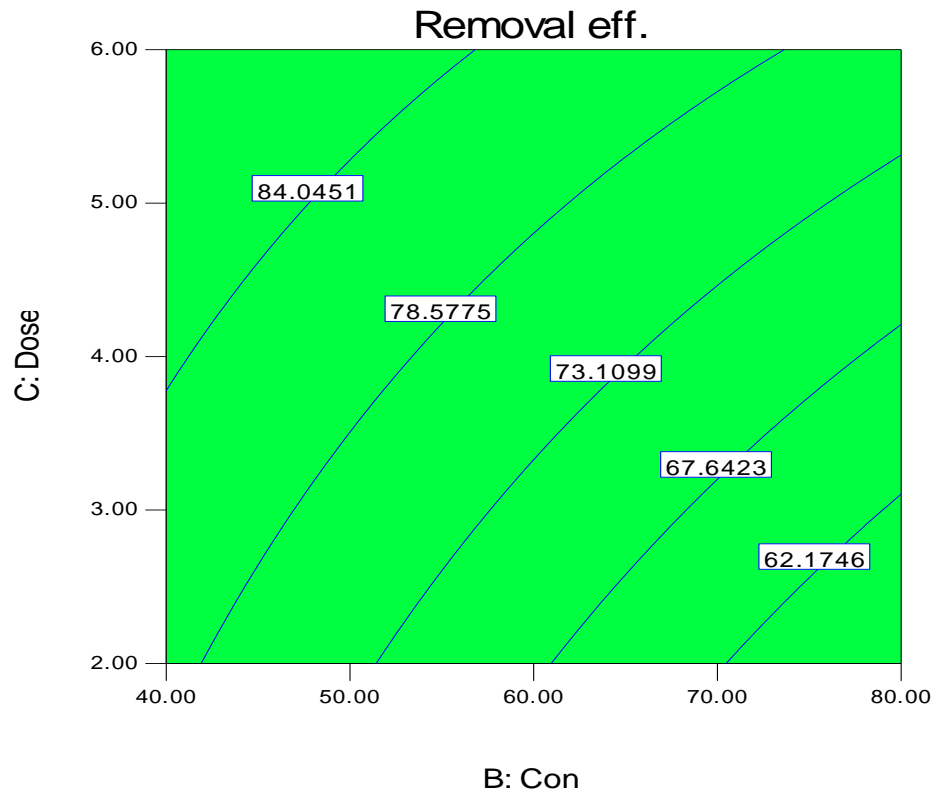
Contour plot and 3D plot of figure 12 a and b shown below respectively shows that percentage removal of the dye increases as biosorbent dose increases due to increased adsorption surface area of the active sites of the adsorbent. But Further increase in the biosorbent dosage did not show an increased removal of reactive dye concentration because the active sites of the biosorbent will be occupied by the adsorbate solution (reactive dye solution) and as initial dye concentration goes down the removal efficiency of reactive dye on using cactus peel as biosorbent increases. At low initial dye concentration and at maximum biosorbent dose percentage removal of reactive dye was found to be high. This indicates that their interaction effect really affects the biosorption process.

Design-Expert® Software

Removal eff.

X1 = B: Con
X2 = C: Dose

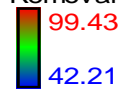
Actual Factors
A: pH = 6.00
D: Time = 80.00



(a)

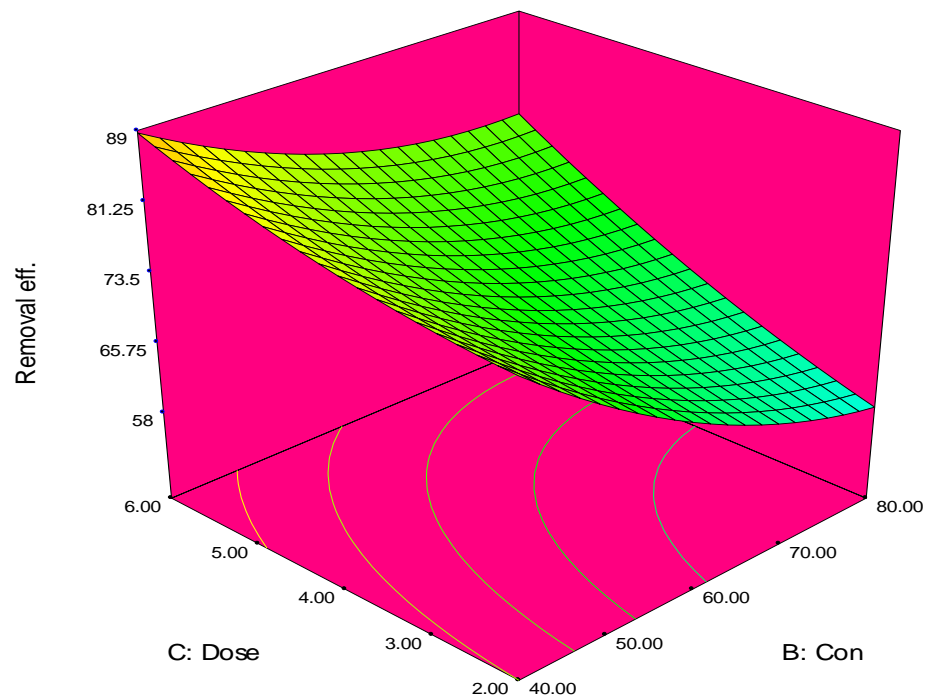
Design-Expert® Software

Removal eff.



X1 = B: Con
X2 = C: Dose

Actual Factors
A: pH = 6.00
D: Time = 80.00



(b)

Figure 12: The interaction effect of initial dye concentration and biosorbent dose on adsorption of reactive dye (a) contour plot, (b). 3D plot

4.3.5 The interaction effect of initial dye concentration and contact time

The interaction effect of initial dye concentration and contact time on adsorption of reactive dye by cactus peel biosorbent is illustrated in figure 13a (contour plot) and 13b (3D plot) below. From these graphs it was concluded that adsorption of reactive dye increases with the increase in the contact time to a certain extent. Further increase in contact time does not increase the dye uptake process due to deposition of dyes on the available active sites of the adsorbent material and removal efficiency of reactive dye decreases with an increase in the initial dye concentration this is due to the reason that at higher concentrations the active sites of the adsorbent were occupied by the dye ions and become saturated.

Therefore, this is a reasonable evidence that their interaction affects the biosorption process.

Design-Expert® Software

Removal eff.

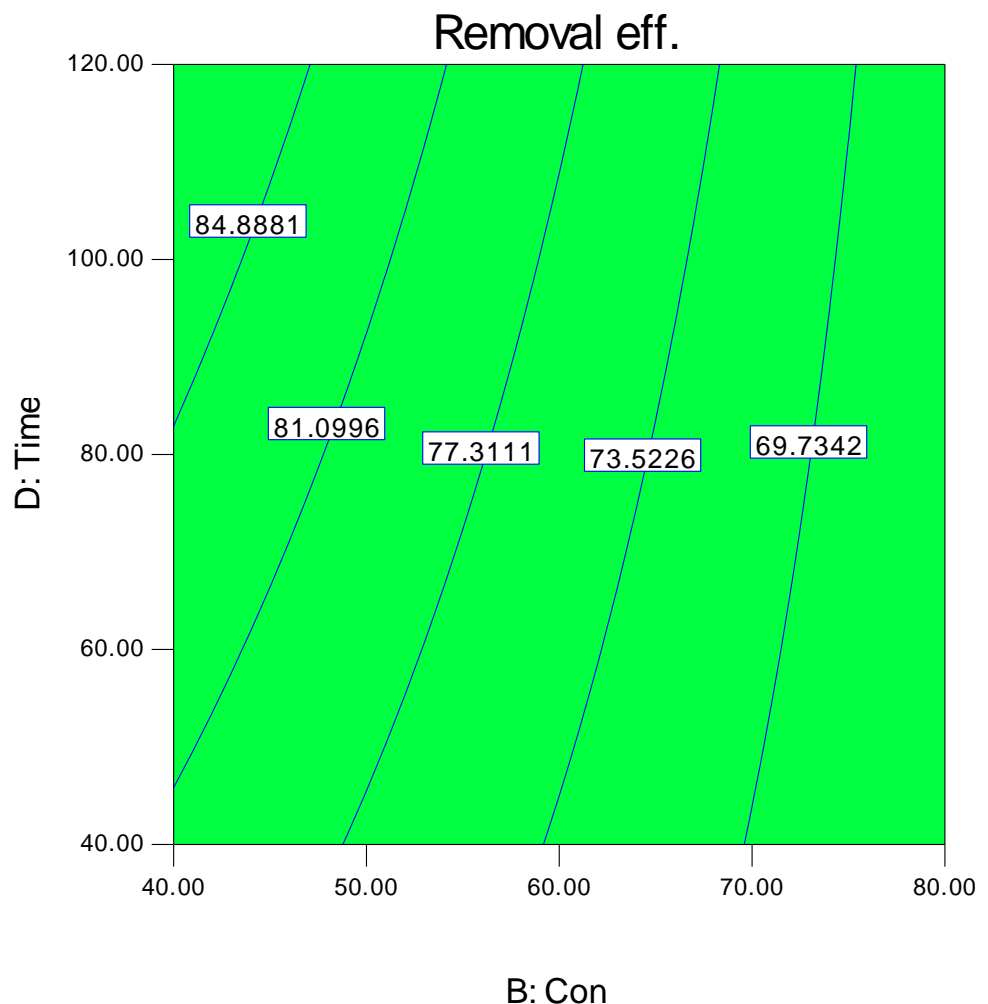
X1 = B: Con

X2 = D: Time

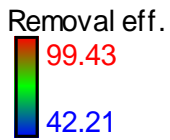
Actual Factors

A: pH = 6.00

C: Dose = 4.00

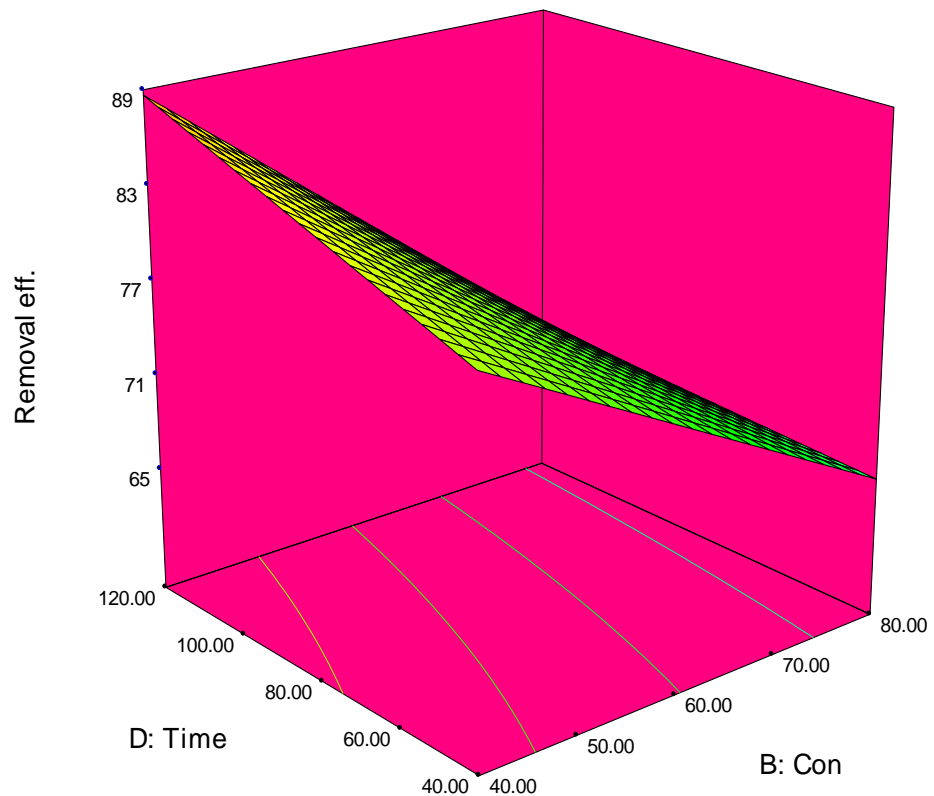


(a)



X1 = B: Con
 X2 = D: Time

Actual Factors
 A: pH = 6.00
 C: Dose = 4.00



(b)

Figure 13: The interaction effect of initial dye concentration and contact time on adsorption of reactive dye (a) contour plot, (b). 3D plot

4.3.6 The interaction effect of biosorbent dose and contact time

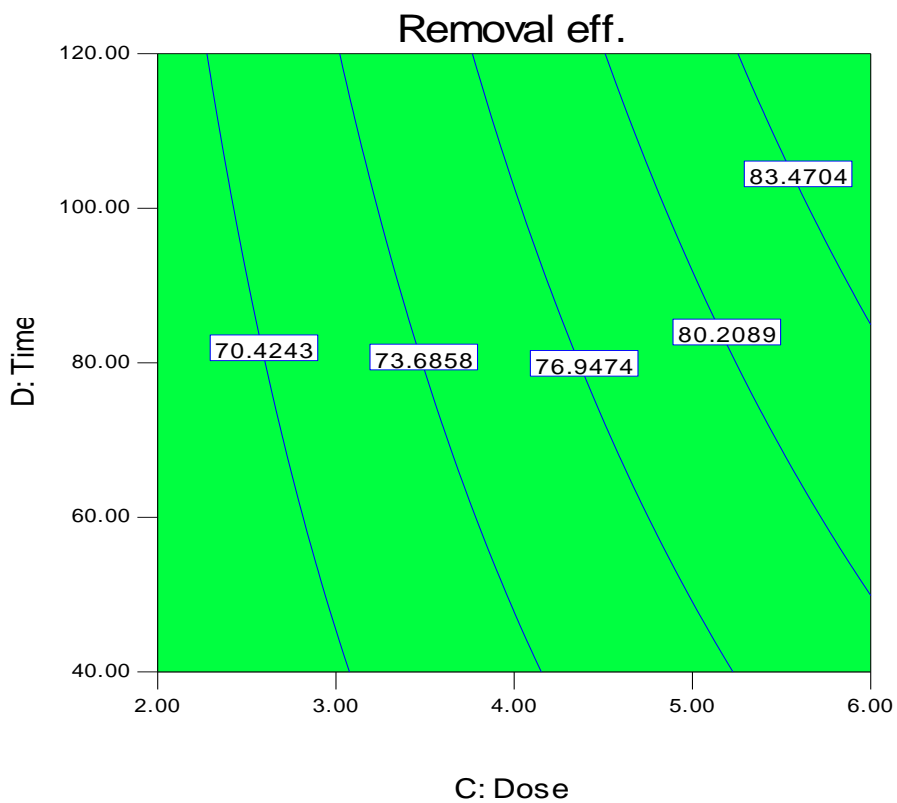
From the interaction effect of biosorbent dose and contact time shown in fig 14a (contour plot) and 14b (3D plot) below it is found that the percentage removal of reactive dye on powder cactus peel increases as biosorbent dose increases because increasing biosorbent dose would make higher number of adsorption sites available and the removal efficiency of reactive dyes on cactus peel increases as contact time increases. So, their interaction basically affects the biosorption. High removal efficiency of reactive dye by using cactus peel biosorbent was found to be at high biosorbent dosage and maximum contact time.

Design-Expert® Software

Removal eff.

X1 = C: Dose
X2 = D: Time

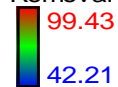
Actual Factors
A: pH = 6.00
B: Con = 60.00



(a)

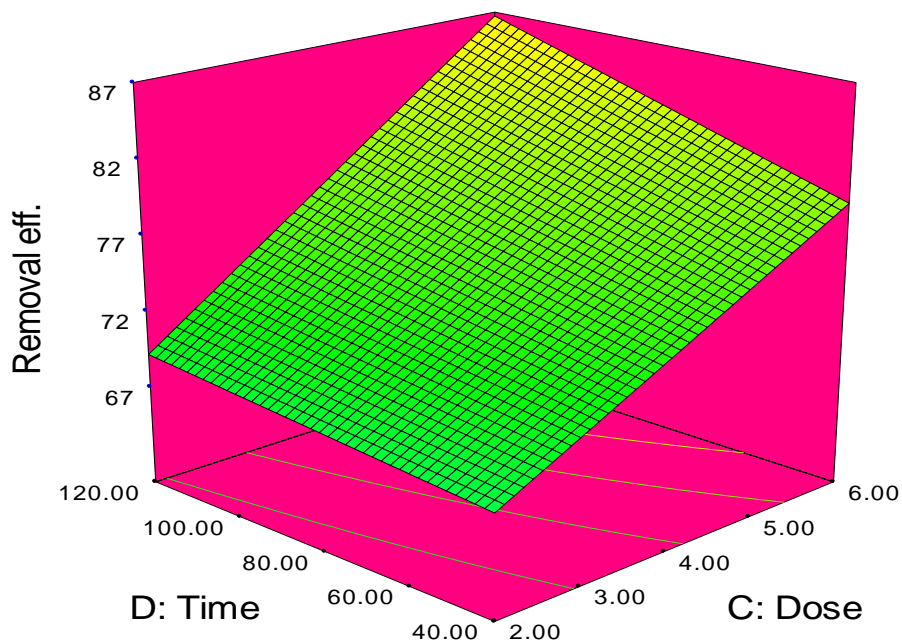
Design-Expert® Software

Removal eff.



X1 = C: Dose
X2 = D: Time

Actual Factors
A: pH = 6.00
B: Con = 60.00



(b)

Figure 14: The interaction effect of biosorbent dose and contact time on adsorption of reactive dye (a) contour plot, (b). 3D plot

Table 4: Analysis of ANOVA for quadratic second order model

ANOVA for Response Surface Quadratic Model						
Analysis of variance table [Partial sum of squares]						
Source	Sum of squares	DF	Mean square	F - value	Prob > F	
Model	3469.693	14	247.8352	33.01731	< 0.0001	significant
A	680.3205	1	680.3205	90.63424	< 0.0001	
B	1295.263	1	1295.263	172.5587	< 0.0001	
C	879.8619	1	879.8619	117.2177	< 0.0001	
D	90.25597	1	90.25597	12.02416	0.0053	
AB	74.17516	1	74.17516	9.881826	0.0093	
AC	51.08676	1	51.08676	6.805924	0.0243	
AD	24.97501	1	24.97501	3.327242	0.0954	
BC	99.15181	1	99.15181	13.20929	0.0039	
BD	46.88826	1	46.88826	6.246588	0.0295	
CD	29.07906	1	29.07906	3.873995	0.0748	
Residual	82.56841	11	7.506219			
Lack of Fit	82.56821	10	8.256821	41284.11	0.0038	significant
Pure Error	0.0002	1	0.0002			
Cor Total	3552.261	25				

The Model F-value of 33.02 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, D, AB, AC, BC, BD are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The "Lack of Fit F-value" of 41284.11 implies the lack of fit is significant. There is only a 0.38% chance that a "Lack of Fit F-value" this large could occur due to noise.

4.4 Dye Biosorption Isotherm Models

Adsorption isotherms are vital models that are applicable when the design of adsorption system is mandatory. The isotherm models designate how the adsorbed molecules disperse themselves between the liquid phase and the solid phase when the adsorption process reaches equilibrium. The data found from these models gives us appropriate information about the capacity of the biosorbent under different conditions. In this research study adsorption isotherm model was used to characterize the interaction of the dye ions with the cactus peel biosorbent. Adsorption isotherms have many important practical implications, for example; it gives as an evident information on how the biosorption process proceeds, and used to observe how efficiently a given adsorbent interacts with adsorbate. The most widely known surface biosorption models for single-solute systems are the Langmuir and Freundlich isotherm [39].

4.4.1 Langmuir isotherm model

The Langmuir model illustrates quantitatively the formation of a monolayer adsorbate (reactive dye solution) on the outer surface of the adsorbent (powder cactus peel), and after that extra adsorption doesn't takes place. By that, the Langmuir signifies the equilibrium distribution of reactive dye ions between the solid and liquid phases.

The Langmuir isotherm is based on the assumption that all binding sites have equivalent affinity resulting in the formation of monolayer of adsorbed molecules [14]. The adsorption takes place at specific sites of the adsorbent. Each site retains one molecule of the dye compound. The Langmuir isotherm model was used to know the maximum sorption capacity of complete mono-layer coverage on cactus peel surface. The experimental data were analyzed according to the linear form of the Langmuir isotherm equation. The linear plots of $\frac{C_e}{q_e}$ versus C_e suggest the applicability of the Langmuir isotherms for the removal of Reactive dye onto cactus peel. The value of qm and KL can be calculated from the slope and intercept of the Langmuir isotherm model plot as shown in Figure 15 below.

Data used for plotting Langmuir and Freundlich models for biosorption of Reactive dye onto cactus peel at initial pH: 4.0, biosorbent dose :6.0gm, contact time 120min

Langmuir Isotherm model			Freundlich Isotherm model	
Ce	qe	Ce/qe	logCe	logqe
11.3465	1.963	5.62	1.055	0.293
6.0256	2.245	2.56	0.78	0.251
18.6636	2.133	8.75	1.271	0.329
11.6412	1.958	5.95	1.066	0.292
1.7298	1.601	1.08	0.238	0.204

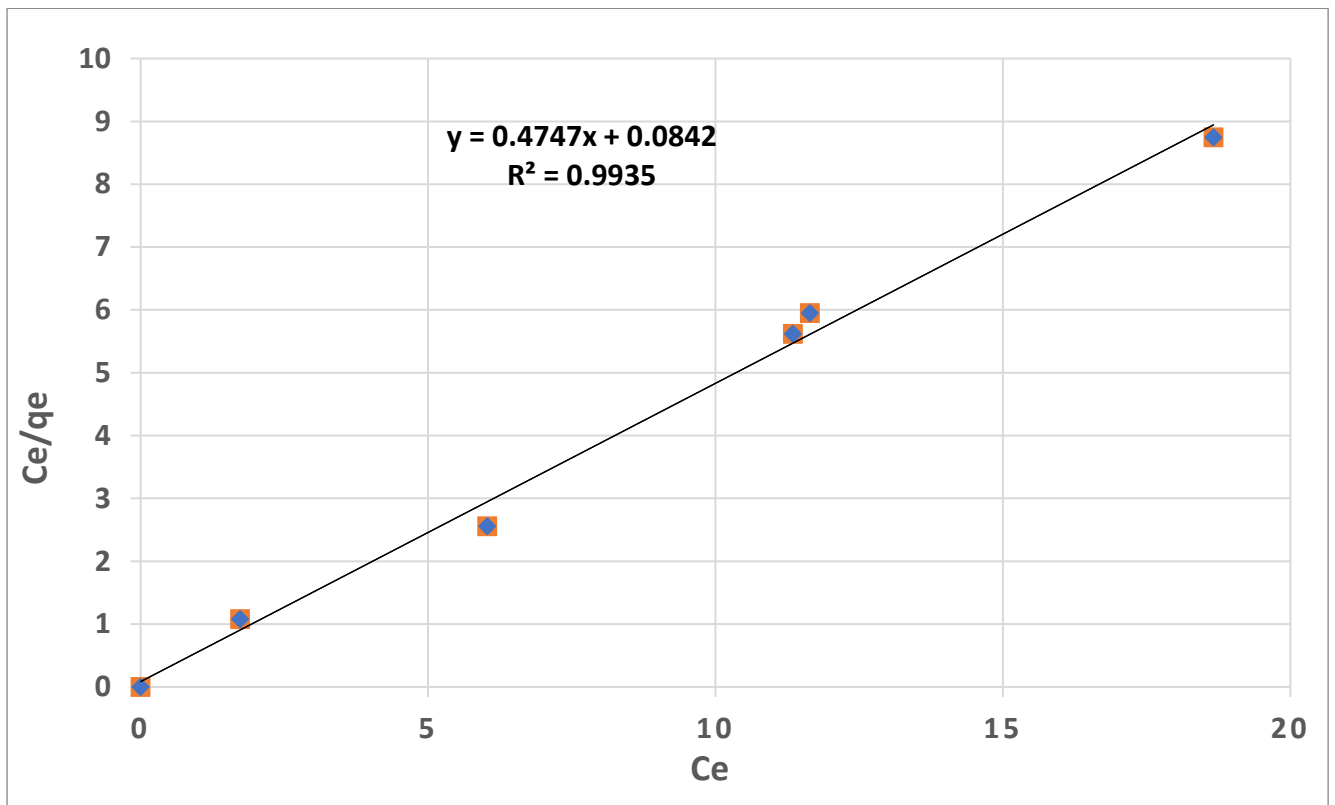


Figure 15: Langmuir isotherm model plot

4.4.2 Freundlich isotherm model

The Freundlich adsorption isotherm is one of the frequently used isotherm model to describe the adsorption process for the heterogeneous surface. The Freundlich isotherm was used to define adsorption to heterogeneous surfaces having adsorption sites of varying affinities. Typical property of heterogenic surface is that the areas where adsorption happens vary in

terms of adsorption energy. Freundlich isotherm is the most basic known model for multilayer adsorption process. This model is applied to adsorption on heterogeneous surfaces with an interaction between dye molecules. Figure 16 below shows the plots of $\log q_e$ versus $\log C_e$. Freundlich isotherm constants (K_f and n) can be obtained from intercept and slope of Figure 16 that shown below. From the Freundlich's plots the calculated values of $K_f = 1.4787$ and $n = 8.48$. If an adsorbent has n value between 1 and 10 it is considered as a convenient adsorption and a good adsorbent [42]. From the calculated results of the constants, it can be observed that the value of n is 8.48 which indicated a normal heterogeneous adsorption process, showing a satisfactory biosorption process. But the value of regression coefficient ($R^2 = 0.9722$) is lower than that of Langmuir isotherm value ($R^2 = 0.9935$). So, we can conclude that Langmuir isotherm model fits best than that of Freundlich isotherm model.

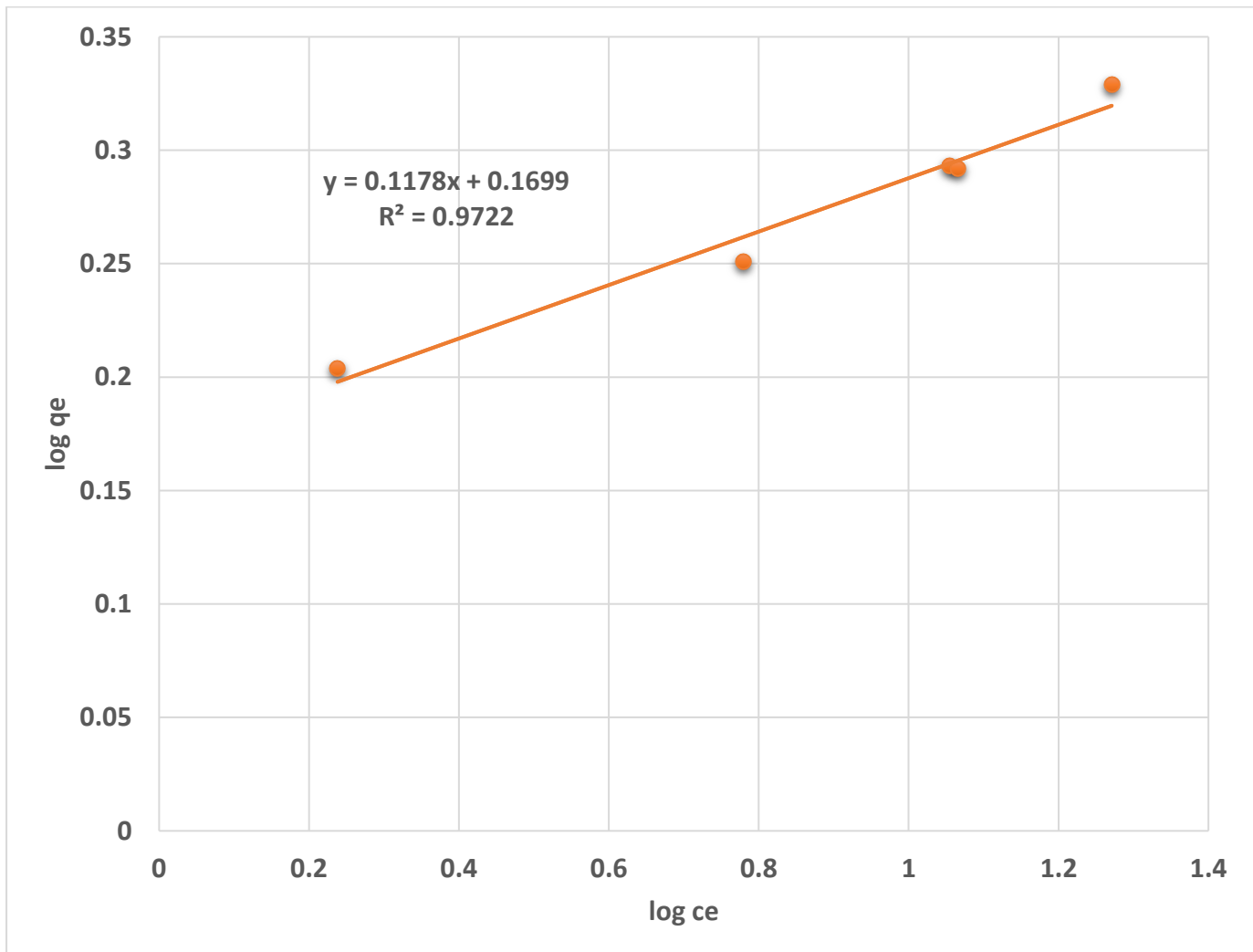


Figure 16: Freundlich isotherm model plot

It can observe from figure 15 and 16 below that regression coefficient of the Langmuir isotherm ($R^2 > 0.99$) is higher than that of the Freundlich isotherm equation model ($R^2 > 0.97$). Therefore, it is a reasonable and good evidence that the biosorption of the reactive dye onto the cactus peel biosorbent follows the Langmuir isotherm represents the best fit of experimental data than the Freundlich isotherm equation.

Table 5: constant parameters of Langmuir and Freundlich isotherm models for biosorption of reactive dye onto cactus peel

Biosorbent name	Dye type	Langmuir Isotherm			Freundlich Isotherm		
		qm (mg/g)	KL (L/mg)	R ²	Kf	n	R ²
Cactus peel	Reactive dye	2.1066	5.637	0.9935	1.4787	8.48	0.9722

4.5 Dye Adsorption Kinetic Models

The sorption mechanism and the rate of the adsorption process are crucial for assessing the biosorption process. To use cactus peel efficiently as a potential biosorbent, contact time is of fundamental importance process parameter. Therefore, the efficiency of the adsorbent will be investigated by studying adsorption kinetics carefully. The kinetics of biosorption designates the solute uptake rate in a given residence time of sorption process. The kinetic properties of adsorbate uptake will be used to select optimum operating conditions for the batch experimental process.

The most common kinetic models that are used to evaluate the performance of the biosorbent for dye removal to fit the biosorption data are the pseudo first order and pseudo second order models.

4.5.1 Pseudo-first-order or Lagergen kinetic model

The Lagergen rate equation is the first equation for sorption of liquid/solid system based on solid capacity.

The pseudo-first-order equation described by Lagergen is given as:

$$\frac{dq}{dt} = k_1(q_e - qt) \dots \dots \dots (4.1)$$

after integration by applying boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ the model can be expressed as:

$$\log(qe - qt) = \log qe - \left(\frac{k_1}{2.303}\right)t \dots\dots\dots (4.2)$$

Where: q_e is the adsorption capacity at equilibrium
 q_t is the adsorption capacity at any time t and
 k_1 is the rate constant of pseudo first order adsorption (min^{-1})

The linear-line plot of $\log(qe - qt)$ against t show the applicability of this model and the values of adsorption rate constant (K_1) and q_e for the adsorption of dyes from textile dye effluents on cactus peel will be determined from the slope and intercept of the plot of $\log(qe - qt)$ against t respectively.

Data for Pseudo first order kinetics, at initial pH: 4.0, dye conc:40mg/l, contact time 120min

Time (min)	Absorbance	Final Conc(mg/l)	q_t (mg/g)	Log (qe-qt)
20	0.2335	15.383	0.615	-0.725
40	0.187	12.262	0.693	-0.958
60	0.155	10.114	0.747	-1.252
80	0.151	9.845	0.753	-1.301
100	0.122	7.899	0.803	-
120	0.122	7.899	0.803	-

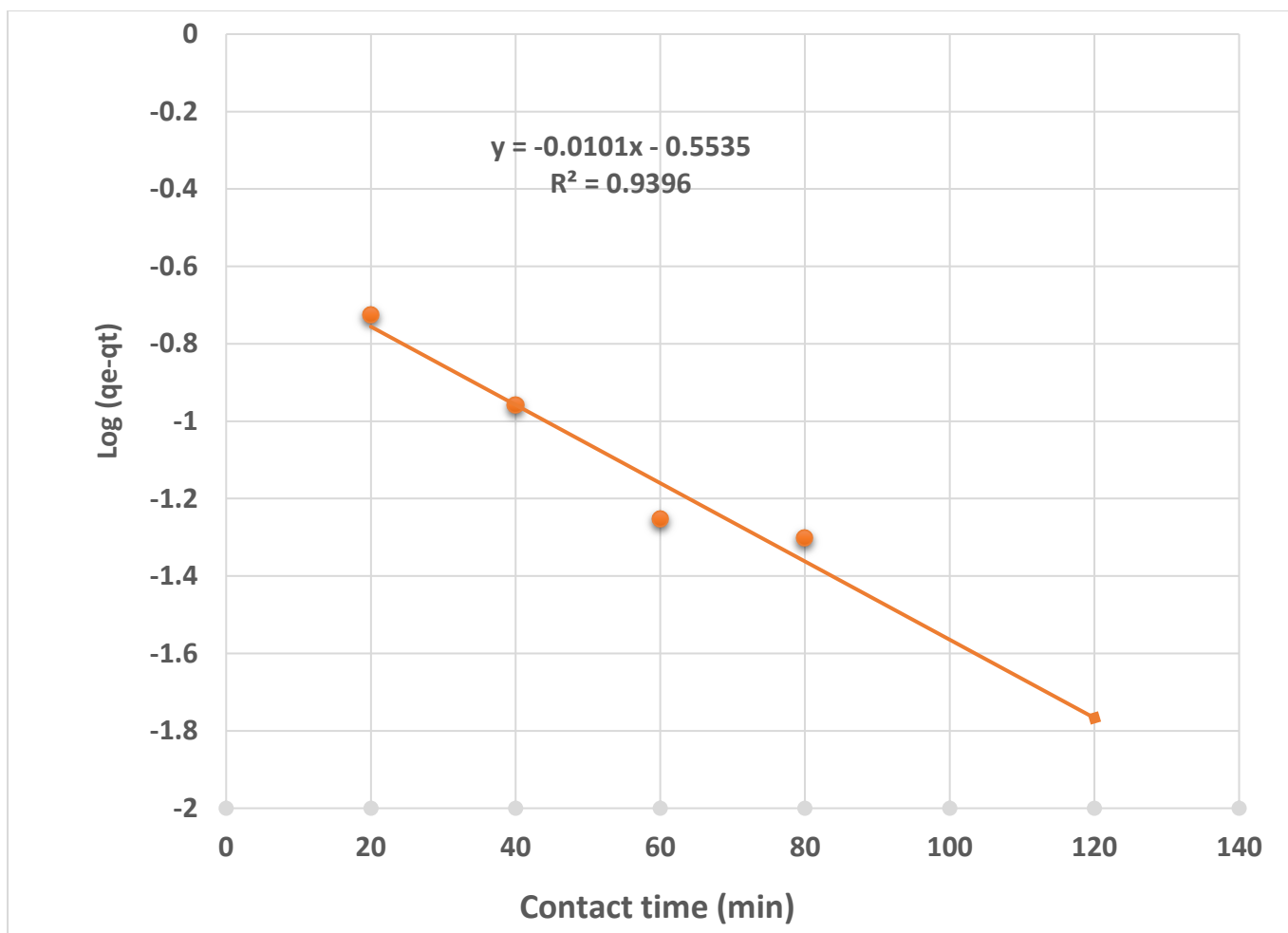


Figure 17: Pseudo first order for biosorption of reactive dye onto cactus peel

4.5.2 Pseudo second order kinetic model

The pseudo-second-order model is based on assumption that the adsorption may be second-order. The pseudo second-order adsorption kinetic rate equation is expressed as:

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \dots \dots \dots (4.3)$$

For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$,

integrating and rearranging equation (4.3) becomes:

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{t}{q_e} \dots \dots \dots (4.4)$$

Where K_2 is the rate constant of sorption, q_e is the amount of dye sorbed at Equilibrium, (mg/g), q_t is amount of dye on the surface of the adsorbent at any time, t .

The pseudo second order rate constant (K_2) and the equilibrium adsorption capacity (q_e) was found from the slope and intercept of the linear plot of t/q_t versus t for the cactus biosorbent respectively.

Data for Pseudo second order kinetics at initial pH: 4.0, dye conc:40mg/l, contact time 120min

Time (min)	Absorbance	Final Conc(mg/l)	qt (mg/g)	t/qt
20	0.2335	15.383	0.615	35.52
40	0.187	12.262	0.693	57.72
60	0.155	10.114	0.747	80.32
80	0.151	9.845	0.753	106.24
100	0.122	7.899	0.803	124.53
120	0.122	7.899	0.803	149.44

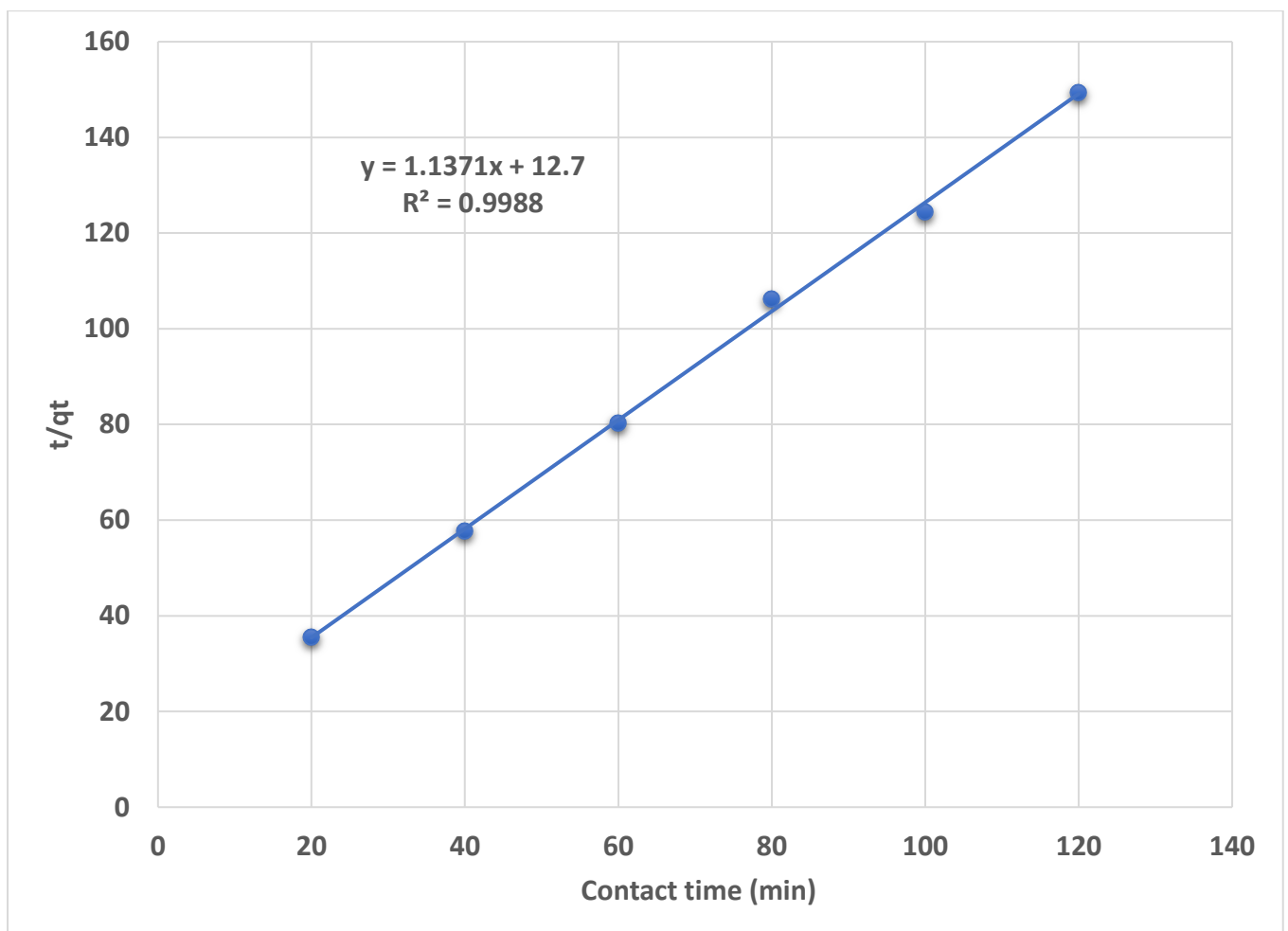


Figure 18: Pseudo second order for biosorption of reactive dye onto cactus peel

Figure 17 and 18 above shows the plotting results of the experiment data fitting with the pseudo-first-order model and pseudo-second-order models respectively. From table 6 below the regression coefficient (R^2) of Pseudo first order is 0.9396 and the calculated q_e value is 0.28 which is much differ from the experimental value of q_e ($q_{exp.} = 0.803$). But the regression coefficient(R^2) of Pseudo second order is approximately unity (0.9988) and the calculated q_e value is 0.8794 which is much closer to the experimental value of q_e ($q_{exp.} = 0.803$). based on these results, it can be concluded that pseudo-second-order model mechanism is the best model for biosorption of reactive dye onto powdered cactus peel.

Table 6: Kinetic parameters for the removal of reactive dye by cactus peel

$q_{\text{experiment}}$	pseudo first order kinetic model			pseudo second order kinetic model		
	$q_{\text{calculated}}$	K_1	R^2	$q_{\text{calculated}}$	K_2	R^2
0.803	0.28	0.0233	0.9396	0.8794	0.102	0.9988

5. Conclusions and Recommendations

5.1 Conclusion

In this research work the biosorption of reactive dye from aqueous solution using powder cactus peel as biosorbent was investigated. The effect of different process variables mainly solution pH, initial dye concentration, contact time and biosorbent dose on the biosorption of reactive dye using cactus peel biosorbent has been investigated from the batch experiment. The results of experiment revealed that the maximum removal efficiency of reactive dye using cactus peel biosorbent was achieved in acidic pH. The removal efficiency of reactive dye increases as pH of the dye solution decreased. The maximum adsorption of reactive dye using cactus peel as adsorbent occurred at solution pH of 3.0. And the removal efficiency of reactive dye increased as biosorbent dose and shaking time increased.

The maximum adsorption of reactive dye using cactus peel as adsorbent occurred at biosorbent dose of 6.0gm and contact time of 120 minute. In addition to this the initial concentration of the dye solution played a significant role on biosorption process of reactive dye. From this study the percentage removal of reactive dye increases as the initial concentration of the dye solution goes down. And the maximum adsorption of reactive dye using cactus peel as adsorbent occurred at initial dye concentration of 40mg/l. At a pH of 3.0, biosorbent dose of 6.0gm, initial dye concentration of 40mg/l and contact time of 120 minute the percentage removal of reactive dye was found to be 99.43%.

The biosorption isotherm Models and kinetic studies were conducted for the biosorption of reactive dye from aqueous solution using cactus peel biosorbent. The dye biosorption isotherm data have been examined by using Langmuir and Freundlich isotherm models. The results showed that the equilibrium data was better fit with the Langmuir isotherm model. This result specifies the formation of a monolayer adsorbate (reactive dye solution) on the surface of the adsorbent (cactus peel).

The most common kinetic models that are used to estimate the performance of the biosorbent for dye removal to fit the biosorption data are the pseudo first order and pseudo second order models. In view of the experimental results pseudo-second-order model mechanism was better fit model for biosorption of reactive dye onto powdered cactus peel biosorbent. Generally, from the experimental results it can be concluded that acid treated powder cactus peel could successfully used for the removal of reactive red dye from aqueous solution at relatively low concentration and acidic pH.

5.2 Recommendations

- ✚ In this research work, only adsorption of reactive dye by cactus peel biosorbent was studied. Furthermore, these adsorbed dyes can be easily desorbed for extra purposes.
- ✚ Researches and developments must be conducted continuously to predict the performance of adsorption process for dye removal from real textile waste water effluents with in various levels of operating parameters using low cost cactus peel biosorbent.
- ✚ The consequence of dye pollutants on human health and aquatic environment as a whole that occur as a result of the disposal of untreated waste water from textile dye effluents can be reduced by proper work practices, increase awareness in textile industries to protect the environment in which they operate and develop waste minimization programs.
- ✚ In Ethiopia textile industry is among the major manufacturing industries, therefore the government should give thoughtful attention so as to minimize disposal of untreated wastewater containing dye effluents to the environment and all the textile industries must involve an effective and commercially viable techniques of color removal from their effluents.
- ✚ Conducting a feasibility study of cactus peel biosorbent to eliminate toxic metal ions and other organic and inorganic pollutants from aqueous solutions and real industrial effluents.
- ✚ In this thesis work hydrochloric acid was used as activating agent so as to remove impurities from the biosorbent material and to increase the adsorption capacity of the biosorbent. Therefore, more studies should be conducted on activation of the biosorbent using different activating agents.

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Appendix A: Experimental Data

Table 7: Data used for calibration of the UV- Spectrophotometer

Concentration (mg/l)	Absorbance
0	0
5	0.084
15	0.226
25	0.378
35	0.521
45	0.674

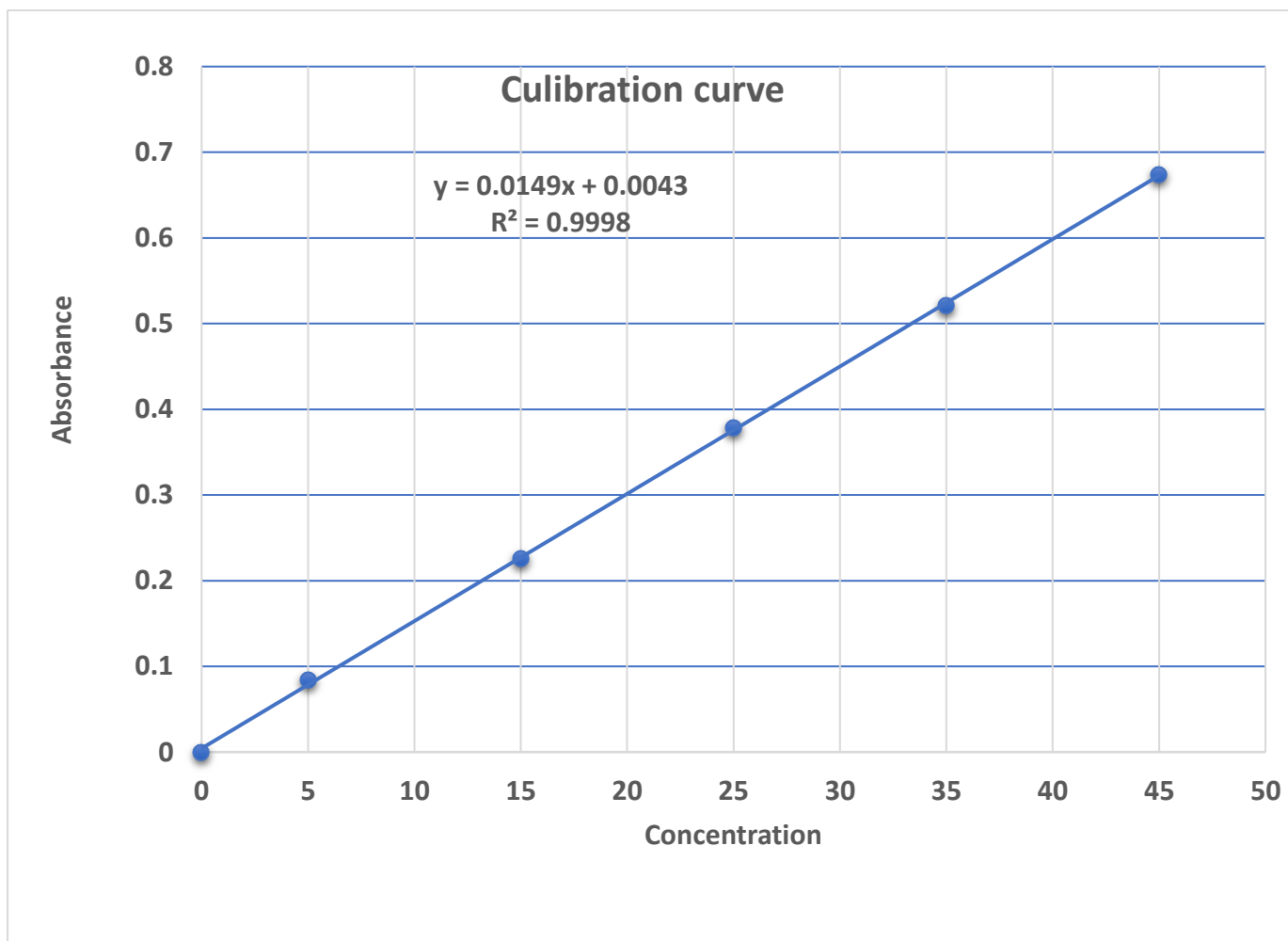


Figure 19: calibration curve to determine final dye concentration

Table 8: Experimental Data for Effect of solution pH on the removal efficiency of Reactive Dye

Solution pH	Absorbance value	Final concentration(mg/l)	Removal efficiency
3	0.111	7.154	82.11
6	0.165	10.772	73.07
9	0.188	12.368	69.08

Table 9: Experimental Data for Effect of initial dye concentration on the removal efficiency of Reactive Dye

initial dye concentration (mg/l)	Absorbance value	Final concentration(mg/l)	Removal efficiency
40	0.096	6.164	84.59
60	0.236	15.558	74.07
80	0.402	26.714	66.61

Table 10: Experimental Data for Effect of biosorbent dose on the removal efficiency of Reactive Dye.

biosorbent dose(gm)	Absorbance value	Final concentration(mg/l)	Removal efficiency
2	0.194	12.728	68.18
4	0.162	10.576	73.56
6	0.106	6.796	83.01

Table 11: Experimental Data for Effect of contact time on the removal efficiency of Reactive Dye.

Time (min)	Absorbance	Final Conc(mg/l)	qt (mg/g)	Removal eff.
20	0.2335	15.383	0.615	61.5
40	0.187	12.262	0.693	69.3
60	0.155	10.114	0.747	74.7
80	0.151	9.845	0.753	75.3
100	0.121	7.898	0.803	80.3
120	0.122	7.899	0.803	80.3

Appendix B: Adsorption Isotherms

Table 12: Data used for plotting Langmuir and Freundlich models for biosorption of Reactive dye onto cactus peel and their respective constant values

Langmuir Isotherm model			Freundlich Isotherm model	
Ce	qe	Ce/qe	logCe	logqe
11.3465	1.963	5.62	1.055	0.293
6.0256	2.245	2.56	0.78	0.251
18.6636	2.133	8.75	1.271	0.329
11.6412	1.958	5.95	1.066	0.292
1.7298	1.601	1.08	0.238	0.204

Biosorbent name	Dye type	Langmuir Isotherm			Freundlich Isotherm		
		qm (mg/g)	KL (L/mg)	R ²	Kf	n	R ²
Cactus peel	Reactive dye	2.1066	5.637	0.9935	1.4787	8.48	0.9722

Appendix C: Adsorption Kinetics

Table 13: Data for Pseudo first order kinetics

Time (min)	Absorbance	Final Conc(mg/l)	qt (mg/g)	Log (qe-qt)
20	0.2335	15.383	0.615	-0.725
40	0.187	12.262	0.693	-0.958
60	0.155	10.114	0.747	-1.252
80	0.151	9.845	0.753	-1.301
100	0.122	7.899	0.803	-
120	0.122	7.899	0.803	-

Table 14: Data for Pseudo second order kinetics

Time (min)	Absorbance	Final Conc(mg/l)	qt (mg/g)	t/qt
20	0.2335	15.383	0.615	35.52
40	0.187	12.262	0.693	57.72
60	0.155	10.114	0.747	80.32
80	0.151	9.845	0.753	106.24
100	0.122	7.899	0.803	124.53
120	0.122	7.899	0.803	149.44

Table 15: adsorption parameters and their constant values of kinetic models

Q _{experiment}	pseudo first order kinetic model			pseudo second order kinetic model		
	Q _{calculated}	K ₁	R ²	Q _{calculated}	K ₂	R ²
0.803	0.28	0.0233	0.9396	0.8794	0.102	0.9988

Appendix D: Results from the statically analysis

Table 16: The experimental design matrix

			Factor 1	Factor 2	Factor 3	Factor 4	Response
Std	Run	Block	A:pH	B:Conc.(mg/L)	C:Dose(gm)	D:Time (min)	% Removal
1	15	Block 1	3.00	40.00	2.00	40.00	82.68
2	25	Block 1	9.00	40.00	2.00	40.00	72.99
3	21	Block 1	3.00	80.00	2.00	40.00	67.84
4	12	Block 1	9.00	80.00	2.00	40.00	53.37
5	2	Block 1	3.00	40.00	6.00	40.00	89.76
6	4	Block 1	9.00	40.00	6.00	40.00	84.67
7	14	Block 1	3.00	80.00	6.00	40.00	81.73
8	19	Block 1	9.00	80.00	6.00	40.00	69.06
9	9	Block 1	3.00	40.00	2.00	120.00	91.86
10	18	Block 1	9.00	40.00	2.00	120.00	79.25
11	7	Block 1	3.00	80.00	2.00	120.00	71.65
12	17	Block 1	9.00	80.00	2.00	120.00	42.21
13	1	Block 1	3.00	40.00	6.00	120.00	99.43
14	16	Block 1	9.00	40.00	6.00	120.00	92.13
15	11	Block 1	3.00	80.00	6.00	120.00	87.94
16	22	Block 1	9.00	80.00	6.00	120.00	75.38
17	13	Block 1	5.70	60.00	4.00	80.00	76.29

18	24	Block 1	6.30	60.00	4.00	80.00	70.62
19	20	Block 1	6.00	58.00	4.00	80.00	76.27
20	26	Block 1	6.00	62.00	4.00	80.00	71.68
21	10	Block 1	6.00	60.00	3.80	80.00	69.82
22	23	Block 1	6.00	60.00	4.20	80.00	74.56
23	3	Block 1	6.00	60.00	4.00	76.00	67.74
24	5	Block 1	6.00	60.00	4.00	84.00	70.49
25	6	Block 1	6.00	60.00	4.00	80.00	73.07
26	8	Block 1	6.00	60.00	4.00	80.00	73.09

Table 17: Diagnostics case statistics

Standard order	Actual value	Predicted value	Residual	Leverage	student Residual	cook's Distance	Outlier t	Run Order
1	82.68	83.86	-1.18	0.687	-0.767	0.086	-0.752	15
2	72.99	74.05	-1.06	0.687	-0.694	0.071	-0.677	25
3	67.84	68.62	-0.78	0.687	-0.511	0.038	-0.493	21
4	53.37	50.21	3.16	0.687	2.063	0.623	2.512	12
5	89.76	87.43	2.33	0.687	1.521	0.339	1.632	2
6	84.67	84.77	-0.10	0.687	-0.068	0.001	-0.065	4
7	81.73	82.15	-0.42	0.687	-0.277	0.011	-0.265	14
8	69.06	70.89	-1.83	0.687	-1.192	0.208	-1.218	19
9	91.86	91.83	0.031	0.687	0.020	0.000	0.019	9

10	79.25	77.03	2.22	0.687	1.449	0.308	1.536	18
11	71.65	69.75	1.90	0.687	1.241	0.225	1.275	7
12	42.21	46.34	-4.13	0.687	-2.693	1.062	-4.400	17
13	99.43	100.79	-1.36	0.687	-0.891	0.116	-0.882	1
14	92.13	93.14	-1.01	0.687	-0.661	0.064	-0.643	16
15	87.94	88.67	-0.73	0.687	-0.478	0.033	-0.460	11
16	75.38	72.41	2.97	0.687	1.940	0.551	2.280	22
17	76.29	74.29	2.00	0.476	1.009	0.061	1.009	13
18	70.62	72.99	-2.37	0.476	-1.192	0.086	-1.218	24
19	76.27	75.06	1.21	0.476	0.612	0.023	0.593	20
20	71.68	73.26	-1.58	0.476	-0.795	0.038	-0.781	26
21	69.82	71.63	-1.81	0.476	-0.913	0.050	-0.905	10
22	74.56	73.11	1.45	0.476	0.729	0.032	0.713	23
23	67.74	69.06	-1.32	0.476	-0.665	0.027	-0.647	3
24	70.49	69.53	0.96	0.476	0.482	0.014	0.464	5
25	73.07	72.35	0.72	0.100	0.276	0.001	0.264	6
26	73.09	72.35	0.74	0.100	0.284	0.001	0.271	8

Table 18: Characteristic IR absorption frequencies of organic functional groups

Functional Group Names	Absorption Ranges(cm ⁻¹)	Type of Vibration causing IR absorption
Alkanes	3000-2800	H-C-H Asymmetric & Symmetric Stretch
	1500-1440	H-C-H Bend
Alkenes	3100-3000	C=C-H Asymmetric Stretch
	1675-1600	C-C=C Symmetric Stretch
Alkynes	3300-3200	=C H Stretch
	2200-2100	C - C Stretch
Aromatic Rings	3100-3000	C=C-H Asymmetric Stretch
	1600-1580	C-C=C Symmetric Stretch
	1500-1450	C-C=C Asymmetric Stretch
Phenols & Alcohols	3600-3100	Hydrogen-bonded O-H Stretch
	1730-1650	C=O Stretch
Ketones	1750-1625	C=O Stretch
	1750-1625	C=O Stretch
Aldehydes	2850-2800	C-H Stretch off C=O
Esters	1755-1650	C=O Stretch
	(1300-1000)	(C-O Stretch)
Ethers	(1300-1000)	(C-O Stretch)
Amines—Primary	3500-3100 (TWO PEAKS!)	N-H Stretch
	1640-1560	N-H Bend
Amines—Secondary	3500-3100 (ONE PEAK!)	N-H Stretch
	1550-1450	N-H Bend

Nitriles	2300-2200	C N Stretch
Nitro Groups	1600-1500	N=O Stretch
	1400-1300	N=O Bend
Amides	3500-3100	N-H Stretch (similar to amines)
	1670-1600	C=O Stretch
	1640-1550	N-H Bend
Aldehydes	2750-2700	C-H Stretch off C=O

Design-Expert® Software
Removal eff.

Color points by value of
Removal eff.:

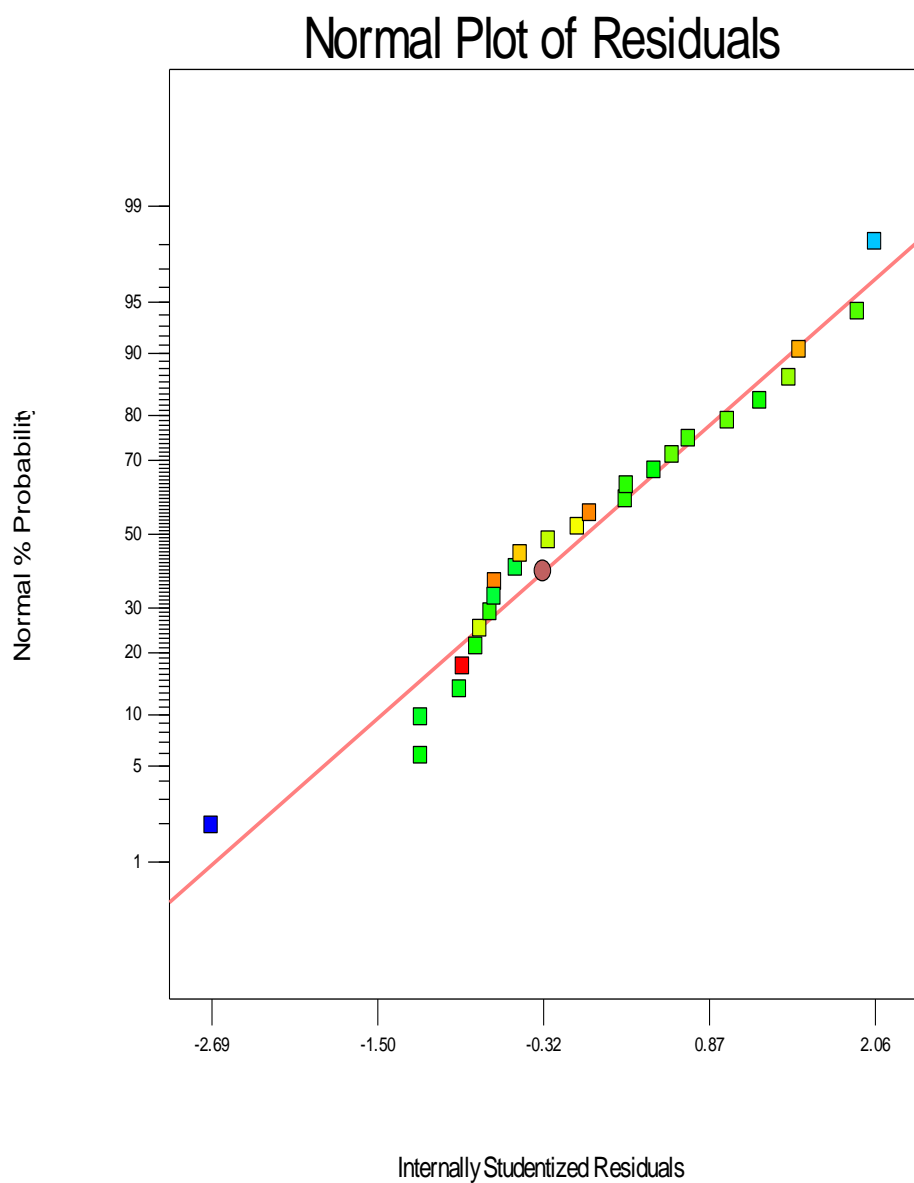
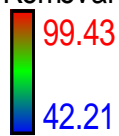


Figure 20: Normal plots of residuals

Color points by value of
Removal eff.:
99.43
42.21

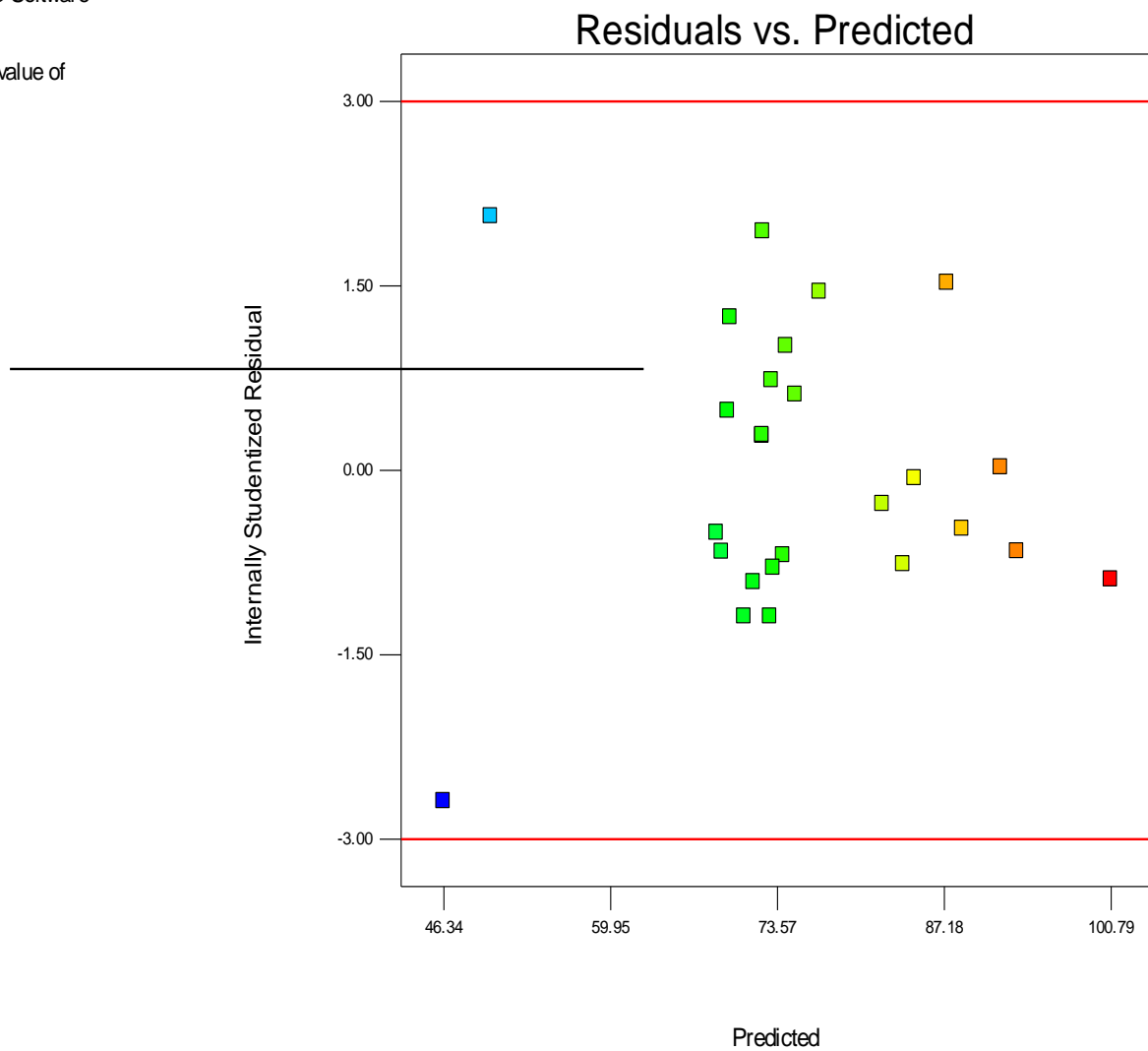


Figure 21: Plot of residual Vs. predicted