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SCHOOL OF CHEMICAL AND BIO ENGINEERING

REMOVAL OF REACTIVE RED DYE FROM AQUEOUS SOLUTION USING LOCALLY AVAILABLE CLAY SOIL AS LOW COST ADSORBENT

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

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Ethiopia

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This is to certify that the thesis prepared by Tehetena Bayssa, entitled*; removal of reactive red dye from aqueous solution using locally available clay soil as low cost adsorbent* and submitted in partial fulfillment of the requirements for the degree of Masters of Science (chemical engineering, Environmental engineering stream) complies with the regulation of the University and meets the accepted standards with respect to originality and quality.

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Chair of school or Graduate program Coordinator

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This thesis is dedicated
To
My parents

Abstract

Textile industry is one of those industries that discharge great amounts of effluents with synthetic dyes to the environment causing public concern. Reactive dyes are applied in textile industries which causes severe problem of water pollution and treatment. This study investigates the potential use of low cost clay soil for the removal of reactive red dye from aqueous solution.

The clay soil washed repeatedly until the dirt was eliminated. Then, it was heated at 105°C for 24hrs and activated with H_2SO_4 in order to increase adsorption sites. The clay soil was characterized for its physicochemical properties. The effects of solution pH, adsorbent dose, initial dye concentration and contact time at room temperature were studied in batch adsorption experiment. Mechanism of adsorption was studied using isotherm and kinetic models .The interaction effect of process parameters and optimization were studied using response surface methodology.

Experimental results have shown that, adsorption capacity was found to increase with higher initial dye concentration and lower solution pH. Maximum adsorption capacity of reactive red dye was found at pH 1 and optimum time of 120min. Langmuir, Freundkich, D-R isotherm models were investigated and the result showed that the adsorption process was most fitted to the Langmuir isotherm model giving correlation coefficient of 0.985.The calculated adsorption free energies from the D-R isotherm model 12.9kJ/mol indicated that the Adsorption process proceeds via chemisorptions. The kinetic study showed that Pseudo second-order model best described the kinetics of adsorption which confirmed the adsorption process was chemisorptions. The optimum condition for reactive red dye removal was found at pH 1.5, 40 mg/L of initial dye concentration 4 g/100 ml of adsorbent dose and contact time of 120 minutes. The results showed that clay soil has the potential to be applied as adsorbent to remove textile dye from textile wastewater.

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List of Abbreviations

Ce	Equilibrium concentration in mg/L
q	Adsorption capacity in mg/g.
q_{max}	Maximum adsorption capacity in mg/g.
q_e	Equilibrium adsorption capacity in mg/g.
q_t	Adsorption capacity in mg/g.
K_1	Pseudo first order kinetics constant (min^{-1})
K_2	Pseudo second order kinetics constant (g/mg.min)
K_{id}	Intra-particle diffusion constant
b	Langmuir constant (L/mg)
K_f	Freundlich constant
n	Freundlich constant
Ɛ	Polanyi potential
K_{DR}	Activity coefficient related to adsorption free energy.
FTIR	Fourier transforms infrared spectroscopy
RSM	Response surface methodology
CCD	Central composite design
ANOVA	Analysis of variance
PZC	Point of zero charge
E	The Adsorption free energy (KJ/mol)

1. Introduction

1.1 Background

Water pollution from textile dyeing industry becomes a matter of concern owing to significant organic matter and dyeing agents that produce colors. As a result, they generate a considerable amount of colored wastewater. It is recognized that public perception of water quality is greatly influenced by the color and odour. Color is the first contaminant to be recognized in wastewater. [1].The presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and undesirable [2] due to their good solubility, synthetic dyes are common water pollutants and frequently found in textile industrial wastewater.10-25% of textile dyes are lost during the dyeing process, and 2-20% are directly discharged as aqueous effluents in different environmental components [3]. Many of these dyes are toxic and even carcinogenic and this poses a serious hazard to aquatic living organisms and to the environment.

The discharge of dye-containing effluents into the water environment is undesirable, not only because of their color, but also because many of dyes released and their breakdown products are toxic, carcinogenic or mutagenic to life forms mainly because of carcinogens, such as benzidine, naphthalene and other aromatic compounds [4].Since, dye can reduce light penetration into the water thereby decreasing the efficiency of photosynthesis in aquatic plants and hence having adverse impact on their growth Dyes can also cause severe damage to human beings, such as dysfunction of kidney, reproductive systems, liver, brain and central nervous system. The occupational exposure of workers in the textile industry is linked to a higher bladder cancer risk. Without adequate treatment these dyes can remain in the environment for a long period of time. For instance, the half-life of hydrolyzed Reactive Blue 19 is about 46 years at pH 7 and 25°C [5] hence the removal of dyes has become an important aspect of textile wastewater treatment.

Wastewater containing dyes is very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion, and are stable to light, heat and oxidizing agents. In developing countries Wastewaters from dyeing industries are released in to nearby land or rivers without any treatment because the available treatment methods are not cost effective and /or

inefficient. There are different reported methods for the removal of pollutants from effluents including filtration, flocculation, chemical precipitation, ion exchange, membrane separation, etc. However, these processes involve use of chemicals and synthetic polymers and disposal of sludge whose impact on the environment has not been entirely studied [6].

The adsorption process provides an attractive alternative treatment, especially if the adsorbent is low cost and readily available. Activated carbon is the most widely used adsorbent, but it is expensive. Therefore, new materials with low cost, easily available, are used for the dye removal such as natural clays [7]. Natural clay minerals due to their low cost, abundance and high sorption potential for ion exchange are strong candidates as adsorbents [8].

This study was investigated the adsorption capacity of locally available low cost adsorbent clay soil (block cotton soil) collected from high land of Ethiopia, for reactive red dye removal from aqueous solutions . Therefore, the dynamic characteristics of adsorption were measured on the effect of process parameters such as solution pH, adsorbent dosage, initial dye concentration and contact time.

1.2 Statement of the problem

Textile industry is one of the most important and oldest industries in Ethiopia which spans over 70 years. Currently, the number of factories that use textile dyes have reached about 50.The wastewater from these factories is highly concentrated, so that small amount of dye can pollute lager amounts of groundwater rendering it unsuitable for of domestic water supply. In addition to potential carcinogens and highly toxic chemicals, the textile industries wastewater contains a variety of conventional pollutants that render a wastewater contaminated ground and surface water unusable. This dye wastewater has been implicated as surface water and groundwater pollution.

Textile industries have shown a significant increase in the use of synthetic complex organic dyes as the coloring material .The presence of dye materials greatly influence the quality of water and the removal of this kind of pollutant is of prime importance. Owing to their complicated

chemical structures, dyes are difficult to treat with municipal waste treatment operations even a small quantity of dye does cause high visibility and undesirability. Moreover, the color produced by dyes in water makes it aesthetically unpleasant. They can have acute or chronic effects on exposed organisms, which depend on the concentration of the dye and the exposed time In addition to that, many dyes are considered to be toxic and even carcinogenic.

Most of dyes are known to be non-biodegradable. Thus the conventional primary and secondary systems are not suitable to treat these effluents. Many physical and chemical processes for color 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, pulp and paper industries seldom apply these to treat their effluents [9]. Most Ethiopian textile industries do not treat their waste before discharging as the cost of implantation and running the treatment plant is high.

Therefore, it is a great necessity for developing inexpensive and efficient adsorbent material that is easily available in large quantity and economically feasible for removal of dye from textile industries.

1.3 Objectives of the research

1.3.1 General Objective

The general objective of the research is to study adsorption of reactive red dye from aqueous solution using locally available clay soil as low cost adsorbent.

1.3.2 Specific Objectives

- Investigation of functional groups on the surface of the adsorbent.
- Investigation of effects of process parameters (solution pH, adsorbent dosage, initial dye concentration and equilibrium time) on reactive red dye removal from aqueous solution.
- Investigation of adsorption isotherm models.

- Investigation of the adsorption kinetics.
- Optimization of experimental parameters.

1.3.3 Research questions

- Does clay soil commonly called black cotton soil can be implemented as low cost adsorbent for the removal reactive red dye from aqueous solution?
- How does physico-chemical nature of the clay soil affects the adsorption of reactive red dye?
- How do the process parameters affect the adsorption process?
- How does the interaction effect of process parameters affect the dye removal?
- What is the mechanism of adsorption?
- What are the optimum conditions for the removal reactive red dye by using clay soil?

1.3.4 Significance of the research

Finding of this research will protect the aquatic environment and solve the problem of textile industries in Ethiopia regarding of treating waste water containing dyes. This study should be significant in the sense that it will

- Produce low cost and locally available adsorbent material which can be used for treatment of textile waste water
- Introduce a solution to dye containing waste water
- Produce environmental friendly adsorbent which can easily be prepared and regenerated
- Provide useful knowledge on factors that might have impact on the adsorption of reactive red dye.

1.3.5 Scope of the research

The scope of this research is to develop abundant and locally available low cost adsorbent for removal of reactive red dye from aqueous solution. For this reason clay soil will be used as an adsorbent. The adsorbent clay soil will be treated with sulfuric acid in order to modify the

surface properties. The reactive red dye removal performances of the adsorbent under different experimental conditions will be investigated. The adsorption data will be then used to investigate the adsorption isotherm models and adsorption kinetics models. Finally, optimization and designing of experiment will be performed using Design expert software.

1.3.6 Limitation of the research

- The time bound set for the thesis work coupled with the financial budget set for the research forced me to exclude some process parameters.
- Severe chemical and Instrumental constrains that greatly restrict the number of analysis that could have been performed.

2. Literature review

2.1 Characteristics of dyes

A dye molecule consists of two key components: the chromophores, responsible for producing the color, and the auxochromes, which in addition to support the chromophore, also render the molecule soluble in water and give enhanced affinity toward the fibers. Dyes have high structural diversity and can be classified in many ways [10].

All dyes are organic aromatic compounds with a conjugated double bond system, to which chromophores and auxochromes are attached. These functional groups reduce the number of conjugated double bonds needed for light absorption and result in molecules that are small enough to diffuse into fibers. Chromophores [11] are unsaturated functional groups. Alone, they absorb visible or near ultraviolet radiation. In a dye molecule, they function as electron acceptors. Auxochromes are saturated functional groups. Auxochromes act as electron donors because the atom attached to the conjugated system has nonbonding electrons. Dye chromogens can be described as electron acceptor(s) (chromophores) interacting with electron donor(s) (auxochromes) through a conjugated double bond system.

The textile dyes are mainly classified in two different ways: (1) based on its application characteristics (i.e. CI Generic Name such as acid, basic, direct, disperse, mordant, reactive, sulphur dye, pigment, vat, azo insoluble), and (2) based on its chemical structure respectively (i.e. CI Constitution Number such as nitro, azo, carotenoid, diphenylmethane, xanthene, acridine, quinoline, indamine, sulphur, amino- and hydroxy ketone, anthraquinone, indigoid, phthalocyanine, inorganic pigment, etc.) .Excepting the colorant precursors such as azoic component, oxidation bases and sulphur dyes, almost two-third of all organic dyes are azo dyes used in a number of different industrial processes such as textile dyeing and printing, color photography, finishing processing of leather, pharmaceutical, cosmetics, etc. Considering only the general structure, the textile dyes are also classified in anionic, nonionic and cationic dyes. The major anionic dyes are the direct, acid and reactive dyes [12] and the most problematic ones

are the brightly colored, water soluble reactive and acid dyes (they cannot be removed through conventional treatment systems).

2.1.1. Theory of Reactive dyes

The first reactive dyes for cellulosic fibers were launched by ICI in 1956 under the trade name Procian. It was the discovery work of Stephen and Rattee which proved that dyes containing the 1,3,5-triazinyl group were capable of reaction with cellulosic fibers under mildly alkaline conditions [13]. Reactive dyes are colored compounds which contain one or two groups capable of forming covalent bonds between a carbon or phosphorus atom of the dye ion or molecule and an oxygen, nitrogen or sulfur atom of a hydroxyl, an amino or a mercepto group, respectively, of the substrate. Such covalent bonds are formed with the hydroxyl groups of cellulosic fibers, with the amino, hydroxyl and mercapto groups of protein fibers and the amino groups of polyamides [14].

Reactive dyes are used extensively in textiles industries regarding favorable characteristics of bright color, water-fast, simple application techniques with low energy consumption [15]. reactive dyes are the largest class of dyes used in textiles industry and it is the azo dyes based on the azo chromogen (-N=N-) and the presence of bright color due to these azo bonds and associated chromophore. These properties as well as the simplicity of the dyeing process, despite their relatively high cost, are widely used on cellulosic fibers.

2.1.2 Structure of reactive dye

From Figure 1.1 there are four important structural features of the molecules in reactive dyes and it can be identified separately. These are the chromogen, the water solubilising group, the bridging group, and the fiber-reactive group [16] The chromogen is the part of the molecule that essential gives the molecule its color and may contribute to other features of the dye such as its light fastness. As encountered in most of the other application classes of textile dyes, these chromogens typically belong to the azo, carbonyl or phthalocynanine chemical.

Most commonly, the water-solubilising group located in the chromogenic part of the reactive dye molecule; although on a number of occasions it is part of the fiber reactive group. The essential structural characteristic of a reactive dye is a functional group that is capable of reacting chemically with the fiber. This feature is, for obvious reasons, termed the fiber-group and the organic chemistry underlying the reaction of these groups with functionality on the fiber forms.

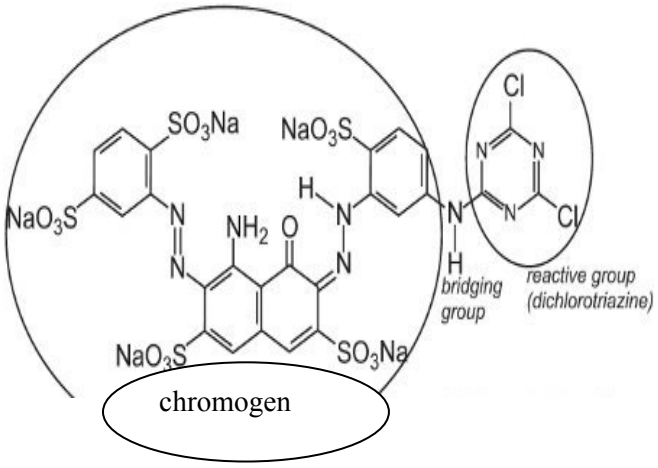


Figure 1.1 structure of reactive dye

2.1.3 Dye contamination and Toxicity

Most industries use dyes and pigments to color their products, which include textile, tannery, food, paper and pulp, printing, carpet and mineral processing industries. Perhaps these are the serious polluters of our environment as for as color pollution is concerned. Discharge of dye effluents into the natural streams may be toxic to the aquatic lives. Color affects the nature of water and inhibits the sunlight penetration into the stream and reduces photosynthetic activity Some of the dyes are carcinogenic and mutagenic .Color is a visible pollutant and the presence of even very minute amount of coloring substance makes it undesirable due to its appearance.

Textile dyes when discharge in to receiving streams will affects the aquatic life and causes the detrimental effects in liver, gill, kidney, intestine, gonads & pituitary gonadotrophic cells. In human it may causes irritation to the respiratory tract if inhaled and causes irritation to the gastrointestinal tract upon ingestion. Contact of dye with skin causes irritation with redness & pain. Upon contact with eye will lead to the human body is composed mainly of proteins, sugars and lipids, and a vast number of our vital metabolic reactions involve these three groups of chemicals. Therefore, introducing chemicals which react with these substances into the body is

likely to be an extremely bad idea. The most powerful dyes are extremely toxic, affecting our biochemical reactions and structures, or even interfering with our DNA to produce mutations or cancer. Reactive dyes are the most commonly used in textile industries for dyeing of cotton, silk, etc... Reactive dyes have properties that make it difficult to remove from aqueous solutions [17].

2.2 Methods of dye removal from wastewater

2.2.1 Overview of current treatment technologies for dye removal

A number of technologies for treating dye containing wastewater are developing. Among the different current dye removal methods, Adsorption, ion exchange, membrane filtration, ozonation, elcetrokinetic coagulation, fenton reagent and photocatalyst could be mentioned. Adsorption technologies for wastewater treatment are becoming more popular in recent years with regard to their efficiency in the removal of pollutants [18]. However, because of the costs and unknown environmental effect associated with some of these methods, it is necessary to develop more cost effective and environmentally friendly remediation system particularly in countries like Ethiopia Adsorption has advantages over the other methods because of its simplicity of design, sludge free and can be of low capital intensive. Adsorption does not have adverse environmental effect for treatment of dye wastewater; in developing countries it is a research area where it becomes interest.

2.2.2 Wastewater management in Ethiopia

In most of Ethiopia dye effluent management systems are not clearly defined and efficiently installed. Inadequate wastewater management system in textile industries triggers inefficiency in environmental management [19]. The world in general and Ethiopia in particular, is facing water quality crisis. Continuing population growth, urbanization and rapid industrialization meant for development are putting pressure on water resources and increasing the unregulated or illegal discharge of contaminated water within and beyond regional borders.

According to the Ministry of Health on the study of liquid waste management, out of 118 industrial establishments assessed in the city of Ethiopia, 40 have solid waste discharges, 61 generate air pollutant discharges while 62 generate liquid wastes that are discharged to the

surrounding. Only 6 out of the investigated factories are found to have some form of wastewater treatment plants and the rest discharge their wastes without any form of treatment [20].

Most of developing countries including Ethiopia often suffer from the absence of efficient institutions; lack of technological knowledge and empirical Know-How of wastewater treatment processes and their implementation; also inappropriate management practices. Textile industries in Ethiopia and elsewhere in Ethiopia, which have treatment facilities, divert their raw wastewaters into the storm water drainage system or directly to the watercourses. The reason could be either for technical reasons related to the wastewater treatment plant operation or for practical reasons since there are no regulations and effective control regarding industrial effluent discharges by concerned parties. Some studies indicate that the industries equipped with some form of effluent treatment facilities have installations undersized and frequently inoperable. It seems that the main function of these facilities appeared to have been obtaining the permit required to build the factories. There are very few industries in the city of Ethiopia that use septic tanks for the disposal of industrial waste effluent [20].

2.2 .3 Conventional Technologies for dye removal

Over the few decades, several methods have been devised for the treatment and removal of dye. The commonly used procedures for removing dye from aqueous streams include chemical treatment and physical treatment.

2.2.4 Chemical Treatment methods

Oxidative processes

This is the most commonly used method of decolourisation by chemical means. This is mainly due to its simplicity of application. The main oxidising agent is usually hydrogen peroxide (H_2O_2). This agent needs to be activated by some means, for example, ultra violet light. Chemical oxidation removes the dye from the dye-containing effluent by oxidation resulting in aromatic ring cleavage of the dye molecules [21].Although these methods are efficient for the treatment of waters contaminated with pollutants, they are very costly and commercially unattractive. The high electrical energy demand and the consumption of chemical reagents are common problems.

Ozonation

Oxidation by ozone is capable of degrading chlorinated hydrocarbons, phenols, pesticides and aromatic hydrocarbons .The dosage applied to the dye-containing effluent is dependent on the total colour and residual COD to be removed with no residue or sludge formation and no toxic metabolites .Ozonation leaves the effluent with no color and low COD suitable for discharge into environmental waterways This method shows a preference for double-bonded dye molecules .One major advantage is that ozone can be applied in its gaseous state and therefore does not increase the volume of wastewater and sludge.

Disadvantage of ozonation is its short half-life, typically being 20 min. This time can be further shortened if dyes are present, with stability being affected by the presence of salts, pH, and temperature. In alkaline conditions, ozone decomposition is accelerated, and so careful monitoring of the effluent pH is required. One of the major drawbacks with ozonation is cost; continuous ozonation is required due to its short half-line [21].

Sodium hypochloride(NaOCl)

This method attacks at the amino group of the dye molecule by the Cl+. It initiates and accelerates azo-bond cleavage. This method is unsuitable for disperse dyes. An increase in decolouration is seen with an increase in Cl concentration. The use of Cl for dye removal is becoming less frequent due to the negative effects it has when released into waterways and the release of aromatic amines which are carcinogenic, or otherwise toxic molecules [22].

Electrochemical destruction

This is a relatively new technique; it has some significant advantages for use as an effective method for dye removal. There is little or no consumption of chemicals and no sludge build up. The breakdown metabolites are generally not hazardous leaving it safe for treated wastewaters to be released back into water ways. It shows efficient and economical removal of dyes and a high efficiency for color removal and degradation of recalcitrant pollutants [21, 22]. Relatively high

flow rates cause a direct decrease in dye removal, and the cost of electricity used is comparable to the price of chemicals.

Electro kinetic coagulation

This is an economically feasible method of dye removal. It involves the addition of ferrous sulphate and ferric chloride, allowing excellent removal of direct dyes from Wastewaters. Unfortunately, poor results with acid dyes, with the high cost of the ferrous sulphate and ferric chloride, means that it is not a widely used method. The optimum coagulant concentration is dependent on the static charge of the dye in solution and difficulty in removing the sludge formed as part of the coagulation is a problem [22] Production of large amounts of sludge occurs, and this results in high disposal costs.

2.2.5 Physical treatment methods

Membrane filtration

This method has the ability to clarify, concentrate and, most importantly, to separate dye continuously from effluent [21] .It has some special features unrivalled by other methods; resistance to temperature, an adverse chemical environment, and microbial attack. The concentrated residue left after separation poses disposal problems, and high capital cost and the possibility of clogging, and membrane replacement is its disadvantages. This method of filtration is suitable for water recycling within a textile dye plant if the effluent contains low concentration of dyes, but it is unable to reduce the dissolved solid content, which makes water re-use a difficult task.

Ion exchange

Ion exchange has not been widely used for the treatment of dye-containing effluents, mainly due to the opinion that ion exchangers cannot accommodate a wide range of dyes [22]. Wastewater is passed over the ion exchange resin until the available exchange sites are saturated. Both cation and anion dyes can be removed from dye-containing effluent this way. Advantages of this method include no loss of adsorbent on regeneration, reclamation of solvent after use and the

removal of soluble dyes. A major disadvantage is cost. Organic solvents are expensive, and the ion exchange method is not very effective for disperse dyes.

Irradiation

Sufficient quantities of dissolved oxygen are required for organic substances to be broken down effectively by radiation. The dissolved oxygen is consumed very rapidly and so a constant and adequate supply is required. This has an effect on cost. Dye-containing effluent may be treated in a dual-tube bubbling rector. This method showed that some dyes and phenol molecules can be oxidized effectively at a laboratory scale only [22].

2.3 Adsorption

Adsorption techniques have gained favour recently due to their efficiency in the removal of pollutants too stable for conventional methods. Adsorption produces a high quality product, and is a process which is economically feasible .Decolourisation is a result of two mechanisms: adsorption and ion exchange and is influenced by many physio-chemical factors, such as, dye/sorbent interaction, sorbent surface area, particle size, temperature, pH, and contact time [21, 22].

2.3.1 Advantage of adsorption over other conventional methods

Adsorption is one of the preferred process for dye removal over conventional methods due to its high efficiency, fast and easy operation and simple and flexible design .moreover the adsorbent can be easily recovered and reused .Adsorption is widely used for the removal of textile pollutants from wastewater due to low capital costs and the wide availability of low cost adsorbents .the adsorption process may generate little or no toxic pollutants and has law initial capital and operating costs [9] Adsorption is safe from the environmental point of view as no sludge is produced .

The effluent produced is after adsorption is generally of high quality [22] in adsorption the pollutants present in the wastewater attach to the surface of the adsorbent. The interaction

between the adsorbate and adsorbent can be expressed by adsorptive characteristics and physical properties.

Physicochemical methods are very simple and feasible compared to all other dye treatment methods. Major drawback associated with most physico-chemical methods is handling and disposal of sludge produced during the removal of dyes .Adsorption is the preferred physico-chemical method due to its wide range of applicability. A wide variety of low cost adsorbents are available [9].The adsorption capacity of these low cost adsorbents can be easily enhanced with simple and economically feasible methods.

2.3.2 Adsorption Mechanism

Adsorption occurs in three steps. First step, the adsorbate diffuses from the major body of the stream to the external surface of the adsorbent particle. Second step, the adsorbate migrates from the relatively small area of the external surface to the pores within each adsorbent particle. The bulk of adsorption usually occurs in these pores because there is the majority of available surface area. Final step, the contaminant molecule adheres to the surface in the pore.

Adsorption, similar to surface tension, is a consequence of surface energy. In the bulk material, all the bonding requirements ionic, covalent or metallic of the constituent atoms of the material are filled. However, atoms on the surface experience a bond deficiency, because they are not wholly surrounded by other atoms. It is then energetically favorable for these dangling bonds to react with whatever happens to be available. The exact nature of the bonding depends on the details of the species involved, which the process is generally classed as experimenting physisorption or chemisorption.

Physisorption or physical adsorption is a type of adsorption in which the adsorbate adheres to the surface only through weak intermolecular interactions. Physisorption is generally considered to be an effective method for quickly lowering the concentration of dissolved dyes in an effluent It is characterized by:

- Low temperature, always under the critical temperature of the adsorbate
- Type of interaction: Intermolecular forces (van der Waals forces)

- Low enthalpy: $\Delta H < 20$ KJ/mol
- Adsorption takes place in multilayer
- Low activation energy

Chemisorption is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond, as opposed to physisorption. It is characterized by:

- High temperatures.
- Type of interaction: strong; covalent bond between adsorbate and surface.
- High enthalpy: $\Delta H \sim 400$ KJ/mol
- Adsorption takes place only in a monolayer.
- High activation energy

2.3.3 Non-conventional low-cost adsorbent

The adsorbent is the separating agent used to express the difference between molecules in a mixture: adsorption equilibrium or kinetics. An adsorbent is a substance, usually porous in nature and with a high surface area that can absorb substances onto its surface by intermolecular forces. Various low cost adsorbents, that have been successfully implement for the adsorption of dyes from wastewater, include clays, spent brewery grain, modified agricultural by products, industrial wastes, coir pith, Chiston, fly ash, peat, coal, baggase, neem leaves and natural and modified clay minerals [23].

2.4 Types of adsorbents used in water treatment

There are generally three broad classes of adsorbents and these include organic, biological and mineral adsorbents. The mineral adsorbents are those adsorbents derived from mineral deposits like activated carbon (from coal), zeolites and clay.

2.4.1 Mineral adsorbents

Mineral adsorbents range from silica gels, activated alumina, activated carbon, oxides of metals, hydroxides of metals, zeolites, clay minerals [24].The most commonly explored mineral

adsorbents for water treatment and purification are zeolites and clay minerals. Clay minerals are now being widely researched for application in water treatment due to their potentially high adsorption capacity owing to their cation exchange capacity and nanoscale size and high surface area. This study will focus on the use of clay soil which has large amount of montmorillonite clay mineral for the adsorption of dye from aqueous solution.

2.4.2 Clay minerals as adsorbents

Clays are widely used as adsorbents due to their high-specific surface area, high chemical and mechanical stabilities, a variety of structural properties and low cost [23]. Clays are abundant, have potentially high adsorption capacities and the potential for ion exchange and therefore, are good candidates for the development of adsorbents. Clay materials possess a layered structure and are considered as good host materials.

Different types of clays are available and they are classified according to the differences in their layered structures. The layered clay minerals classified into three broad classes based on their surface charge. The classes are: uncharged (kaolin, talc and pyrrophylite), negatively charged (paragonite, vermiculites, and smectites) and positively charged (layered double hydroxides).

Montmorillonite clay is a widely studied 2:1 phylosilicate of the smectite clays due to its high cation exchange capacity (CEC) compared with other clays, and is reported to have the highest surface area. A comparison of the adsorption properties of kaolinite and montmorillonite clays showed that montmorillonite had a higher adsorption capacity than kaolinite for the adsorption of dye [24].There has been an increasing interest to utilize clays for the adsorption of not only organic, but also inorganic molecules from aqueous solution [25].

2.5 Adsorption mechanism of dye onto clay surface

If adsorption is performed from liquid solution, e.g. aqueous ion exchange, solvent-surface interactions and solvent-molecule interactions come into play. The final organization of the molecules at the clay mineral surface will be determined by the subtle balance between all possible interactions [26].

The interaction of organic dyes with clay minerals has been studied extensively for decades and reviewed [27]. The aggregation behavior is sensitive to the kind and amount of metallic ions present in the lattice of the clays, the amount of adsorbed water as well as the structure of the organic guests to be intercalated [28].

In the vicinity of clay particles, dye aggregation takes place due to an enhanced polarity of water molecules induced by present inorganic ions in electric double layer [29]. The presence of water as a polar solvent is essential for the aggregation of dye cations [30].Increasing the polarity of the environment increases the degree of aggregation. Enhanced aggregation is observed in aqueous solutions of inorganic salts and is found to be related to the polarizing effects of ions. A re-arrangement of the dye cations occurs in extant aggregates, which is directed by the charge distribution so that each cation balances one negatively-charged site, thus mapping an intrinsic distribution of the negative charge on the clay surface. The dye/ silicate dispersions are dynamic systems, where complex re-organization and re-distribution of the dye assemblies take place. The layer charge of the silicate substrate controls the formation of the dye's molecular assemblies, such as dimmers and aggregates. The dye species (monomers, aggregates) are characterized by distinctly different optical properties using UV/ visible and fluorescence spectroscopes. New bands in the spectra of the dye/ clay dispersions are due to the formation of dye cation dimmers and/ or higher aggregates [31].The aggregation of dye cations on a clay surface may significantly vary depending on the clay specimen.The dye-clay suspension's spectra depend on parameters like dye loading, clay type, exchangeable cation, clay concentration and age of the suspension [32].

When smectites are suspended in aqueous solutions, the expansion of the clay mineral structure occurs the swelling process relates to the expansion of interlayer spaces and is important for adsorption (intercalation) of various organic species. In aqueous suspensions, the exchangeable cations and water form a diffuse double layer around the charged alumino-silicate leaflets. Exchangeable cations facilitate the dissociation of interlayer water, producing local acidity. Organic compounds are adsorbed into the interlayer space of montmorillonite either as cations, by electrostatic attraction, or by van der Waals forces [33].

2.5.1. Clay soil deposit in Ethiopia

Clay soils, predominately black cotton and other clayey soils occur in various parts of Ethiopia. In the central, western, north-western, south-western and some parts of southern and eastern Ethiopia they often occur covering an extensive area. Such soils commonly occur in flat and gently sloping landscapes such as on the Highland plateau, low land flood plains and valley floors. These soils are notorious for exhibiting harmful geotechnical characteristics and causing costly hazards particularly in the construction .In wet season, these soils become highly plastic, thick, slick, and heavy [34].

2.6 Factors that affect the adsorption process

Numerous works have reported on the significant influence of clay minerals on optical properties of organic dyes .Several works have studied the factors affecting spectral properties of dyes adsorbed on clay mineral surfaces. Molecular aggregation and electronic properties of chromophores are strongly influenced by various parameters, including dye concentration and structure, pH and ionic strength, temperature and presence of organic co-solvents, etc [35].

2.6.1 Effect of initial dye concentration

The initial dye concentration of an effluent is important since a given mass of sorbent material can only adsorb a fixed amount of dye [36]. The effect of the initial of dye concentration factor depends on the immediate relation between the concentration of the dye and the available binding sites on an adsorbent surface normally the dye removal will decrease with increase in initial dye concentration. This is because for a given mass of adsorbent; the amount of dye it can absorb is fixed. The higher the concentration of the dye, the smaller the volume it can remove .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. [37] also reported that the time taken to reach equilibrium increased with increasing concentration. But the actual amount of dye adsorbed per unit mass of adsorbent increased with increase in dye concentration.

2.6.2 Effect of adsorbent dosage

Generally, the percentage of dye removal increases with increasing adsorbent dosage. Initially the rate of increase in the percent dye removal has been found to be rapid which slowed down as the dose increased. This phenomenon can be explained, based on the fact that at lower adsorbent dose the adsorbate (dye) is more easily accessible and because of this, removal per unit weight of adsorbent is higher. With rise in adsorbent dose, there is less commensurate increase in adsorption, resulting from many sites remaining unsaturated during the adsorption [38]. But after a certain dosage the increase in removal efficiency is insignificant with respect to increase in dose.

2.6.3 Effect of contact time

The rate of removal of dye increases with an increase in contact time to a certain extent. Further increase in contact time does not increase the uptake due to deposition of dyes on the available adsorption site on adsorbent material [39].At this point, the amount of the dye desorbing from the adsorbent is in a state of dynamic equilibrium with the amount of the dye being adsorbed onto the adsorbent. The time required to attain this state of equilibrium is termed the equilibrium time, and the amount of dye adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operating conditions.

2.6.4 Effect of pH

PH is a measure of acidity (pH<7) or basicity (pH>7) of an aqueous solution. The pH factor is very important in the adsorption process especially for dye adsorption. The pH of a medium will control the magnitude of electrostatic charges which are imparted by the ionized dye molecules. As a result, the rate of adsorption will vary with the pH of an aqueous medium .Generally, at low pH solution, the percentage of dye removal will decrease for cationic dye adsorption, while for anionic dyes the percentage of dye removal will increase. In contrast, at a high pH solution the percentage of dye removal will increase for cationic dye adsorption and decrease for anionic dye adsorption [40].

Cationic dye adsorption is favored at pH > pHpzc, due to the presence of functional groups such as OH-, COO^-groups. Anionic dye adsorption is favored at pH< pHpzc where the surface

becomes positively charged .Solution pH influences both the carbon surface dye binding sites and the dye chemistry in water. At lower pH values, the carbon will have a net positive charge. Higher uptakes obtained at lower pH may be due to the electrostatic attractions between negatively charged functional groups located on the reactive dye and positively charged adsorbent surface. Hydrogen ion also acts as a bridging ligand between the adsorbent wall and the dye molecule [41].

2.6.5 Effect of ionic strength

The wastewater containing dye has commonly higher salt concentration, and effects of ionic strength are of some importance in the study of dye adsorption onto adsorbents Theoretically, when the electrostatic forces between the adsorbent surface and adsorbate ions were attractive, as in this system, an increase in ionic strength will decrease the adsorption capacity. Conversely, when the electrostatic attraction is repulsive, an increase in ionic strength will increase adsorption. [42] Reported that the extent of adsorption is sensitive to changes in concentration of supporting electrolyte (chloride sodium) indicates that electrostatic attraction may be a significant component of the overall adsorption in this system.

2.6.6 Effect of temperature

Temperature appears to be a less important factor in adsorption temperature studies and has no significant influence to the adsorption efficiency over the range 20-35 ^{O}C. higher temperature will increase the kinetic energy of dye ions, which facilitates attachment of dye ions on the surface [43]. However, very high temperature may cause distortion of some sites of the cell surface available. Hence, adsorption processes are normally operated at temperature range from 5 to 40 ^{O}C.

2.6.7 Effect of agitation speed

In the batch adsorption systems, agitation speed plays a significant role in affecting the external boundary film and the distribution of the solute in the bulk solution [22]. The effect of agitation speed on adsorption of dye can be carried out by changing the speed of rotation of

adsorbate–adsorbent solution .Generally removal of dyes increases with agitation speed. Increasing agitation speed decreases the boundary layer resistance of the transfer of adsorbate molecules from the bulk solution to the adsorbent surface. Due to this, the adsorbate is forced towards the adsorbent surface and it leads to an increase in the diffusion of adsorbate into the surface of the adsorbent .

2.7 Previous studies

Natural minerals

The adsorption mechanism of three reactive azo dyes (Everzol Black B, Everzol Red 3BS, Everzol Yellow 3RS H/C) were studied by two natural minerals. Batch adsorption tests as a function of pH, solids concentration, mixing time and dye concentration using sepiolite and zeolite carried out. Selected solids concentration as 0.05 g/mL (5 %) for sepiolite and zeolite. It is stated that most of the adsorption was found to take place within the first 2 h of mixing. Taking into account the extreme changes like pH and concentration, the mixing period was selected as 4 h for further testing. Adsorption capacity of sepiolite as 0.5–1 mg/g and negative adsorption of zeolite on reactive dyestuffs was observed [44].

Barley husk

The adsorption of five reactive dyes onto barley husk in static-batch mode and in a continuous flow, packed-bed reactor it is investigated effective adsorption, thermodynamics and various initial concentrations of dye solutions for static batch conditions. In addition, the effects of initial dye concentrations and retention time, by varying height and weight of packing, along with the kinetics of dye adsorption in CFPBR were examined. It is stated that the Langmuir Isotherm was used to predict adsorption capacity that was obtained as approximately 8.5 mg/g in static batch condition after 24 hours. Also, barley husks were found to remove 8 mg/g of dyes at initial concentration of 100 mg/L in CFPBR with a residence of 11 minutes with 90% adsorption being achieved [15].

Agricultural residues

In another study the effect of pretreatment of three agricultural residues, wheat straw, corncob, and barley husk, on adsorption process was investigated In order to increase the surface area of untreated sorbents, steam, alkali, ammonia steeping and milling were applied as pretreatment processes. It is stated 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 [21].

Activated carbon

one gram of activated carbon to shake for 48 hours with the aqueous solutions containing dye concentration, Rhomadine 6G (Basic Red 1), about 5-45 mg/L and examined the effects of pH (7-9), temperature (30-60oC) and particle sizes (0.5, 0.7, 1.0 mm) on the adsorption capacity of the activated carbon. It is reported that adsorption capacity of the adsorbent will increase if the particle size decreases, and temperature increases and also pH at neutral range gives the maximum adsorption capacity. In that study, maximum adsorption capacity of the activated carbon was obtained as 44.7 mg/g at T: 60oC, pH: 7.0, particle size: 0.5 mm. In addition, the kinetic data for dye adsorption at the same conditions and indicated the validity of first-order rate expression was investigated [45].

Activated clay

Kinetics and mechanism of adsorption of one basic dye (BB 69) and one direct dye (DR 227) onto activated clay in the temperature range 15-75oC was studied. Activation of clay was made by treatment with 1 molar sulfuric acid at 80oC for 2 hours. Pseudo first and second-order kinetic models were tested. It was shown that the adsorption process of the dyes was well defined by the pseudo second-order equation. The related rate constants and apparent activation energies were evaluated. It was reported that adsorption capacity of BB 69 on activated clay Increases with increasing temperature, but that of DR 227 decreases probably due to different adsorption nature; that is, the adsorption of BB 69 was extremely favorable and that of DR 227 was classified as reversible adsorption. In that study, it was concluded that the reaction mechanism might be partly as a result of the Complication or ion exchange between the charged

groups in dye molecules and the SiO_2 or Al_2O_3 groups on the adsorbent surface. Also, relatively large pore size of the adsorbent (20-50 nm) was considered as a possible reason of adsorption. The apparent activation energy for adsorption of BB 69 and DR 227 was found as 8.03 and 17.5 kJ/mol, respectively [46].

Combustion of coal wastes

Adsorption of a dyestuff, Rifazol Black B (Reactive Dye) from aqueous solution on different adsorbents that are activated carbon, natural sepiolite, activated sepiolite and slag which is generated from combustion of Soma coal in a Textile Factory was studied. Effects of pH, temperature and particle size on adsorption were investigated. Activation of sepiolite was done by using 0.75 M HCl and HNO3. Maximum adsorption capacities of the adsorbents are given as follows; activated carbon > slag > activated sepiolite > natural sepiolite [47].

Eucalyptus bark

Eucalyptus bark that is a very abundant, inexpensive, 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. it was found the maximum adsorption capacity about 90 mg of dye/g of drybark at pH 2.50 for a sodium chloride concentration of 50 g/L, an initial dye concentration equal to 500 ppm, a bark concentration equal to 2 g/L and at 18oC. 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 [48].

Chitosan

In another study, the removal of some reactive dyes, Reactive Red 222, Reactive Yellow 145, and Reactive Blue 222, from aqueous solutions by adsorption on “chitosan” was examined. Effects of dye concentration, the amount and particle size of “chitosan” were investigated during experiments. Maximum adsorption capacity of “chitosan” was obtained as 380, 179, and 87 g/kg

for RR222, RY145, and RB 222, respectively. Among the most frequently used isotherm equations, Langmuir, Freundlich and Redlich-Peterson Equations, the equilibrium data could be best fitted by the Redlich-Peterson equation over entire concentration range. In addition, the smaller the "chitosan" particles, the greater the capacity of dye [49].

Silica particles

The adsorption of several anionic dyes, D&C Red 6, Acid Yellow 1, Acid Blue 25, Guinea Green B, on nanosize 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 Al lake. The advantage of the adsorbent was its small size (<20 nm) and the ability of the dyes to form chemical bonds with surface groups of the core particles. In that study adsorption capacities of the adsorbent for different dyestuffs were obtained at some values that were between 0.12-0.70 g dye/ g adsorbent [50].

Palm fruit particles

The adsorption of three basic dyes, namely, Basic Yellow, Basic Red and Basic Blue, from an aqueous solution on palm-fruit Particles was investigated. It was stated that the maximum adsorption capacities of the palm-fruit particles were found to be 327 mg yellow dye per gram of adsorbent, 180 mg red dye per gram of adsorbent and 92 mg blue dye per gram of adsorbent. In addition, a comparative cost study, based on the adsorption capacity alone, showed that the costs of the adsorbent required were 1.9%, 4.4%, 7.1%, respectively, compared with the case of commercial activated carbon granules [51].

Sunflower stalks

A study to determine adsorption capacity of Sunflower stalks for two basic dyes, Methylene Blue and Basic Red 9, and two direct dyes, Congo red and Direct Blue 71 was performed. The maximum adsorption capacity of the adsorbent was much higher for basic dyes, i.e. 205 and 317 mg/g for Methylene Blue and Basic Red 9, respectively, than that for direct dyes. It was stated

that the components of sunflower stalk have different adsorption capacities. The pith, the soft and porous material in the center of stalks, has twice the adsorptive capacity of the skin. Adsorption capacity of the adsorbent and its components for anionic dyes was obtained in the range 15 –76 mg/g that are much lower than that of cationic dyes [52].

3. Material and Methods

3.1 Materials

3.1.1 Equipments and apparatus

Table 3.1 List of equipments and instruments used for the thesis.

INSTRUMENT OR APPARUTUS	MANUFACTURER AND MODEL	USE
Analytical balance	Ohaus,EP 214C (Switzerland)	sample weighing
Analytical sieves with shaker	Retsch AS200 (Germany)	sample sieving
cross beater mill	Retsch (Germany)	size reduction of adsorbent
drying oven	Memmert,100-800(Germany)	sample drying
Furnace	Nebertherm LHT 02/16 (Germany)	To convert sample to ash
low temperature freezer	Hot point	preservation of dye samples
Micro pipette	Socorex Acura835 (Switzerland	Volume measurements
pH meter with glass electrode	Jenway 3505 (England)	pH measurement
Spectrophotometer	Jenway 6300 (England)	reactive dye analysis
Temperature controlled shaker	Stuart SBS 40(England)	Shaking samples
FTIR	Perkin Elmer Spectrum 65	Functional group determination

3.1.2 Chemicals and reagents

All chemicals used in this research were of analytical-laboratory grade. Distilled water was used throughout the study. Commercially quality reactive red dye was obtained from Ayka Addis textile industry. The reactive red dye was used without further purification as adsorbate. It has a maximum visible absorbance at a wave length of 540nm.

- Stock solution preparation: The stock solution was prepared by dissolving 1 g of the reactive dye in 1 L of distilled water to obtain working solutions of varying concentrations for further experiments. All working solutions were prepared by diluting the stock solution with distilled water.
- Calibration standards: lower concentration standards were prepared from the stock solution.
- pH adjustment: 0.1-1M NaOH(RANKEM, India) and 0.1-1M HCL(RANKEM, India) were used .
- Adsorbent modifier: 0.1M H_2SO_4 (RANKEM, India) was used.
- Point of zero charge: 0.1M KNO_3 (BDH, England) was used.

3.2 Experimental Methods

3.2.1 Preparation of adsorbent

Clay soil commonly called black cotton soil which is locally available was used as an adsorbent. The clay soil sample was obtained from geotechnical laboratories as there are adequate tested clay soil samples. The collected clay sample washed extensively in running tap water to remove dirt and earthly materials adhered to the surface. The washed sample dried in oven at 105 °C for 24hrs. Chemical composition of clay soil sample was given in Table 3.2.

Table 3.2 Chemical composition of sample clay soil [53]

Components	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**MgO**	**CaO**	**Na_2O**	**K_2O**	**TiO_2**	**P_2O_5**	**LOI**
Compositions %	52.8	17.7	7.57	1.05	1.43	0.61	1.42	1.12	0.09	15.37

3.2.2 Modification of adsorbent materials

The modified clay soil was prepared in the laboratory by contacting the pre-prepared raw adsorbent with 0.1M H_2SO_4. 345g of sample clay soil mixed with 600 mL of sulfuric acid and agitated at 150 rpm for 24 hours. The clay soil was separated by filtration, during the filtration process, the treated clay washed several times using distilled water. Acid activated clay soil dried

in the oven at 52^0c for 12hrs .the dried sample crushed and sieved with particle size of 180-710μm and stored in the plastic bag used for adsorption studies.

3.2.3 Characterization of the adsorbent

3.2.3.1 Proximate Analysis on raw adsorbent

- **Determination of % Moisture content**

To determine the % moisture contents of the clay soil sample, 1 g sample was taken in a clean and dry crucible (W1) and kept in an oven at 105ºC for 2 hrs. The sample was then transferred desiccators to cool and weight, again it was transferred in to an oven until constant weight after drying was obtained (W2) and % moisture was determined by following the formula:

$$(\%)\ \text{Moisture} = \frac{(w_1)-(w_2)}{(w_1)} \times 100 \qquad (3.1)$$

Where: w_1= weight of sample and crucible before drying (gram)

w_2= weight of oven dried sample and crucible (gram)

- **Determination of % Ash content**

An empty crucible and cover was ignited in the muffle at 600^oC for 1 hour and cooled in a dessicator and weighed to the nearest 0.1 mg. 2 gram sample of air-dried laboratory prepared Adsorbent was placed in the crucible, the weight of crucible plus specimen was noted. The crucible and contents was placed in the muffle furnace and ignited until all the carbon was eliminated. The temperature of final ignition was set at 600^oC; and kept for four hours. After four hour time, the crucible with its contents was removed and placed in a dessiccator to cool to 3^0C. The crucible with its contents was weighed accurately. The following formula was used to obtain the ash content in the adsorbent.

$$\%\ \text{Ash content} = \left(\frac{W_2}{W_1}\right) \times 100 \qquad (3.2)$$

Where: W_1= weight of ash (grams).

W_2= weight of oven –dried sample (grams).

3.2.3.2 Apparent density measurement

The pycnometer was cleaned using acetone and dried. The mass of the dry pycnometer was determined (Wo). Then the pycnometer was filled with the laboratory prepared biosorbent to 1/3 volume and the weight of the pycnometer plus the sample was measured (W1). Distilled water was added to the pycnometer with sample, until capillary hole in the stopper is filled with water. The spare water that leaked through the capillary hole was dried with a filter paper and the total weight of the pycnometer , the sample and distilled water was measured (W2). The particle density was calculated using formula.

$$\rho = \rho_w * \left(\frac{W_1 - W_O}{W_2 - W_1}\right) \quad (3.3)$$

Where: ρ_W = Density of water at 20^0C.

W_0= Mass of dry pycnometer

W_1= Mass of sample plus pycnometer

$W_{2=}$ Total mass of distilled water, sample and pycnometer.

3.2.3.3 pH of zero charge determination

The point of zero charge (pH pzc) of the solid adsorbent is a function of pH. The pH at which the charge of the solid surface is zero is referred to as the point of zero charge (pH pzc) and is typically used to quantify or define the electro kinetic properties of adsorbent surface. The point of zero charge (pH pzc) of the adsorbent was determined by the solid addition method. For this purpose a series of 100 mL of Erlenmeyer flasks 45 mL of standard solution of 0.1 M KNO_3 was transferred. The initial pHs of the solution (pHi) were approximately adjusted from 1.0 to 8 by adding either 0.1M HCl or NaOH using pH meter. The total volume of the solution in each flask was made exactly to 50 ml by adding the 0.1 M KNO3 solution of the same strength. The pHi of the solutions was then accurately noted, and 1g of adsorbent was added to each flask, which were securely capped immediately. The suspensions were then manually shaken and allowed to equilibrate for 48h with intermittent manual shaking. The final pH values of the supernatant liquid (pHf) were noted. The difference between the initial and final pH (Δ pH) values

(Δ pH=pHi−pHf y-axis) was plotted against the initial pHi (x-axis). The point of intersection of the resulting curve with the x axis gave the pHpzc.

3.2.3.4 FTIR analysis

The FTIR analysis was conducted using Perkin Elmer spectrum 65 FTIR spectrometer in average Wave length from 4000 to 400cm^{-1}. Laboratory prepared adsorbent samples for the analyses were first milled in a ceramic pestle to powdery conditions. The powder was mixed with KBr particles to make it suitable to infrared analysis. The mixture was then press to a small thickness, slightly below 1mm, required for FTIR analysis.

3.2.4 Batch Adsorption experiments

The adsorption studies were carried out at room temperature by shaking specific amount of clay soil and 100ml of reactive red dye solution in conical flasks (250ml), the samples were agitated at the rate of 150rpm for 2 hours. The dye solution with desired concentration placed in flask at desired pH, agitation, and temperature. The timing will be started upon the addition of adsorbent. After agitation, the powder was removed by filtration using Whatman number 1 filter paper. The concentration of dye in the filtrate was determined using Jennway UV-VIS spectrophotometer .All samples were carried out in duplicate under the same conditions and the average results were taken.

Solutions of different dye concentrations (0.1, 0.2, 0.4, 0.6, 0.8, 1, 2, 4, 6, 8 and 10mg/l) were pipette out into 5ml standard volumetric flasks and the total volume was made up to 50ml using distilled water. The absorbance values of these solutions were measured at maximum wavelength of 540 nm and plotted against the concentration values. The calibration curve in the concentration range that falls in the region of applicability of Beer-Lamberts 'law was employed The uptake of dye concentration was calculated using equation 3.4, while the metal uptake q(mg dye ion g^{-1} of adsorbent) was calculated from the mass balance of equation 3.5

$$\% \text{ Cr removal} = \frac{(C_0 - C_f) \times 100}{C_o} \quad (3.4)$$

$$q = \frac{(C_o - C_f)V}{W} \quad (3.5)$$

Where: C_o and C_f are the initial and equilibrium concentrations of dye solution (mg/l).

V is the volume of solution in liter and

W is the mass of adsorbent in gram

q is adsorption capacity

3.2.4.1 Effect of solution pH

The adsorption of dye was studied for solution pH ranging from 1-4.4g of adsorbent was contacted with 100 ml of 40 mg/l of dye solution shaken at 150 rpm for two hours at 20°c.
0.1 N HCl or NaOH solutions were used to adjust pH values. All pH measurements were taken using a laboratory pH meter.

3.2.4.2 Effect of Initial Concentration

The initial concentration of dye was varied from 20 to 100 mg L^{-1}. 4g of adsorbent was contacted with 100 ml of different concentrations of dye. Samples were shaken at150rpm for two hours at 20°c.

3.2.4.3 Effect of adsorbent concentration

The concentration of adsorbent was varied from 2 to 8 g. Each sample was contacted with 100 ml of 40 mg/ L of dye solution for two hours.

3.2.4.4 Effect of contact time on dye ion adsorption.

4g of the adsorbent was contacted with 300ml of dye (40 mg/ L) for different periods of time. The solution was mixed using a laboratory rotary shaker at rate of150rpm. 5 mL of samples was taken in 15 minutes time interval using a micro pipette, and filtered through No. 1 Whatman filter paper. The effect of contact time analyzed for up to 3 hours.

3.2.5 Adsorption Kinetic Models

The kinetics of sorption describes the solute uptake rate, which in turn governs the residence time of sorption reaction. It is one of the important characteristics in defining the efficiency of

sorption. Sorption kinetics shows a large dependence on the physical and/or chemical characteristics of the sorbent material. Different models have been used to investigate the mechanism of sorption. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (R^2 values close or equal to 1). A relatively high R^2 value indicates that the model successfully describes the kinetics of reactive red dye adsorption.

3.2.5.1 Pseudo-first-order or Lagergen kinetic model

It is the first equation for sorption of liquid/solid system based on solid capacity [54] The Pseudo-first-order equation is generally expressed as in Eq. (3.6).

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{3.6}$$

Here q_e and q_t are the adsorption capacities at equilibrium and at time t, respectively (mg/g) and k_1 is the rate constant of pseudo first- order adsorption (min^{-1}). Integrating Eq. (3.6) for the boundary conditions t = 0 to t = t and qt = 0 to qt = qt, gives

$$\log\left(\frac{q_e}{q_e - q_t}\right) = \frac{K_1 t}{2.303} \tag{3.7}$$

Eq. (3.7) can be rearranged to obtain the more useful form Eq. (3.8).

$$\log(q_e - q_t) = \log q_e - \left(\frac{k1}{2.303}\right) t \tag{3.8}$$

The values of log ($q_e - q_t$) will linearly correlate with t. The plot of log (qe −qt) vs. t should give a linear relationship from which k_1 can be determined from the slope.

3.2.5.2 Pseudo-second-order kinetic model

If the sorption rate of system is a pseudo-second-order mechanism, the rate-limiting step may be chemical sorption or chemisorption involving valency forces through sharing or the exchange of

electrons between sorbent and sorbate as covalent forces. There are certain assumptions in description of this kinetic model [55]

1. There is a monolayer of dye ion on the surface of sorbent.
2. The energy of adsorption for each ion is the same and independent of surface coverage.
3. The adsorption occurs only on localized sites and involves no interactions between sorbed ions.
4. The rate of adsorption is almost negligible in comparison with the initial rate of sorption.

The pseudo-second-order adsorption kinetic rate equation is expressed in Eq. (3.9)

$$\frac{dq}{dt} = K_2(q_e - q_t)^2 \qquad (3.9)$$

Where K_2 is the rate constant of sorption, (g/mg min), $q$eq is the amount of metal ion sorbed at equilibrium, (mg/g), qt is amount of metal ion on the surface of the adsorbent at any time, t, (mg/g).

Separating the variables in Eq. (3.9) gives:

$$\frac{dq_t}{(q_{e-q_t})2} = K_2 dt \qquad (3.10)$$

For the boundary conditions t = 0 to t = t and q_t = 0 to qt = q_t ; the integrated form of Eq. (3.10) becomes:

$$\frac{1}{(q_{e-q_t})} = \frac{1}{q_e} + K_2 t \qquad (3.11)$$

The linear form of equation (3.11) becomes

$$\frac{t}{q_t} = \frac{1}{(K_2 q_e^2)} + \frac{t}{q_e} \qquad (3.12)$$

Where, K_2 is the rate constant for the pseudo-second order adsorption process. The rate parameters K_2 and q_e can be calculated obtained from the intercept and slope of the plot of t/qt vs.t according to Eq (3.12).

3.2.5.3 Intra-particle diffusion model

Intra-particle diffusion can be described by three consecutive steps [56]

1. The transport of sorbate from bulk solution to outer surface of the sorbent by molecular diffusion, known as external (or) film diffusion.
2. Internal diffusion, the transport of sorbate from the particles surface into interior sites.
3. The sorption of the solute particles from the active sites into the interior surface of the pores.

The overall rate of the sorption process will be controlled by the slowest, the rate limiting step. The nature of the rate-limiting step in a batch system can be determined from the properties of the solute and sorbent. In adsorption systems where there is the possibility of intra-particle diffusion being the rate-limiting step, the intra-particle diffusion approach described by Weber and Morris. The rate constants, for intra-particle diffusion (k_{id}) are determined using equation given by Weber and Morris [57]

$$q_t = K_{id} t^{0.5} + C \qquad (3.13)$$

Where q_t is the amount of dye adsorbed, t is the contact time; k_{id} is the intra-particle diffusion coefficient and c is constant.

A plot of qt against $t^{0.5}$ should give a straight line which pass through the origin for intra-particle diffusion controlled adsorption process. The value of k_{id} can be calculated from slope of such plot. The values of the constant illustrate the effect of boundary layer on the rate of adsorption

3.2.6 Adsorption isotherm model

An adsorption isotherm is used to characterize the interaction of the dye ions with the adsorbent. This provides a relationship between the concentration of dye ions in the solution and the amount of dye ions adsorbed to the solid phase when the two phases are at equilibrium.

3.2.6.1 The Langmuir Isotherm

This is proposed by Langmuir [58] for homogeneous adsorption. It assumes a uniform adsorbent surface with energetically identical sorption sites. The Langmuir formula is proposed as follows:

$$q_e = \frac{q_{max}\, bC_{eq}}{1+bC_{eq}} \tag{3.14}$$

Where, q_{max} is the maximum metal sorption (mg metal/g of biomass) and b is the Langmuir isotherm constant (l/mg metal). Two derivatives of the Langmuir equation are Eq. (3.15) and (3.16):

$$\frac{C_{eq}}{q_e} = \frac{1}{q_{max}} + \frac{C_{eq}}{q_{max}} \tag{3.15}$$

$$\frac{1}{qe} = \frac{1}{q_{max}} + \frac{1}{q_{max}b}\frac{1}{C_{eq}} \tag{3.16}$$

The Langmuir isotherm considers sorption as a chemical phenomenon. It was first theoretically examined in the adsorption of gases on solid surfaces. Langmuir constant b is related to the energy of adsorption through the Arrhenius equation. The higher the value of b, the higher is the affinity of the sorbent for the sorbate. A $q$max can also be interpreted as the total number of binding sites that are available for adsorption and q_{eq} as the number of binding sites that are in fact occupied by the sorbate at the concentration $C_{eq.}$ Langmuir assumed that the forces that are exerted by chemically unsaturated surface atoms (total number of binding sites) do not extend further than the diameter of one sorbed molecule and, therefore, sorption is restricted to a monolayer. In the simplest case the following assumptions were made:

a) Fixed number of adsorption sites: at equilibrium, at any temperature, and gas pressure a fraction of the surface sites θ is occupied by adsorbed molecules and the fraction 1–θ is free.
b) All sorption sites are uniform (i.e., constant heat of adsorption).
c) Only one sorbate.
d) One sorbate molecule reacts with one active site.
e) No interaction between sorbed species.

Generally, the Langmuir isotherm does not describe equilibrium behavior accurately, especially with heterogeneous adsorption systems where adsorption continued beyond a monolayer. However, it is of practical importance because it is mathematically convenient and easily integrable.

3.2.6.2 The Freundlich Isotherm

The Freundlich isotherm, first proposed in 1906, is based on multilayer adsorption with interaction between adsorbed molecules [59].The model applies to adsorption onto heterogeneous surfaces with a uniform energy distribution and reversible adsorption. The Freundlich isotherm is the earliest known relationship describing the adsorption equation. The application of the Freundlich equation suggests that adsorption energy exponentially decreases on completion of the adsorptional centers of an adsorbent. For adsorption from solution, the Freundlich isotherm is represented by Eq. (3.17).

$$q_e = K_f C_{eq}^{1/n} \qquad (3.17)$$

Where K_f and n are the Freundlich constants. K_f related to the adsorption capacity; the larger its value, the higher the capacity. '***n'*** is the adsorption intensity or the heterogeneity of the sorbent; the more heterogeneous the surface, the larger its value. Equation (3.17) can be linearized in logarithmic form and the Freundlich constants can be determined.

$$\log q_e = \log K_f + \frac{1}{n}\log C_{eq} \qquad (3.18)$$

This isotherm is widely recommended due to its accuracy. It gives more accurate results than the Langmuir isotherm for a wide variety of heterogeneous adsorption systems. Though accurate and mathematically convenient, one drawback is that Freumdlich isotherm does not converge to Henry's law at low surface coverage and, therefore, fails to describe equilibria as $q \rightarrow 0$ and is thermodynamically inconsistent.

3.2.6.3 Dubinin-Radushkevich (D-R) sorption isotherm

Dubinin-Radushkevich (D-R) sorption isotherm model is postulated within the sorption space close to the sorbent space to evaluate the sorption free energy and to help determine the nature of bonding, i.e. physisorption or chemisorptions [60]

The Dubinin-Radushkevich sorption isotherm can be presented as follow:

$$\ln q_m = \ln q_e - K_{DR}\varepsilon^2 \qquad (3.19)$$

Where qm is the amount of heavy metal adsorbed [mole/g], qe is the maximum adsorption capacity [mole/g], KDR is the activity coefficient constant related to the adsorption free energy of the transfer of the solute from the bulk solution to the solid adsorbent[mol2/J2], and ε Ɛ is the polany potential which is given by the following equation:

$$\varepsilon\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \qquad (3.20)$$

Where: R is universal gas constant (8.314 J.mol^{-1} .K^{-1}), T absolute temperature in Kelvin, C_e is the equilibrium metal concentration [mole/L]. The value of K_{DR} can be determined from the plot of Ɛ ^{2} vrs. ln qm . The K_{DR} value can be used to determine the mean free energy (E) required to transfer 1 mole of heavy metal from infinity to the surface of the adsorbent from Eq.(3.21)

$$E = - \frac{1}{\sqrt{2K_{DR}}} \qquad (3.21)$$

If the value of E is between 8 and 16 KJ/mole, then the adsorption process is supposed to proceed via chemisorptions, while the values of E< 8 KJ/mol the adsorption process is of a physical nature [61]

3.3 Statistical Analysis of adsorption Process and optimization design of experiments.

Experimental design of the adsorption of reactive red dye process was carried out by using the Response surface methodology (RSM). RSM is a collection of mathematical and statistical techniques that are beneficial for the modeling and analysis of problems in which a response of interest is influenced by several variables and the objective is to search the optimum conditions of variables to predict targeted responses. RSM consists of an empirical modeling technique devoted to the evaluation of relations existing between a group of controlled experimental factors and the observed results. This could eliminate the time consuming phase which could not to be achieved using conventional method (one-factor-at-a-time approach). Besides, the central composite design (CCD) is well suited for fitting a quadratic surface, which usually works well for the process optimization and it requires a minimum number of experiments to be carried out.[15]. pH of the solution(X_1), dye concentration (X_2), adsorbent dose (X_3) and time (X_4) were identified as the set of four independent process variables to investigate their influence on the output variable (response), the removal of the dye from aqueous solution by clay soil.

The CCD method was adopted to decide the number of the sorption experiments to be performed for optimization of the process variables. For a design of four independent variables (n = 4), each with two different levels, the total number of experiments (N) was worked out as

$$N= 2^n+2n+n_c = 2^4+ 2(4) + 6 = 30 \qquad (3.22)$$

Here, this includes the standard 2n factorial points with their origin at the center, 2n axial points fixed at a distance, α from the center to generate the quadratic terms, and n_c replicate points at the center. [17] After having defined the range of each of the process variables, they are coded to

lie at ± 1 for the factorial points, 0 for the center points and ±α for the axial points. The numerical values of the variables were transformed into their respected coded values as:

$$Z_i = \frac{x_i - x_i^*}{\Delta x_i} \qquad (3.23)$$

Where Z_i is the coded value of i-th test variable, xi the uncoded value of the i-th variable , Xi^* is the uncoded value of the i-th variable at center point and ΔXi is the step change. The selected process variables with their limits, units and notations are given in Table 3.3.

Table 3.3 Experimental range and levels of independent process variables.

variables	Ranges and levels				
	-2	-1	0	+1	+2
pH	0.25	1.5	2.75	4	5.25
Adsorbent dose [g/100ml]	0.06	2.375	4.688	7	9.31
initial dye concentration [mg/l]	20	40	60	80	100
time [min]	22.5	75	127.5	180	232.5

4. Results and discussions

4.1 Adsorbent Characterization

The result obtained from the proximate analysis and the physicochemical characterization of acid activated clay soil is presented in table 4.1.

Table 4.1 Proximate analysis and physicochemical characterization of acid activated clay soil.

	Acid activated clay soil
Moisture content (%)	8.3
Ash content (%)	1.09
Apparent density g/cm3)	1.67
point of zero charge (p_{pzc})	2

From the result Table 4.1 clay soil sample had high percentage of moisture content and plasticity and strength of clays depend on the amount of water present. Between 1.2 to 14.26% moisture content, the clay will form an aggregate to develop strength [62]. The non combustible volatile matter content of the clay soil sample was low as evidenced on the low ash content of 1.09% obtained.

4.2 Point of zero charge

The pHpzc of clay soil adsorbent was assessed from the graph of the difference between the initial and final pH values (ΔpH = pHf–pHi) that was plotted against the initial pH value (pHi) as displayed in Figure 4.1. The pH_{PZC} was determined to be 2. From the graph it can be seen that the adsorbent was positively charged at PH less than 4. However, above pH 4 there was charge reversal which indicates decrease in acid groups on the surface of the adsorbent.

Due to the presence of functional group such as OH^- group, cationic dye adsorption is favoured at pH> pHpzc, whereas, anionic dye adsorption is favoured at pH< pHpzc where the surface becomes positively charged [63]. At pH values below the pHpzc, the adsorbent surface has a net

positive charge, and the surface will attract anionic reactive red dye and here the electrostatic interaction occurs at PH < 2, the more the lower value from the PHpzc the more positive the surface of the adsorbent. This behavior explains the acid modification gave a positive surface charge for the adsorbent which enhance adsorption capacity of acid activated clay soil for reactive red dye.

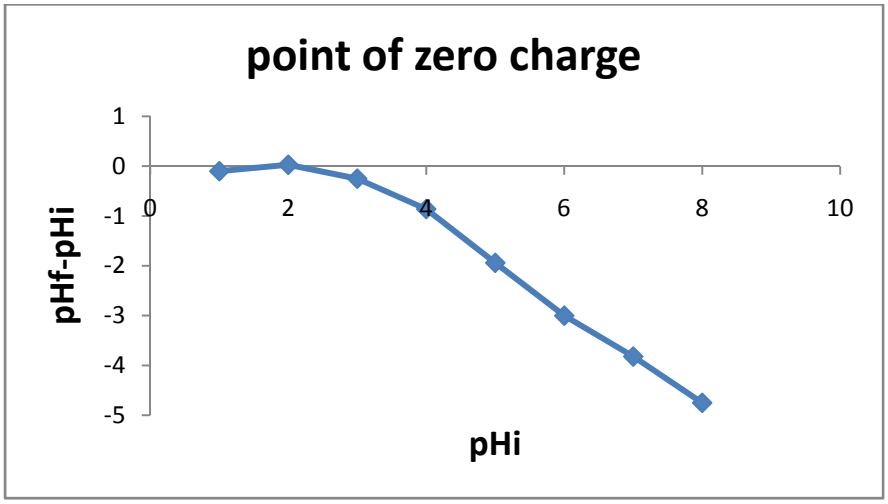


Figure 4.1 Point of zero charge graphs for sample clay soil

4.1.2 FTIR (Fourier Transform Infrared) Spectroscopy Analysis of clay soil

In the present study, FTIR spectra of clay soil before and after acid modification as well as after adsorption were recorded in the range of 4000cm^{-1} to 400cm^{-1}. (Appendix B) shows the recorded spectra of the three forms of clay soil samples.

All the three clay soil samples show a broad absorption band around at 3300 cm^{-1} along with the weak band at around 1700 cm^{-1} are due to absorbed water. The pair of peaks appeared at around 2915 and 2844 cm^{-1} in all samples due to the C-H stretching vibrations of some organic contribution .Carboxyl groups were the most important functional groups in natural organic matter. The organic substances have a high specific surface and good molding capacity, improving the plasticity of the clays [64]. The Si – O stretching and bending as well as the OH bending absorption in the range of 1290 – 400cm^{-1} tells us more about the kaolinite and

Montmorillonite minerals present in the clay soil samples. The peak around 1027cm^{-1} and 464cm^{-1} reprecents Dissociated silanol groups (-Si-O) in the tetrahedral sheets. The band around 3612cm^{-1} represents -OH groups, originating from the smectite and kaolinite minerals .band around 3410cm^{-1} and 1620cm^{-1} represents -H-O-H molecules of water adsorbed in the smectite minerals. The vibrational bands at 514cm^{-1} and 463cm^{-1} are strong bending vibrations corresponding to Al-O-Si and Si-O-Si respectively. The appearance of Doublet bands at around (820cm^{-1} and 793cm^{-1},720cm^{-1} and 692cm^{-1},649cm^{-1}) represents -Al_2-OH and Si – O Stretching an indication of smectite and quartz clay minerals respectively. All these mentioned peaks and bands were shown by all three clay soil in variable intensity.

During acid activation of clay soil the protons penetrate into the clay layers attacking the OH groups causing the alteration in the adsorption bands attributed to the OH vibrations and octahedral cations .the intensity of stretching bands observed at 3612cm^{-1} decreases with acid activation .the acid treatment resulted in the increasing peak sharpness associated with the the water adsorbed in the smectite minerals at 3410cm^{-1} (H-O-H). Calcite was dissolved (according to the reaction: $CaCO_3 + H_2SO_4^{\ 2+} \rightarrow Ca^{2+} + SO_4^{\ 2} + CO_2 + H_2O$), which was demonstrated by the complete disappearance of the intensity of a band at 1436cm^{-1}(C=O).the acid activation leads to the formation amorphous silica, which may be exposing more adsorption sites [65].

The FTIR spectrum of the activated clay soil after adsorption 40mg/L of reactive red dye showed either a reduction or shift in wave number and intensity of peaks. For instance wave number 3402cm^{-1} and 3579cm^{-1} were shifted to 3382cm^{-1} and 3575cm^{-1} which indicates the involvement of -H-O-H molecule .the participation of Montmorillonite mineral and silanol groups (-Si-O) were confirmed by the resulted shift in wave number from 1027cm^{-1} to 1013cm^{-1} and 464cm^{-1} to 462cm^{-1} respectively. The participation of smectite (-Al_2-OH) and quartz (Si -O) of clay minerals were also confirmed by the shift in doublet wave number 820cm^{-1} to 819cm-1 and 668cm^{-1} to 667cm^{-1} respectively.

4.4 Batch adsorption Studies

4.4.1 Effect of solution pH

Figure 4.2 showed the reactive red dye ions removal and adsorption capacity of acid treated clay soil variable solution pH values. From the Figure 4.2 it is evident that the solution pH affects the adsorption process. The increase in solution pH from pH 1 to 4 resulted in sharp decrease in both percentage removal and adsorption capacity. . The maximum adsorption of reactive red dye ions are obtained at pH1.0. Therefore pH1.0 was selected as optimum pH for reactive red dye ion adsorption onto acid activated clay soil.

[66] studied the effect of solution pH on the adsorption of Congo red by pine cone and they noticed that the adsorption was maximum at lower pH. this suggest lower pH solution results in an increase in the percentage of anionic dye removal because of the electrostatic attraction between anionic dye and the positive surface charge of the adsorbent .At higher solution pH, electrostatic repulsion is found between the negatively charged surface and dye molecules, this is due to the negative charge surface sites on the clay soil were not favorable to the adsorption anionic dye due to electrostatic repulsion. Moreover, there was a competition between the hydroxide ions and the dye anions. The repulsion between anionic dye molecules and the excessive hydroxide ions resulted in a sharp decrease in adsorption, thus decreasing the adsorption capacity and percentage removal of anionic dyes [67].

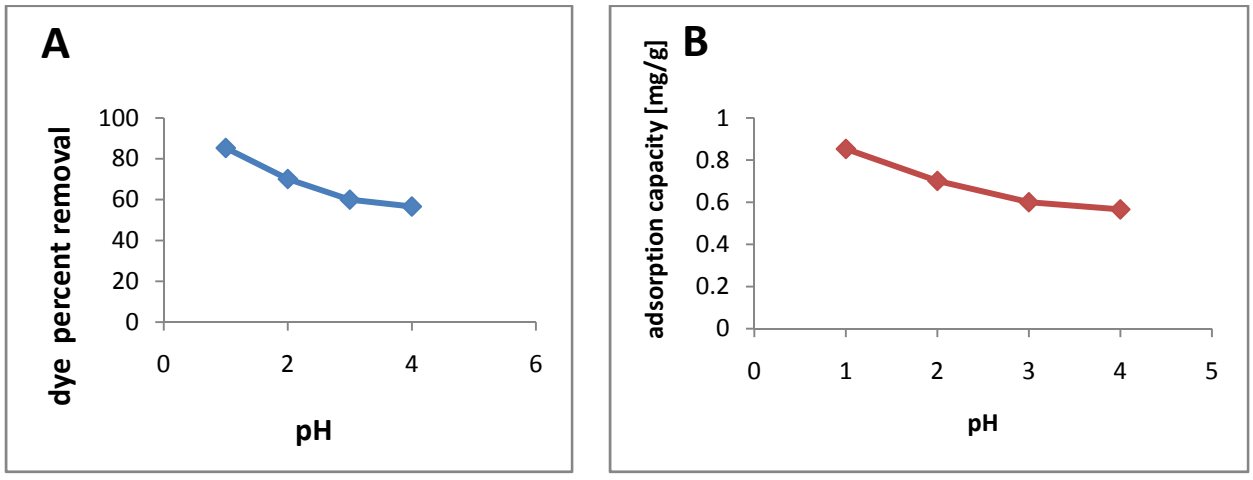


Figure 4.2 Effect of solution pH on adsorption of reactive red dye (A) adsorption efficiency (B) adsorption capacity

4.4.2 Effect of initial dye concentration

The relationship between initial dye concentrations, percentage removal and the adsorption capacity has been investigated. The adsorption of dye was carried out at different initial dye concentration ranging from 20-100 mg/L at pH 1. The effect of different initial dye concentration on adsorption of dye onto clay soil is presented in Figure 4.3. The result indicated the percentage of dye removal decreases with an increase in the initial dye concentration, which may be due to the saturation of adsorption sites on the adsorbent surface. This can be explained by the fact that all adsorbents have a limited number of active sites and at a certain concentration the active sites become saturated. [68] studied the adsorption of Methyl Orange by Chitosan/Alumina interface and they found that when the Methyl Orange concentration increased from 20 mg/L to 400 mg/L, the percentage of dye removal decreased from 99.53% to 83.55%.

On the other hand the increase in initial dye concentration will cause an increase in the capacity of the adsorbent and this may be due to the high driving force for mass transfer at a high initial dye concentration .The increase in the initial dye ions concentration also enhances the interaction between the dye ions in the aqueous phase and the adsorbent surface. This also resulted in higher uptake of dye for the given amount of adsorbent [67]. Thus, effect of initial dye concentration depends on the immediate relation between the concentration of the dye and the available sites on an adsorbent surface. The initial concentration provides an important driving force to overcome all mass transfer resistance of dye ions between the aqueous and solid phases.

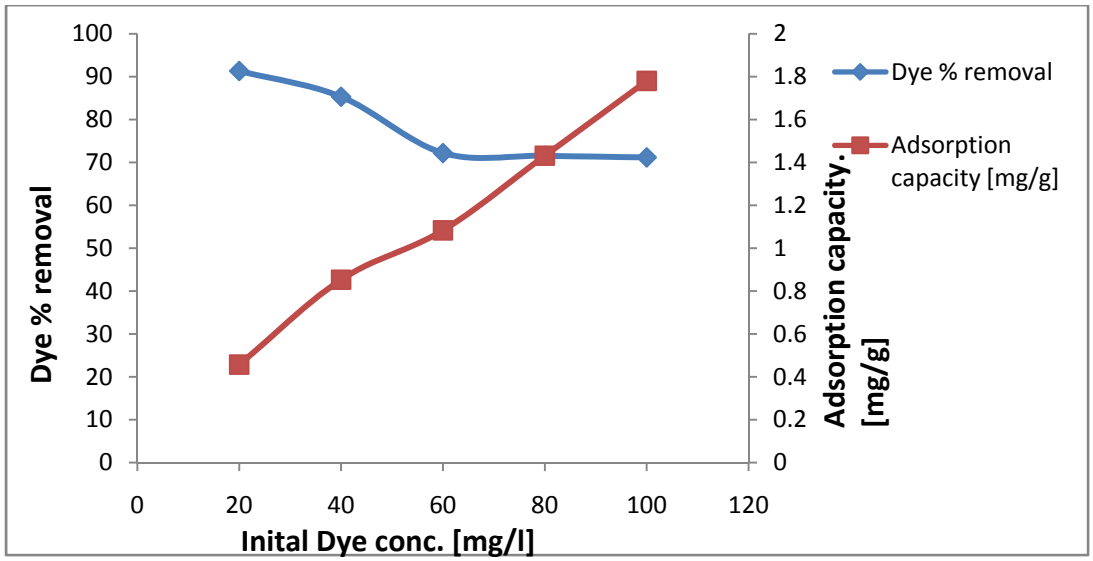


Figure 4.3 Effect of initial dye concentration on adsorption efficiency and capacity.

4.4.3 Effect of adsorbent dose

In this study, adsorbent dosages were selected ranging from 1to 8gm while the pH of the solution was fixed at 1. The results are presented in Figure 4.4. It was observed that percentage of dye ion removal increased with increase in adsorbent dose. Such a trend is mostly attributed to an increase in the sorptive surface area and the availability of more active binding sites on the surface of the adsorbent. [22] Studied the effect of adsorbent dosage gives an idea for the ability of a dye adsorption to be adsorbed with the higher amount of adsorbent.

However, the equilibrium adsorption capacity showed an opposite trend. As the adsorbent dosage was increased from 1to 8gm, the adsorption capacity reduced. Optimum dye adsorption capacity was recorded at 4gm of clay soil of 40mg/l dye concentration and further increase in adsorbent dose decreases the adsorption capacity. This may be due to the decrease in total adsorption surface area available to dye ion resulting from overlapping or aggregation of adsorption sites. Thus with increasing adsorbent mass, the amount of dye ion adsorbed onto unit mass of adsorbent gets reduced, causing a decrease in qe value with increasing adsorbent mass concentration.

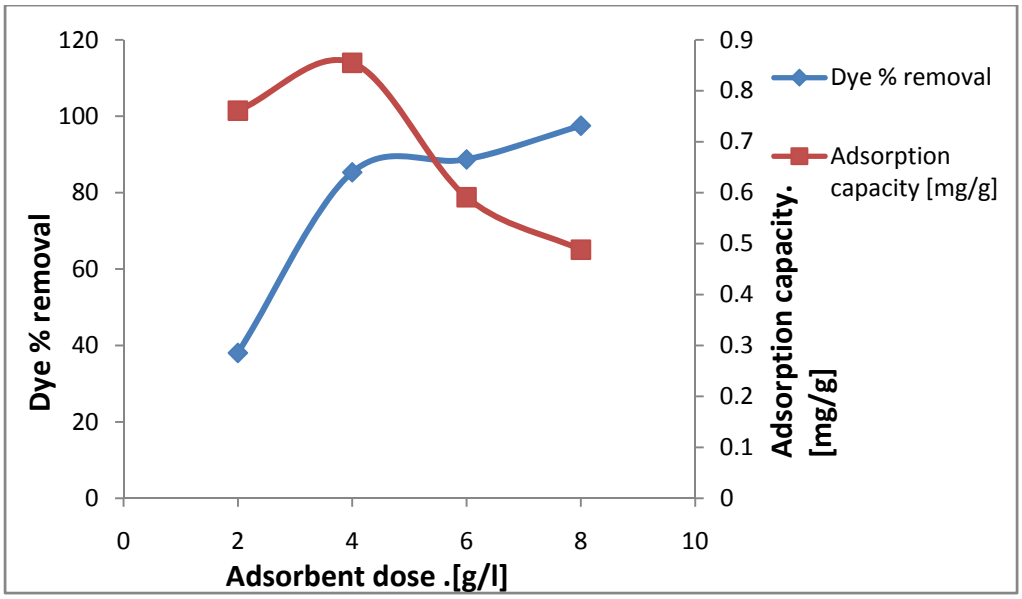


Figure 4.4 Effect of adsorbent dose on adsorption efficiency and capacity.

4.4.4 Effect of contact time

In general the adsorption capacity and the removal efficiency of dye will increase with increase in contact time. However, in practice it is necessary to optimize the contact time, considering the adsorption process. Figure 4.5 shows the percentage removal of dye ions and the adsorption capacity of clay soil as a function of contact time**.** Adsorption of dye ion increased with rise in contact time up to 105min. Further increase in contact time did not increase both percentage removal and adsorption capacity. The equilibrium was nearly reached after 120 min. Hence, 120 min was chosen as the equilibrium time. [43] Also stated the most of adsorption was found to take place within the first 2hrs of mixing. This is due to the fast adsorption rate before equilibrium may be explained by an increased availability in the number of active binding sites on the adsorbent surface. The adsorption rapidly occurs and normally controlled by the diffusion process from the bulk to the surface. At equilibrium stage the adsorption is likely an attachment-controlled process due to less available sorption sites [69].

It should be noted that there are several parameters which affect the equilibrium adsorption time. Some of these parameters are the stirring rate, the physicochemical properties of the adsorbent, adsorbent dose, initial metal concentration, presence of the competitive ions and the properties of the dye under study.

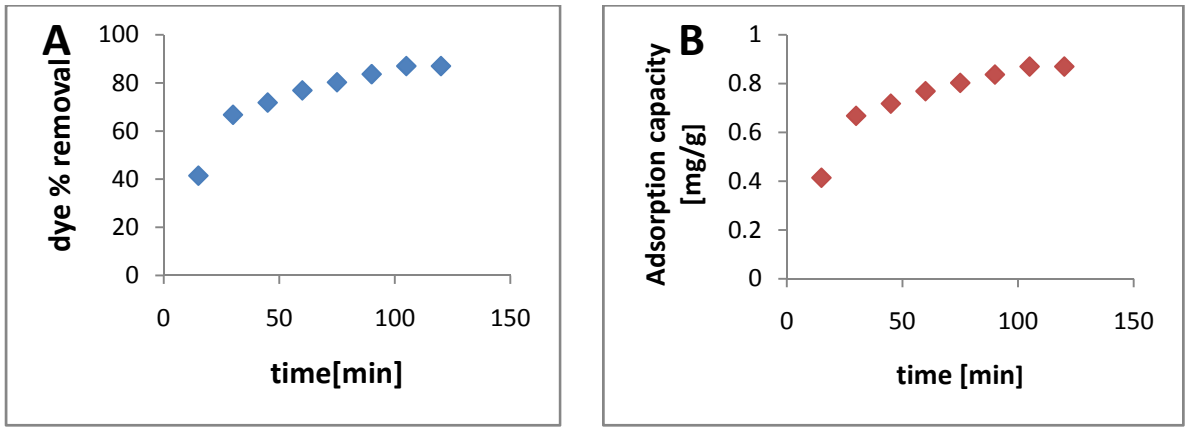


Figure 4.5 Effect of contact time on adsorption of reactive red dye (A) adsorption efficiency (B) adsorption capacity

4.5 Dye Adsorption Kinetics Models

4.5.1 Pseudo first order kinetics model

Figure 4.6 showed the plot of log ($q_e - q_t$) vs. t gives a linear relationship from which k1 and qe be determined from the slope and intercept of the plot, respectively. The pseudo first order graphs showed that the values of Log (qeq -qt) versus time decreased with time giving the dye ions more opportunity to be taken up by the adsorbent .

The regression correlation coefficients for the pseudo first order model is found to be 0.976.The values of regression correlation coefficient and the value of the adsorption capacity (q_{eq}) obtained from the graphs seemed to be good showing the applicability of the pseudo first order model for removal of dye ions using clay soil. The value of adsorption capacity (q_{eq}) calculated from the pseudo first order kinetic model is also in a good agreement with the true adsorption capacity(q_{ep}) .The values of the pseudo first order rate constant K_1 (min -1), calculated q_{eq} (mg/g) and the regression correlation coefficient calculated from the slope and intercept of the corresponding plot is clumped in table 4.2.

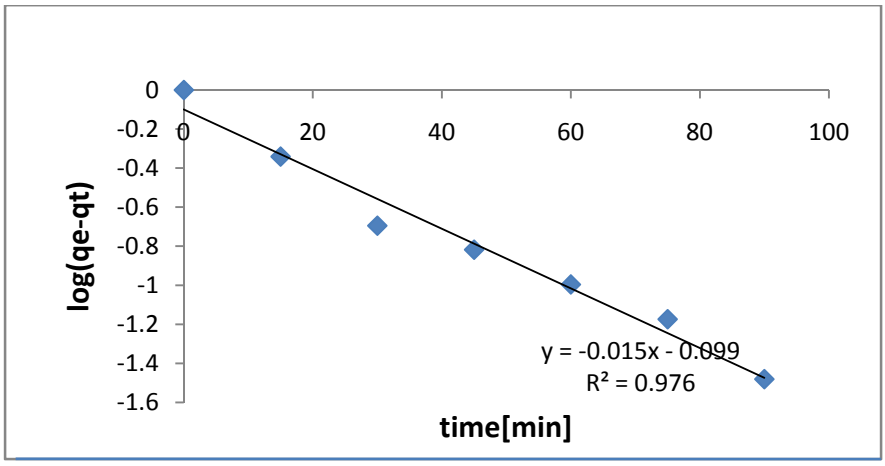


Figure 4.6 pseudo first order model plot

4.5.2 Pseudo second order kinetics model

The pseudo second order rate constant (K_2) and the equilibrium adsorption capacity (q_{eq}) were calculate from the slope and intercept of the linear plot of *t/q* versus *t* for the clay soil adsorbent. Figure 4.7 showed the linear plot of pseudo second order kinetic model. The calculated constant values of K_2, q_{eq}, and R_2 for pseudo second order kinetic model are summarized in table 4.2.

From table 4.2 it is evident that, there is a very good agreement between the experimental q_{eq} and the calculated q_{eq} values as compared to the pseudo first order kinetic model. Data obtained from the adsorption of kinetics, when modeled with pseudo second order equation showed excellent fitting having regression correlation coefficient value of 0.994. The experimental results obtained suggested that the reactive red dye adsorption by clay soil followed a pseudo second order kinetics.

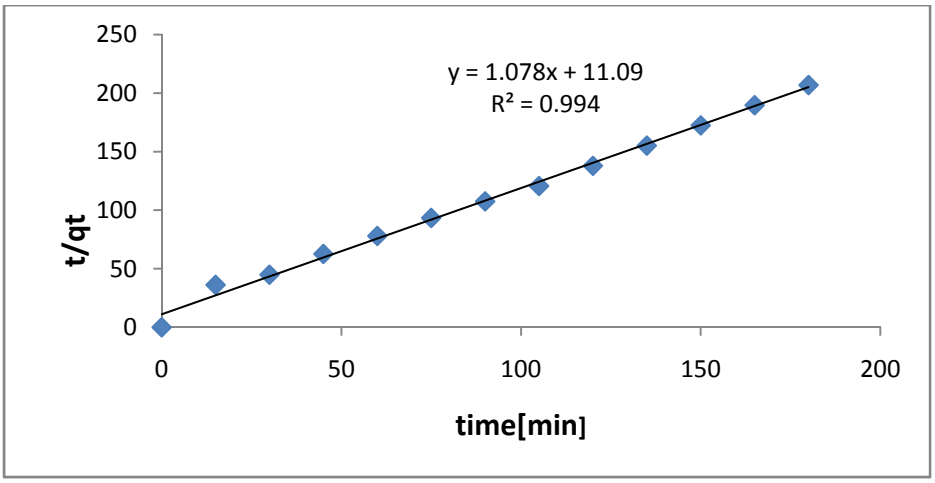


Figure 4.7 pseudo second order model plot

4.5.3 Intra-particle diffusion model

A plot of q_t versus $t^{0.5}$ should be a linear line which pass through origin with a slope of K_{id} and intercept C when the adsorption mechanism follows the intra-particle diffusion model [70]. The plot of q_t versus $t^{0.5}$ for the corresponding adsorbent is given in figure 4.8. The calculated values of K_{id} with the regression correlation coefficient are summarized in table 4.2.

From the figure 4.8 it is clear that the graphs linear within certain range, but the trend of the data did not pass through the origin. The calculated values of K_{id} and C were 0.058 mg/g.min and 0.284. The value of the intercept gives idea about the thickness of boundary layer i.e. the larger the intercept the larger the boundary layer effect [71]. The deviation of the straight line from the origin may be due to the difference in the rate of mass transfer in the initial and final stage of the adsorption Process. Furthermore such deviation of the straight line from the origin indicates that pore diffusion is not the sole rate controlling step [72].

Over all analysis of the pseudo first order, pseudo second order and the intra-particle diffusion model data revealed that, the kinetics of reactive red by using acid activated clay soil best described by assumption of the pseudo second order kinetics model. This tendency comes as an indication that the rate-limiting step in adsorption of reactive red dye onto clay soil is a chemical sorption (chemisorptions) involving valence forces through the sharing or exchange of electrons between adsorbent and adsorbate. The high values of the regression correlations coefficient of

the graphs and the high proximity of calculated and experimental equilibrium adsorption capacity (q_{eq}, mg/g) supports the present study

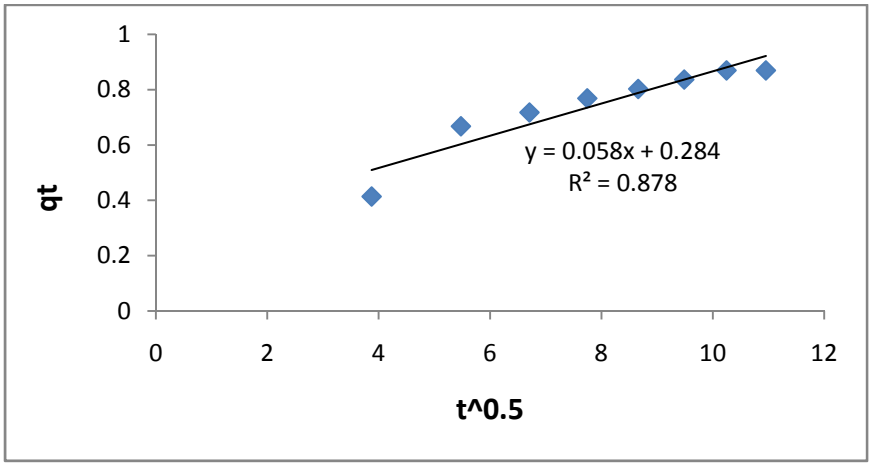


Figure 4.8 Intra-particle diffusion model plot

Table 4.2 Adsorption Kinetics constants

	pseudo first order kinetic model			pseudo second order kinetic model			Intra-particle diffusion	
q_{EXP} mg/g	q_{cal} mg/g	K_1 min^{-1}	R^2	q_{cal} mg/g	K_2 g/mg.min	R^2	K_{id} mg/g.min	R^2
0.87	0.796	0.0345	0.976	0.93	0.104	0.994	0.058	0.878

4.6 Dye adsorption Equilibrium Isotherm Models

The adsorption isotherm is significant for the explanation of how the adsorbent will interact with the adsorbate and give an idea of adsorption capacity. They play an important role in understanding the mechanism of adsorption. The surface phase may be considered as a monolayer or multilayer. Several isotherm models are presented in the literature [73].

The adsorption data collected in this study were fitted in to three well known adsorption isotherm models, namely Langmuir, Freudlich and Dubnin- Radushkevich isotherm models.

4.6.1 Langmuir isotherm model

The Langmuir model is based on the assumption [74] that adsorption takes place at specific homogenous sites within the adsorbent and once a dye molecule occupies a site, no further adsorption takes place at that site indicating that only one dye molecule could be adsorbed on one adsorption site.

To determine the Langmuir constants, experiments were conducted by varying the initial dye concentration from 20-100 mg/L at temperature of 20 °C, pH 1 and agitation speed of 150 rpm. The results obtained were plotted as 1/qe vs 1/Ce and the values of Langmuir's constants qmax (mg/g) and b (L/mg) were determined from the plots presented from figure 4.9. The Langmuir constant calculated are presented in table 4.3 with respective regression correlation coefficient (R^2= 0.985) showing that Langmuir equation represents the best fit of experimental data than the other isotherm equation.

The fact that Langmuir isotherm fits the experimental data very well confirms the monolayer coverage of dye onto activated clay soil and also the homogeneous distribution of active sites on the adsorbent, since the Langmuir equation assumes that the surface is homogeneous.

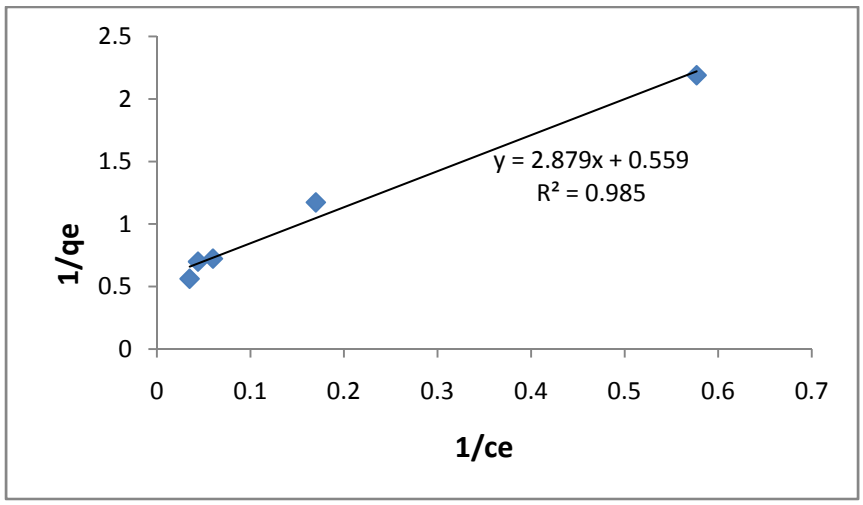


Figure 4.9 Langumir isotherm model plot

4.6.2 Fruendlich isotherm model

The empirical Freundlich equation which is based assumption adsorption on a heterogeneous surface was used to determine the Freundlich constants (1/n and K_f) which are given in table 4.3. K_f(L/mg) and n are Freundlich's constants , indicates the degree of linearity between the solution concentration and the adsorbent . Figure 4.10 shows the plots of Log q_e versus Log C_e. the Fruendlich isotherm constants (K_f and n) were also determined from the Figure.

From the Freundlich's plots the calculated values of K_f= 0.362 and n where 2.26. An adsorbent with n value between 1 and 10 is considered as a favorable adsorption and a good adsorbent. [75] From the calculated results, it can be seen that the value of n is 2.26 indicating a favorable adsorption process. But the value of correlation coefficient (R^2 = 0.965) is lower than the Langmuir isotherm value.

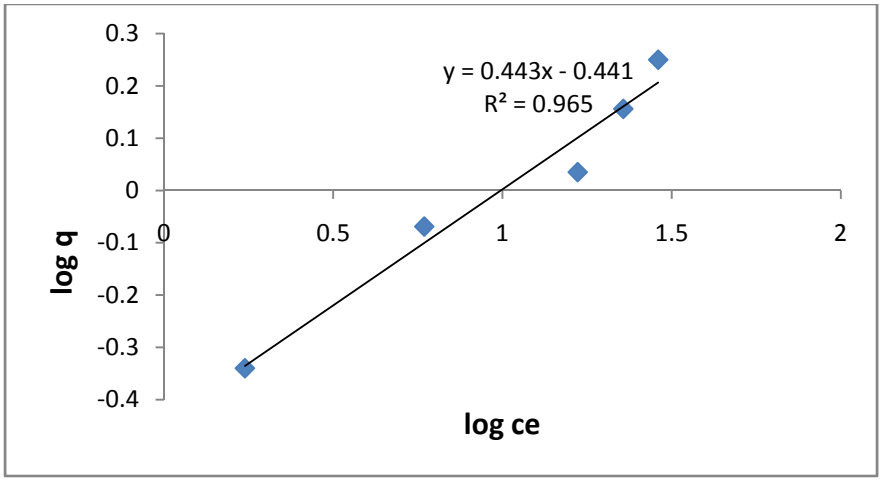


Figure 4.10 Fruendlich isotherm model plot

4.6.3 Dubnin- Radushkevich (D-R) isotherm model

The adsorption equilibrium data were further subjected to D-R isotherm model to identify the adsorption mechanism. The linear plots of ln qe versus ε^2 were used to determine D-R isotherm Constants K_{DR} (mole2/KJ2) and adsorption free energy E (KJ/mole). The results are reported in Figure 4.11 and Table 4.3**.**

From the D-R plots, it is clear that the regression correlation coefficient obtained for the D-R Isotherm model was lower than that of the Langmuir isotherm model and Fruendlich isotherm. However, the calculated adsorption free energy was found to be 12.9KJ/mol which indicated the adsorption process proceeds via chemisorptions, here a covalent bond is formed between the adsorbate and adsorbent. It is also called specific adsorption and limited to monolayer coverage of the substrate [76] which is also confirmed by the Langmuir isotherm model and pseudo second order kinetic model in section 4.6.1 and section 4.5.2 respectively.

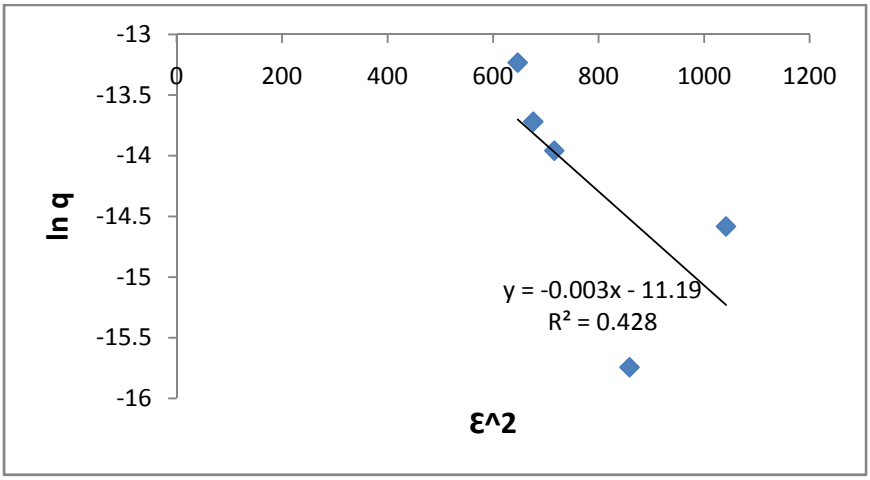


Figure 4.11 Dubnin-Raduskevich model plot.

Table 4.3 Adsorption isotherm constants

Langmuir			Freundlic			Dubnin-Radushkevich		
q_{max}	b	R^2	K_F	n	R^2	K_{DR}	E	R^2
1.789	0.194	0.985	0.362	2.26	0.965	0.003	12.9	0.428

4.7 Statistical Analysis of adsorption Process

Central composite design (CCD) approach was adopted for investigating the individual and interactive effects of the selected process variables on the adsorption of reactive red dye from aqueous solution. The measured dye removal (%) were entered as a response in the design lay out given in table C-1(appendix C. the major statistical analysis of the adsorption process (model generation, model fitness test, and ANOVA analysis) are presented and discussed.

A quadratic model was selected for developing the mathematical relationship between the response and the process variables pH, initial dye concentration (mg/l), dose (g/L) and contact time (s).

The CCD based experiment to obtain a quadratic model, here consisted of 2^4 standard factorial runs, a star configuration ($\alpha = \pm 2$) of size, 2n, and six replicates at the center point (n_c) used to determine experimental error. A Polynomial regression modeling was performed between the response variable and the corresponding coded values (A, B, C, D) of the four different process variables, and finally, the best fitted model equation was obtained as,

$$\text{Dye \% removal} = +71 - 1 - 16.30*A - 7.88*B + 10.20*C + 3.77*D + 0.051*A*B - 0.48*A*C - 0.59*C*D - 1.51*A^2 - 2.73*B^2 - 0.49C^2 - 4.15*D^2 \quad (4.1)$$

In terms of actual factors empirical relation between dye % removal and variables has been expressed by following second order polynomial equation

$$\text{Dye \% removal} = +71 - 1 - 16.30*pH - 7.88*conc + 10.20*dose + 3.77*time + 0.051*pH*conc - 0.48*pH*dose - 0.59*dose*time - 1.51*pH^2 - 2.73*conc^2 - 0.49dose^2 - 4.15*time^2 \quad (4.2)$$

Model Eq. (4.2) was used to evaluate the influence of the process variables on the removal of dye in aqueous medium by clay soil. The quality of the model developed was evaluated based on the value of coefficient of determination (R^2). The R^2 value for the model was calculated to be 0.9984 which was relatively high (close to unity). This implied that more than 99.84% of the experimental data were compatible with the data predicated by the model (table C-2, Appendix C) and only 0.167% of the total variability in the response was not explained by the model. The high R^2 value indicated that the model obtained was able to give a convincingly good estimate of response in the studied range.

The actual and predicted dye percent removals are shown in Fig.4.12. Actual values are the measured response data for a particular run, and the predicted values are evaluated from the model that are generated by using the approximately functions. In Fig.4.12, the values of pred. R^2 and Adj. R^2 were found to be 0.9908 and 0.9969, respectively. From this figure, it is noted that the values calculated using the predictive quadratic model was in good agreement with the experimental values with satisfactory correlation between these values. Thus, the model developed is suitable for predicting the removal efficiency of dye in the conditions investigated.

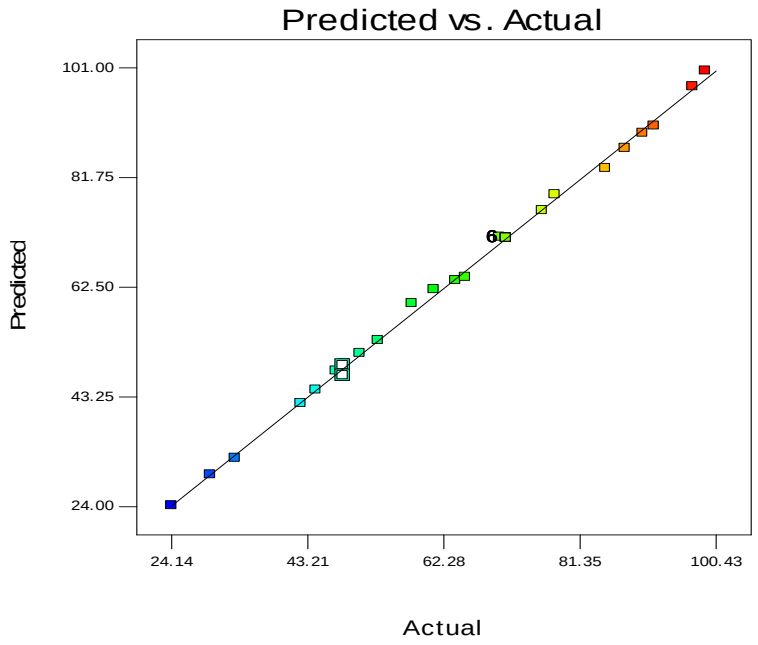


Figure 4.12 Actual and predicated values of removal reactive dye (R^2=0.9984)

ANOVA is statistical tool that subdivides the total variation in set of data into components parts associated with specific sources of variation for the purpose of testing hypotheses on parameters of the model. F-values represent most variation in response can be explained by empirical model however F-value must be larger for better empirical model. If F values are lager enough then P value signifies effect of parameters on response. The model F-value of 670.43 implies the model is significant for reactive red dye removal and there is only a 0.01% chance that a model F-value of this large could occur due to noise.

ANOVA table 4.4 shows the analysis of variance of regression parameters of predicated response surface quadratic model for reactive red dye removal by activated clay soil using the

result of all experiment performed. The adequate precision ratio 97.922 indicates an adequate signal where it measures the signal to noise ratio; a ratio greater than four is desirable .As shown in ANOVA table values of "prob>F" less than 0.05 indicates model terms are significant. In this case model terms pH(A) ,initial dye concentration (B), adsorbent dose(C), time (D) , interaction between pH and time (AD), interaction between initial dye concentration and adsorbent dose(BC), interaction between adsorbent dose and time (CD), interaction between effect of square of solution pH(A^2), interaction effect of square of initial dye concentration (B^2), interaction effect of square of adsorbent dose (C^2) and interaction effect of square of adsorption time (D^2) were significant model terms. Values greater than 0.1 indicates the model terms are not significant.

Additionally, from the ANOVA analysis the lower value of coefficient of variation (C.V%=1.72) indicates the better precession and reliability of the experiments carried out. The C.V. as a ratio of the standard error of estimate to the mean value of the observed response as (% dye removal) is the measure of reproducibility of the model and as general rule a model can be considered reasonably reproducible, if the model C.V. value is not greater than 10% [77].

4.7.1 Effect interaction of adsorption parameters on percentage removal of dye

The results obtained from 30 experimental runs conducted to observe the effect of the four adsorption factors (solution pH, initial dye concentration, adsorbent dose and time) using activated clay soil which are presented in table C-1 (Appendix C). In this section the interaction effects of the four factors on the (% removal) of dye are discussed in detail. The analyses are supported by the 3D and contour plots of the interaction effects of the four factors on the percentage removal of dye

Table 4.4 Analysis of ANOVA for quadratic second order model

Source	Sum of squares	df	Mean square	F values	p-value Prob > F	
Model	11395.30315	14	813.9502252	670.4261417	< 0.0001	significant
A-pH	6377.864067	1	6377.864067	5253.253413	< 0.0001	
B-conc	1488.690017	1	1488.690017	1226.188867	< 0.0001	
C-dose	2494.5126	1	2494.5126	2054.654457	< 0.0001	
D-time	341.8640167	1	341.8640167	281.5830337	< 0.0001	
AB	0.042025	1	0.042025	0.034614719	0.8549	
AC	3.705625	1	3.705625	3.05221105	0.1011	
AD	25.7049	1	25.7049	21.17234739	0.0003	
BC	37.027225	1	37.027225	30.49820348	< 0.0001	
BD	2.3716	1	2.3716	1.953415072	0.1825	
CD	5.5225	1	5.5225	4.548715945	0.0499	
A^2	62.60893333	1	62.60893333	51.56908164	< 0.0001	
B^2	204.3600048	1	204.3600048	168.3251448	< 0.0001	
C^2	6.675504762	1	6.675504762	5.498411037	0.0332	
D^2	472.5783048	1	472.5783048	389.2484328	< 0.0001	
Residual	18.21118333	15	1.214078889			
Lack of Fit	18.21118333	10	1.821118333			
Pure Error	0	5	0			
Cor Total	11413.51434	29				

Std. Dev. 1.10; **R^2** 0.9984; **Adj.R^2** 0.9969; **Pred.R^2** 0.9908; **C.V. %** - 1.72; **Adeq. Prec**. 97.922

4.7.1.1 The interaction effect of solution pH and initial dye concentration

The plot for combined effect of the solution pH and dye concentration (Fig. 4.13) suggests that increasing dye concentration results in a decreasing removal of the dye, whereas, it increases with decreasing the pH value. Ascending trend in dye uptake with decreasing pH may be attributed to the positive charges on the dye molecules in the acidic medium, from figure it can be seen that at low pH value (pH<2) more than 83% of initial dye percent in the solution was

removed While the increase in the solution pH (pH > 2) with increase in the initial dye concentration resulted in significance reduction in the percentage removal. The presence of these positively charged functional groups will also increase the percentage removal due to the attraction of the negatively charged dye ions by the positively charged surface functional groups and the trend reverses when the dye adsorption decreases with increasing concentration. This behavior can be understood as the increasing adsorbate concentration with fixed adsorbent dose would result in saturation of the binding sites on the surface and subsequently declining of the adsorbate uptake with increasing concentration.

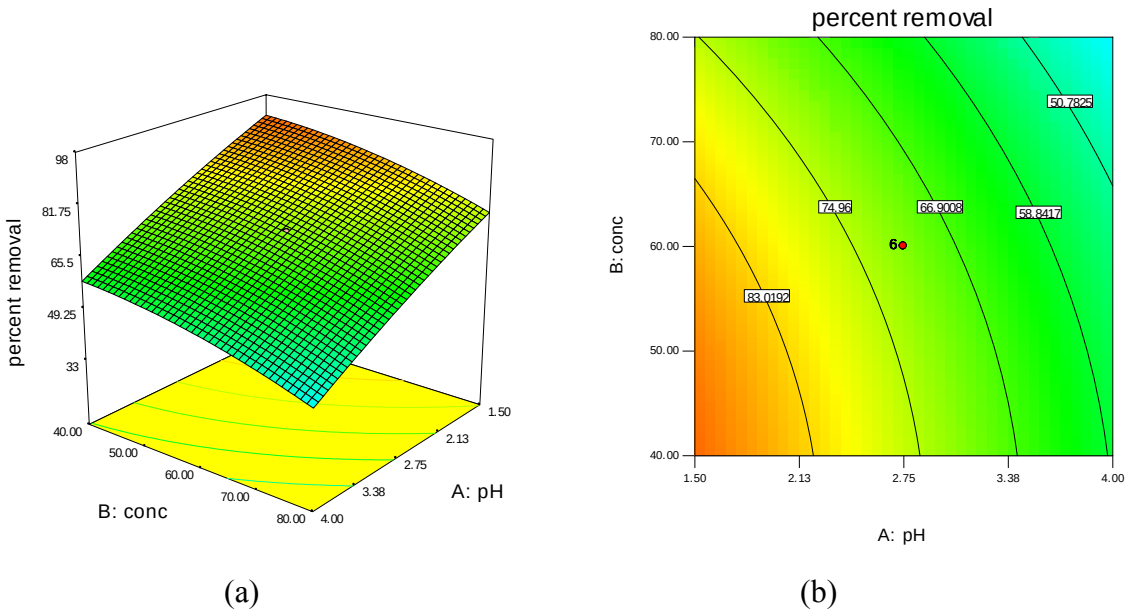
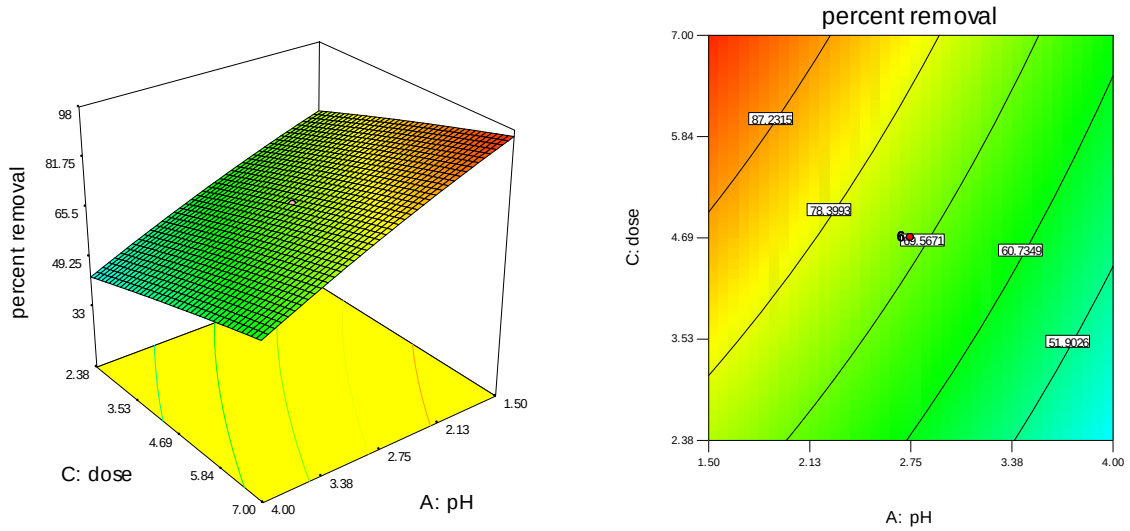


Figure 4.13 The interaction effect of solution pH and initial dye concentration on adsorption of reactive red dye (a) 3D plot, (b) contour plot.

4.7.1.2 The interaction effect of solution pH and adsorbent dose

The effect of pH and adsorbent dose on dye removal is shown in 3D and counter plot in Fig. 4.14 Percent removal increased with increasing adsorbent dose and decreasing pH. At lower pH (pH<2) more than 87% of dye was removed , this result showed the significance of solution pH on the adsorption process of dye ions .the maximum percentage removal was predicated at

solution pH<1.5) .such behavior justified by the presence of large quantity of positively charged surface functional groups at lower solution pH and large amount of adsorbent dose .

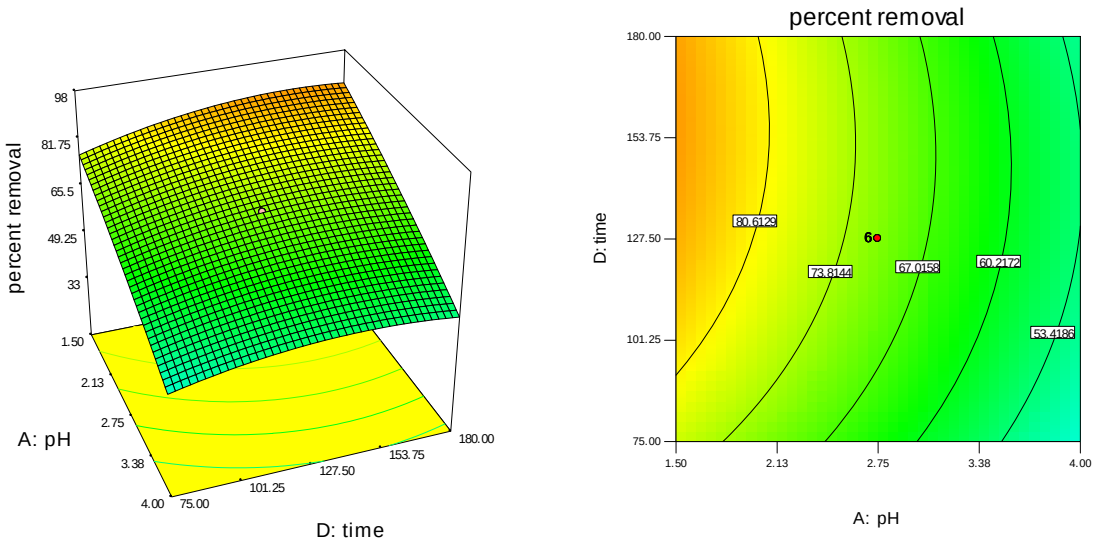


(a) (b)

Figure 4.14 The interaction effect of solution pH and adsorbent dose on adsorption of reactive red dye (a) 3D plot, (b) contour plot.

4.7.1.3 The interaction effect of solution pH and contact time

The counter and 3D surface plot for combined effect of pH and contact time (Fig. 4.15) shows at lower pH, the dye removal increases with increasing contact time. as the time of adsorption increases, dye % removal increase . This result indicates that both adsorption factors have significant effect on the % removal of dye. The ANOVA analysis also showed the interactions effect of solution pH and contact time have "Prob.>F" value of 0.0003, which indicates the significance of the factors on the % removal of dye.

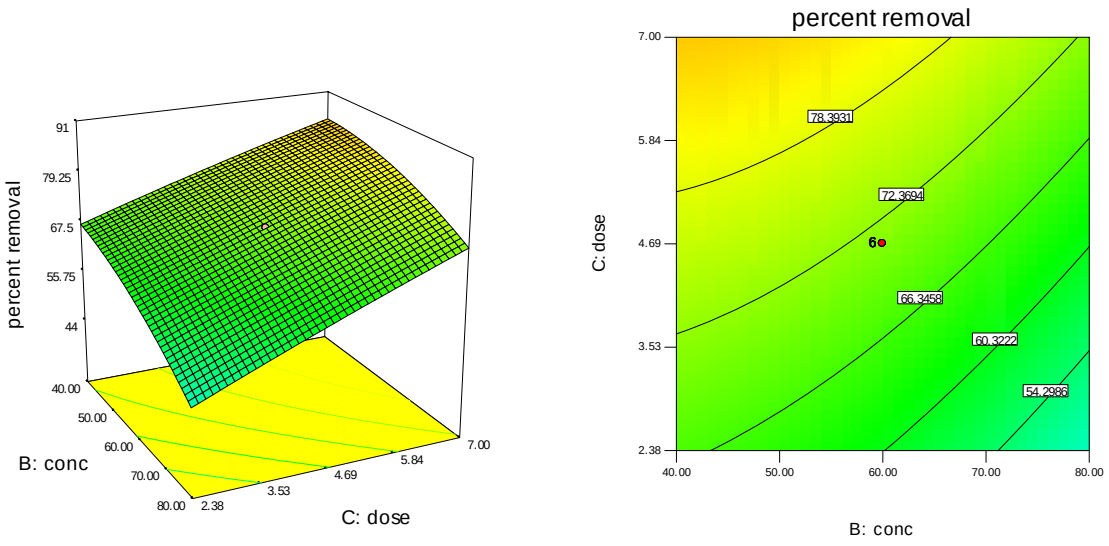


(a) (b)

Figure 4.15 The interaction effect of solution pH and contact time on adsorption of reactive red dye (a) 3D plot, (b) contour plot.

4.7.1.4 The interaction effect of adsorbent dose and initial dye concentration

The combined effect of adsorbent dose and initial dye concentration on removal dye in counter and 3D surface plot is shown in Fig 4.16. It may be noted that the dye removal increased with increasing adsorbent dose and decreasing dye concentration. This is due to increase in initial dye concentration, adsorption sites, surface area of the adsorbent are saturated, resulting in decrease in the adsorption efficiency. The ANOVA analysis also showed the interactions effect of adsorbent dose and initial dye concentration have "Prob.>F" value of 0.0001, which indicates the significance of the factors on the % removal of dye.

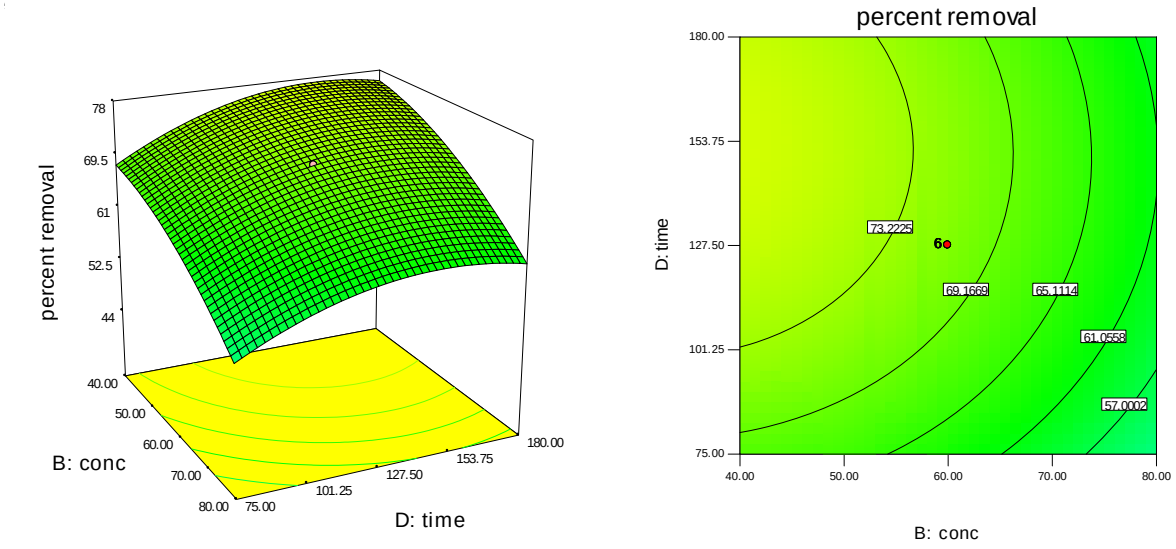


(a) (b)

Figure 4.16 The interaction effect of adsorbent dose and initial dye concentration on adsorption of reactive red dye (a) 3D plot, (b) contour plot.

4.7.1.5 The interaction effect of initial dye concentration and contact time

The interactive effect of initial dye concentration and contact time on dye removal is shown in counter and 3D surface plot in Fig 4.17. However beyond time 120min increasing the adsorption time has no considerable improvement in % dye removal. This is due at equilibrium stage the adsorption achieves its saturation, possibility no further adsorption occur and the contact time has no longer effect on % removal of dye. The ANOVA analysis showed the interaction of initial dye concentration and contact time has no significant effect on the % removal of dye since calculated value of "Prob. > F" was 0.1825, which is greater than 0.05.

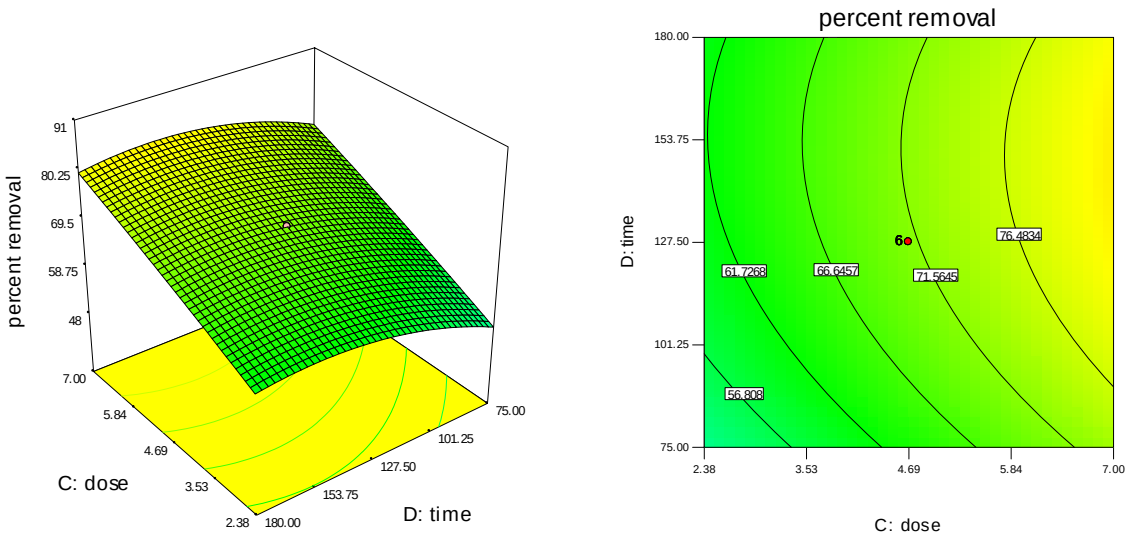


(a) (b)

Figure 4.17 The interaction effect of contact time and initial dye concentration on adsorption of reactive red dye (a) 3D plot, (b) contour plot.

4.7.1.6 The interaction effect of adsorbent dose and contact time

Fig 4.18 shows the interactive influence of adsorbent dose and contact time on the dye removal from aqueous phase. It is evident that the dye removal increased with the increase in both the adsorbent dose and contact time. The observed trend may be understood the increase in adsorbent dose would make higher number of adsorption sites available. The ANOVA analysis also showed the interactions effect of adsorbent dose and contact time has significance on the % dye removal.



(a) (b)

Figure 4.18 The interaction effect of contact time and adsorbent dose on adsorption of reactive red dye (a) 3D plot, (b) contour plot.

4.7.2 Optimization of dye removal

The main objective of optimization is to have the optimum values of process variables for reactive red dye removal using clay soil. The optimum conditions for four factors i.e. solution pH, adsorbent dose, initial dye concentration and time were determined using design expert software. The software searches for a combination of factors that satisfied the requirements placed on the response and on each of the factor. Table 4.5 shows the optimum working condition (ultimate goals, high and low limits) of the response and the factors. In the optimization the desired goal for response (% dye removal) was chosen to be maximized.

The goals are combined into an overall desirability function .desirability is an objective function that ranges from zero outside of the limits, to one at the goal. The program seeks to maximize this function.

Table 4.6 presents the optimum conditions in uncoded units (solution pH, adsorbent dose, initial dye concentration and contact time) which give the highest composite desirability (0.919) from the Design expert software. The predicted (87.439 %) and experimental (87.01 %) values of %

dye removal of under the optimum conditions are also presented. The very small deviation, i.e., 0.43%, between the predicted and experimental values of % removal of dye indicates that the experimental value was in a good argument with the value predicated from the quadratic model. This result confirmed that response surface methodology (RSM) was an effective and reliable method for optimization the removal of reactive red dye.

Table 4.5 working conditions of response and factors for optimization

variables	ultimate goal	Experimental region	
		Lower limit	upper limit
pH	In the range	1.5	4
Adsorbent dose [g/100ml]	In the range	4	8
initial dye concentration [mg/l]	In the range	40	80
time [min]	In the range	15	120
% dye removal	Maximize	24.2	98.99

Table 4.6 Optimum conditions and model validation

variables	Optimum result
pH	1.5
Adsorbent dose [g/100ml]	4
initial dye concentration [mg/l]	40
time [min]	120
% removal of dye	87.439
Desirablity	0.919
Experimental % removal of dye	87.01
% deviation	0.43

5. Conclusion and Recommendation

5.1 Conclusion

- The mechanism and kinetics of adsorption of dyes on clay soil depends on the physic-chemical nature of the soil and experimental conditions such as solution pH, adsorbent dosage, initial dye concentration and contact time. Therefore, these factors should be taken into account while evaluating the adsorption capacity of clay soil.
- The parameters obtained from different models provide important information on the adsorption mechanism and the surface properties of the adsorbent.
- The present study has showed that adsorption isotherm data fitted well to the Langmuir isotherm model and the kinetic data results obtained follows the pseudo-second order model.
- The results from the Dubnin- Radushkevich isotherm model indicated that the adsorption process proceed through a chemisorptions.
- The results from the statistical analysis of the adsorption process using the response surface methodology revealed that the adsorption process can be represented by a quadratic regression model based on the determination coefficient of R^2 =0.9984 and adequate precision ratio of 97.922
- The ANOVA analysis showed that the removal of reactive red dye is highly affected by the solution pH, adsorbent dose, the initial dye concentration, contact time and the interaction between the solution pH with contact time, the interaction between initial dye concentration with adsorbent dose and adsorbent dose with contact time.

The overall results obtained showed that Clay soil is a cheap and easily available material in large quantity which can be used as an adsorbent for the removal of reactive red dye form aqueous solution. Being naturally occurring material, the use of clay soil as an adsorbent would also solve its disposal problem. And the adsorption experiment can be effectively modeled by using the response surface methodology.

5.2 Recommendations

- In this research, only clay soil is considered for the adsorption process but additional potential locally available clay mineral adsorbents should be identified and assessed with geologist and other related specialist.
- More research is necessary to predict the performance of adsorption process for dye removal from actual effluent under wide range of operation conditions.
- Investigate the adsorption capacity of the adsorbent from mixed dye effluent.
- Investigate the application of the adsorbent to remove other organic and inorganic pollutants from aqueous and actual wastewater.
- Analysis on BOD and COD of the effluent after adsorption treatment.
- Conduct feasibility of clay soil and other low cost adsorbents at an industrial scale.

References

1. Banat, I.M., Nigam, P., Singh, D., Marchant, R. (1996). Microbial decolorization of textile-dye containing effluents: a review. Bioresour. Technol. 58, 217–227.

2. Robinson, T., McMullan, G., Marchant, R., Nigam, P. (2001). Remediation of dyes in textile effluent:a critical review on current treatment technologies with a proposed alternative. Bioresour. Technol. 77, 247–255.

3. Neill, C., Hawkes, F.R., Hawkes, D.L., Lourenco, N.D., Pinheiro, H.M., Dele´e, W. (1999). Colour in textile effluents sources, measurement, discharge consents and simulation: a review. J. Chem. Technol. Biotechnol. 74, 1009–1018.

4. Suteu, D.; Zaharia, C.; Muresan, A.; Muresan, R. & Popescu, A. (2009b). Using of industrial waste materials for textile wastewater treatment. Vol.8, No.5, pp.1097-1102.

5. Hao, O.J.; Kim, H. & Chang, P.C. (2000). Decolorization of wastewater. Critical Reviews in Environmental Science and Technology, Vol.30, pp. 449-505.

6. M. Malakootian, A. Almasi, 1H. Hossaini. (2008). Pb and Co removal from paint industries effluent using wood ash

7. Bouberka, Z., S. Kacha, M. Kameche, S. Elmaleh and Z. Derriche.(2005). Sorption study of an acid dye from aqueous solution using modified clays. J. Hazard. Mater. B, 119: 117-124 .

8. Preeti Sagar Nayak and B K Singh. (2007). Instrumental characterization of clay by XRD, XRF and FTIR, 235-238.

9. Rytwo, G., Tropp, D. and Serban, C. (2002). Adsorption of diquat, paraquat and methyl green on sepiolite: experimental results and model calculations. 20,273– 282.

10. Bhattacharyya, K. G.; Gupta, S. S. (2008).Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: A review. Advances in Colloid and Interface Science, 140, 114–131

11. Rivlin, J.(1992).The dyeing of textile fibers: Theory and practice.

12. Robinson, T., Chandran, B., Naidu, G. S., Nigam, P. (2002a). Studies on the Removal of Dyes from a Synthetic Textile Effluent Using Barley Husk in Static- Batch Mode and in a Continuous Flow, Packed-Bed, Reactor, Bioresource Technology, **85**, 43-49

13. R.M.Christie.(2007). Environmental aspects of textile dyeing,Woodhead, Boca Raton, Cambridge.

14. R.S. Juang, R.K.L. Tseng, F.C.Wu, S.H. Lee. (1997).Adsorption behavior of reactive dyes from aqueous solution on chitosan, J. Chem. Technol. Biotechnol. 391–399.

15. Robinson, T., Chandran, B., Naidu, G. S., Nigam, P. (2002a), Studies on the Removal of Dyes from a Synthetic Textile Effluent Using Barley Husk in Static- Batch Mode and in a Continuous Flow, Packed-Bed, Reactor, Bioresource Technology, **85**, 43-49

16. R.M.Christie.(2007). Environmental aspects of textile dyeing,Woodhead, Boca Raton, Cambridge.

17. Zouboulis, A.I., Rousou, E.G., Matis, K.A., Hancock, I.C.(1999). Removal of toxic dye from aqueous mixtures. Part 1: biosorption. J. Chem. Technol. Biotechnol. 74, 429– 436.

18. Pang YL,Abdullah AZ(2013) Current Status of Textile Industry wastewater Management and Research Progress in Malaysia:A review .Clean(Weing) 41:751-764.

19. UNIDO.(2000)the scope for decreasing pollution load in leather processing, Regionalm Programme for Pollution Control in the Tanning Industry in South-East Asia.

20. UNESCO,(2004)National Water Development Report for Ethiopia Pollutants in textile effluents.

21. Robinson, T.; McMullan, G.; Marchant, R. & Nigam, P. (2001). Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. Bioresource Technology, vol.77, pp.247-255

22. Crini, G.(2006). Non-conventional low-cost adsorbents for dye removal: A review, Bioresour. Technol., 97**,** 1061- 85 **.**

23. Dabrowski, A. (2001).Adsorption - from theory to practice. Advances in Colloid and Interface Science, 93, 135-224.

24. Bouchenafa-Saïb, N.; Khouli, K.; Mohammedi, O.(2007) Preparation and characterization of pillared montmorillonite: application in adsorption of cadmium. Desalination, 217, 282–289

25. Ahmaruzzaman, M.(2008). Adsorption of phenolic compounds on low-cost adsorbents: A review. Advances in Colloid and Interface Science, 143, 48–67.

26. B. K. G. Theng. (1974). The Chemistry of Clay-Organic Reactions.343pp.

27. Tetsuya Shichi and Katsuhiko Takagi (2000). Clay minerals as photochemical reaction fields Rev.; **1 (2)**, p 113–130.

28. K. Bergmann and C. T. O'Konski .(1963). 'A spectroscopic study of methylene blue monomer, dimer, and complexes with montmorillonite'. J. Phys. Chem.; **67 (10)**, p 2169 -2177.

29.J. Bujdák, N. Iyi and T. Fujita. (2002). The aggregation of methylene blue in montmorillonite dispersions. Clay Minerals.; **37 (1)**, p 121-133.

30. Ching-Hsing Yu, Susan Q. Newton, Mya A. Norman, David M. Miller, Lothar Schäfer and Brian J. Teppen .(2000). Molecular dynamics simulations of the adsorption of methylene blue at clay mineral surfaces. Clays and Clay Minerals; **48 (6)**, p 665-681.

31. Juraj Bujdák and Nobuo Iyi. (2002). Visible spectroscopy of cationic dyes in dispersions with reduced-charge montmorillonites. Clays and Clay Minerals; **50 (4)**, p 446-454.

32. Katrien Y. Jacobs and Robert A. Schoonheydt. (1999). Spectroscopy of methylene blue–smectite suspensions Colloid Interface Sci.**220 (1)**, p 103-111.

33. Z. Chernia, D. Gill and S. Yariv .(1994). 'Electric Dichroism. The Effect of Dialysis on the Color of Crystal Violet Adsorbed to Montmorillonite'. Langmuir; **10 (11)**, p 3988–3993.

34.ERA.(2002) site Investigation manual : Addis Ababa, the Ethiopian Roads Authority.

35. Adriana Czímerová, Alexander Ceklovský and Juraj Bujdák .(2009). 'Interaction of montmorillonite with phenothiazine dyes and pyronin in aqueous dispersions: A visible spectroscopy study'. **7 (3)**, p 343-353.

36. Benaı¨ssa H. (2005). Removal of acid dyes from aqueous solutions using orange peel as a sorbent material. Ninth International Water Technology Conference. 1175–1185.

37. Kannan N, Sundaram MM .(2001). Kinetics and mechanism of removal of methylene blue by adsorption on various carbons—a comparative study. Dyes Pigment. 51:25–40.

38. Jain AK, Gupta VK, Bhatnagar A, Jain S, Suhas S. (2003). A comparative assessment of adsorbents prepared from industrial wastes for the removal of cationic dye. 80:267–270.

39. Ansari R, Mosayebzadeh Z. (2010). Removal of basic dye methylene blue from aqueous solutions using sawdust and sawdust coated with polypyrrole. 7:339–350

40. Salleh MAM, Mahmoud DK, Karim WAWA, Idris A. (2011). Cationic and anionic dye adsorption by agricultural solid wastes: a comprehensive review. 280:1–13

41. Aksu Z, Tezer S. (2005). Biosorption of reactive dyes on the green alga Chlorella 40:1347–1361

42. Wang XU, Zhou Y, Jiang Y, Sun C. (2008) .The removal of basic dyes from aqueous solutions using agricultural by-products. J Hazard Mater 157:374–385

43. Greenwood, N. N. and Earnshow, A. (1984). Chemistry of the Elements, Pergamon Press, Oxford

44.Armagan, B., Turan, M., Çelik, M. S. (2003b). Adsorption of Dyestuffs onto Natural Clay Minerals: Effects of Solids Concentration and Mixing Time, V. National Environmental Engineering Congress of UCTEA The Chamber of Environmental Engineers, 179-186.

45. Annadurai, G., Juang, R. S., Lee, D. J. (2001), Adsorption of Rhodamine 6G from Aqueous Solutions on Activated Carbon, Journal of Environmental Science Health, **36** (5), 715-725.

46. Wu, F. C., Tseng, R. L., Juang, R. S. (2001). Kinetics of Color Removal by Adsorption from Water Using Activated Clay, Environmental Technology, **22**, 721-729.

47.Öztürk, N., Bektaş, T. E., Özdemir, M., Kıpçak, I. (2000), Investigation of Effectiveness of Sepiolite and Other Adsorbents in Removal of Dyestuffs, IV. National Chemical Engineering Congress, 158-163.

48. Morais, L. C., Freitas, O. M., Goncalves, E. P., Vasconcelos, l. T., Gonzalez Beca, C. G. (1999). Reactive Dyes Removal from Wastewaters by Adsorption on Eucalyptus Bark: Variables That Define the Process, Water Research, **33** (4), 979- 988.

49.Juang, R. S., Tseng, R. L., Wu, F. C., Lee, S. H. (1997b).Adsorption of Behavior of Reactive Dyes from Aqueous Solutions on Chitosan, Journal of Chemical Technology Biotechnology, **70**, 391-399.

50. Wu, G., Koliadima, A., Her, Y. S., Matijevic, E. (1997), Adsorption of Dyes on Nanosize Modified Silica Particles, Journal of Colloidal and Interface Science, **195**, 222-228.

51. Nassar, M. M., Magdy, Y. H. (1997). Removal of Different Basic Dyes from Aqueous Solutions by Adsorption on Palm-Fruit Bunch Particles, Chemical Engineering Journal, **66**, 223-226.

52. Sun G., Xu X. (1997). Sunflower Stalks as Adsorbents for Color Removal from Textile Wastewater, Industrial Engineering Chemical Research, **36**, 808-812.

53. Yitagesu, Fekerte Arega, van der Meer, F. D, and Van der Werff, H. (2010). Geotechnical Investigation and Spectral Characteristics of clay soils.

54. .Ho, Y.S., McKay, G. (1998) , Trans IChemE 76B, 332.

55. Baral, S.S., Das, N., Roy Chaudhury, G., Das, S.N. (2009) . Hazard. Mater. 171, 358.

56. Dubinin .M.M., and Radushkevich, L.V. (1947), Equation of the characteristics curve of activated charcoal. 875-889

57. W.J. Weber, J.C. Morris,(1963). Kinetics of adsorption on carbon from solution. 89 31–60.

58. Langmuir I (1916), the adsorption of gases on plane surface of glass, mica and platinum.40:1361–1368.

59. Freundlich HMF (1906). Over the adsorption in solution. 57:385–470.

60. Dubinin .M.M., and Radushkevich, L.V. (1947). Equation of the characteristics curve of activated charcoal. 875-889.

62. Stephen, G. and Martin, R.T. (1995) Definition of Clay and Clay Minerals: Joint Report of the Aipea Nomenclature and CmS Nomenclature Committees, Clay and Clay Minerals, 43, (2), 255–256.

61. Jain M, Garg VK, Kadirvelu K. (2011). Investigation of Cr(VI) adsorption onto chemically treated Helianthus annuus: Optimization using Response Surface Methodology, Bioresour. Technol.;102:600-605.

63. Liu W, et al. (2012) .Kinetics and thermodynamics characteristics of cationic yellow X-GL adsorption on attapulgite/rice hull-based activated carbon nanocomposites.;32(3):655–62

64. H. H. Murray, Appl. Clay Miner.(2007) Developments in Clay Science .

65. Komandel ,P.,Schmidt, D., Madejova,J., Cicel, J.(1990). Alteration of smectites by treatment with hydrochloric acid and sodium carbonate solutions .5,113-122.

66.Dawood Sen Tk. (2012). Removal of anionic dye from aqueous solution by raw pine .water Res 2012;46(6):19.

65. Foo KY, BH Hameed .(2011.) Microwave assisted preparation of activated carbon from pomelo skin for the removal of anionic and cationic dyes. 173: 385-390.

67. Salleh MAM, et al.(2011). Cationic and anionic dye adsorption by agricultural solid wastes: a comprehensive review.280(1):1–13.

68.Zhang J,Zhou Q Ou L .(2012). Kinetic ,isotherm and thermodynamics studies of the adsorption of methyl orange from aqueous solution ;67:412-9.

69. Sen TK, Afroze S, Ang HM. (2011). Equilibrium, kinetics and mechanism of removal of methylene blue from aqueous solution by adsorption onto pine cone biomass of Pinus radiata. Water, Air, & Soil Pollution 218: 499-515.

70. Langmuir I .(1916). the adsorption of gases on plane surface of glass, mica and platinum.40:1361–1368.

71. Kannan, K., and Sundaram, M. M. (2001). Kinetics and mechanism of removal of methylene blue by adsorption on various carbons e a comparative study, Dyes Pigments
51, 25-40.

72. Mall, I.D., Srivastava, V. C., Kumar, G. V., and Mishra, I. M. (2006). Characterization and utilization of Mesoporous fertilizer plant waste Carbone for adsorptive removal of dyes from aqueous solution. Colloid Surf. A. 278, 175-187.

73. Srinivasan A, Viraraghavan T. (2010).Decolorization of dye wastewaters by biosorbents. 91(10):1915–29.

74. Wang Y.C., Szeto Y.S., Cheung W.H., McKay G. (2003).Equilibrium studies for acid dye adsorption onto chitosan, Langmuir, **19**, 7888-7894 **.**

75. S. Goldberg. (2005).Equations and Models Describing Adsorption Processes in Soils. SSSA Book Series, no. 8.

76. Atkins P.(1999). Physical chemistry 6th Edn. Oxford University press: 857- 864.

77. Montgomery, D. C. (2001). Design and analysis of experiments.

Appendix A: EXPERIMENTAL DATA

Table A- 1: Data for calibration of the spectrophotometer.

Concentration (mg/l)	Absorbance
0	0
0.1	0.006
0.2	0.009
0.4	0.013
0.6	0.017
0.8	0.019
1	0.021
2	0.034
4	0.065
6	0.092
8	0.125
10	0.153

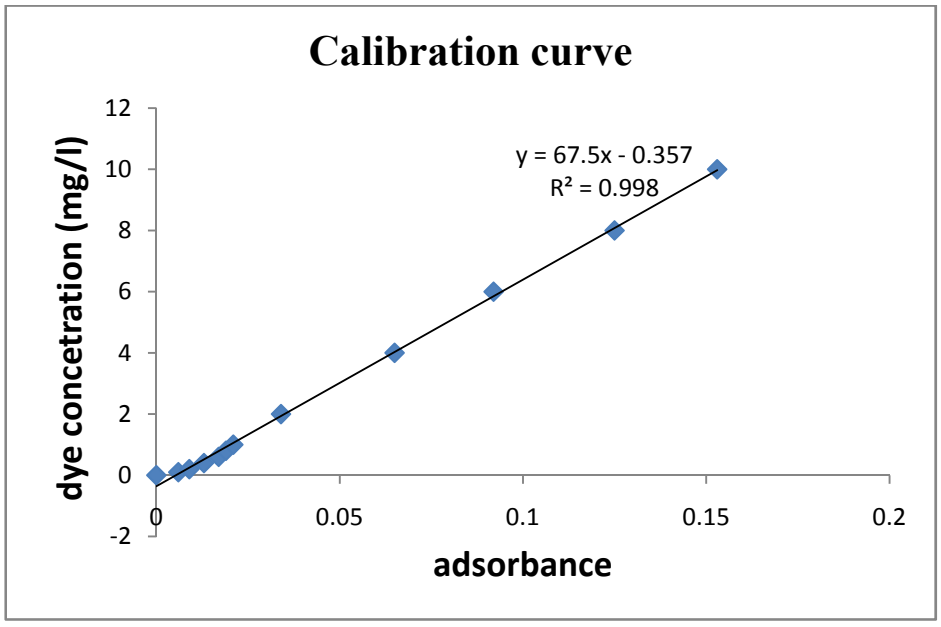


Figure A 1. Calibration graph for determination of dye concentration.

Table A- 2: Data for Effect of solution pH on the Adsorption of Reactive Red Dye.

solution pH	Absorbance	Final conc C_e(mg/L)	Adsorption capacity qe(mg/g)	Dye percentage removal
1	0.014	5.871	0.853	85.323
2	0.023	11.946	0.701	70.135
3	0.029	15.996	0.6	60.01
4	0.031	17.346	0.566	56.635

Table A- 3: Data for effect of initial dye concentration on the Adsorption of Reactive Red Dye.

Initial dye conc.(mg/L	Absorbance	Final conc C_e(mg/L)	Adsorption capacity q_e(mg/g)	Dye percentage removal
20	0.031*	1.7346	0.457	91.327
40	0.014	5.871	0.853	85.323
60	0.03	16.679	1.083	72.202
80	0.039	22.746	1.431	71.568
100	0.048	28.821	1.78	71.179

Table A- 4: Data for effect of adsorbent dose on the Adsorption of Reactive Red Dye.

Adsorbent dose(g/100ml)	Absorbance	Final conc Ce(mg/L)	Adsorption capacity qe(mg/g)	Dye percentage removal
2	0.042	24.771	0.761	38.073
4	0.014	5.871	0.855	85.323
6	0.012	4.521	0.591	88.698
8	0.02*	0.992	0.488	97.52

Table A- 5: Data for Effect of contact time on Adsorption of Reactive RED Dye.

Time (min)	Absorbance	Final conc (mg/L)	q_t (mg/g)	% Removal	$Log(q_e-q_t)$	t/q_t	t^0.5
15	0.04	23.421	0.414	41.45	-0.341	36.232	3.873
30	0.025	13.296	0.668	66.76	-0.695	44.91	5.477
45	0.022	11.271	0.718	71.82	-0.818	62.674	6.708
60	0.019	9.246	0.769	76.89	-0.996	78.023	7.746
75	0.017	7.896	0.803	80.26	-1.174	93.4	8.66
90	0.15	6.546	0.837	83.64	-1.481	107.527	9.487
105	0.13	5.196	0.87	87.01	-	120.69	10.247
120	0.13	5.196	0.87	87.01	-	137.931	10.954

Table A-6: Data for Langmuir isotherm model parameters.

Initial dye conc.(mg/L	Absorbance	Final conc C_e(mg/L)	1/Ce	Adsorption capacity q_e(mg/g)	1/qe
20	0.031*	1.7346	0.577	0.457	2.19
40	0.014	5.871	0.17	0.853	1.173
60	0.03	16.679	0.06	1.083	0.723
80	0.039	22.746	0.044	1.431	0.699
100	0.048	28.821	0.035	1.78	0.562

Table A- 7: Data for Freundlinch isotherm model parameters

Initial dye conc.(mg/L	Absorbance	Final conc Ce(mg/L)	Log Ce	Adsorption capacity qe(mg/g)	Log qe
20	0.031*	1.7346	0.239	0.457	-0.34
40	0.014	5.871	0.769	0.853	-0.069
60	0.03	16.679	1.222	1.083	0.035
80	0.039	22.746	1.357	1.431	0.156
100	0.048	28.821	1.46	1.78	0.25

Table A- 8 : Dubnin- Radushkevich (D-R) isotherm model parameters.

Initial dye conc.(mg/L	Absorbance	Final conc Ce(mg/L)	Ce(mol/g)	Adsorption capacity qe(mg/g)	qe(mol/g)	Ln(qe)	Ɛ2
20	0.031*	1.7346	1.76E-06	0.457	4.64E-07	-14.583	1041.66
40	0.014	5.871	5.97E-06	0.853	1.45E-07	-15.744	858.73
60	0.03	16.679	1.70E-05	1.083	8.67E-07	-13.959	716.1
80	0.039	22.746	2.31E-05	1.431	1.10E-06	-13.72	676.26
100	0.048	28.821	2.93E-05	1.78	1.81E-06	-13.233	646.61

Appendix B: FTIR Spectrum of Clay Soil.

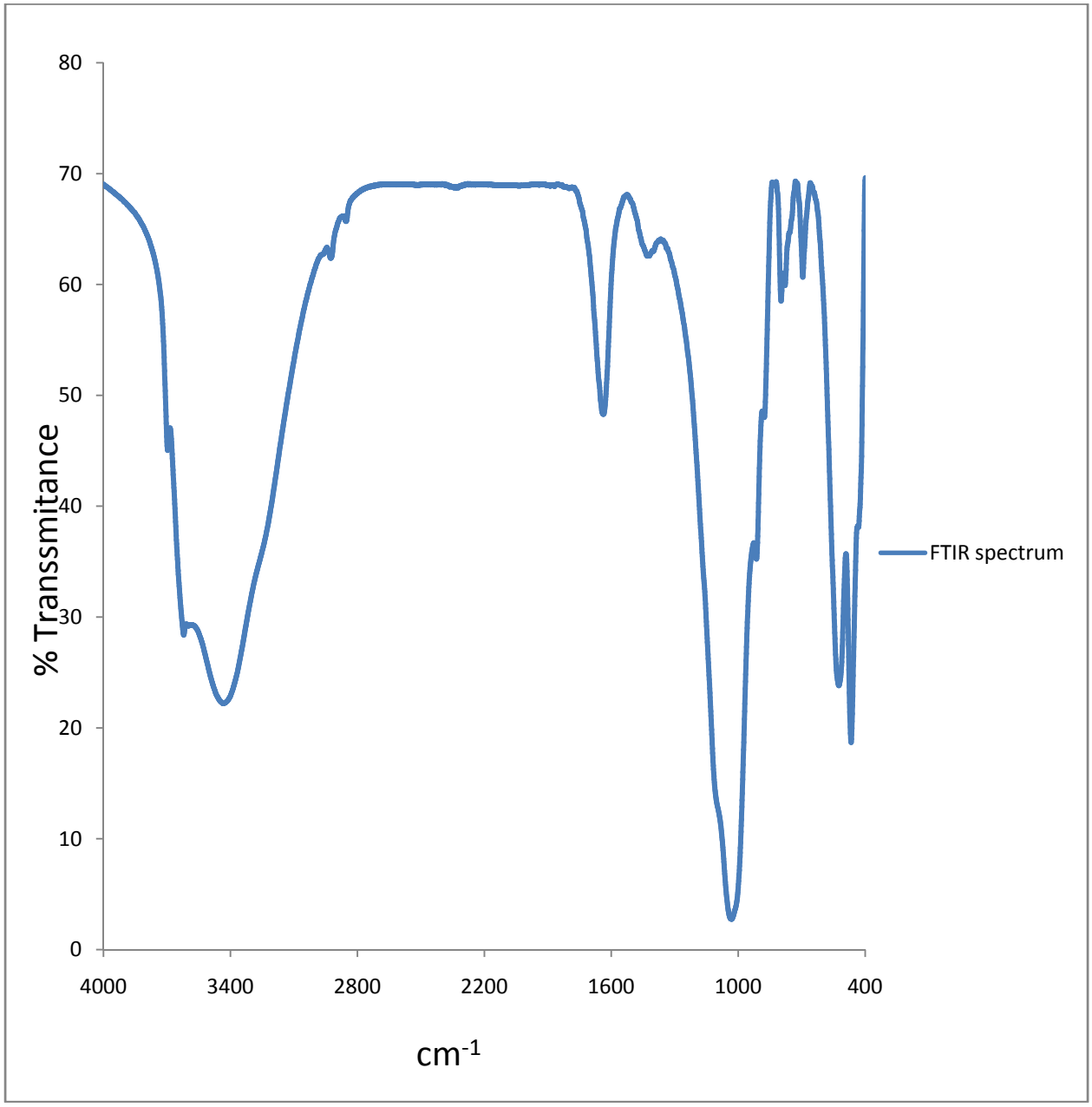


Figure B-1: FTIR Spectrum for clay soil before Acid Activation and Adsorption.

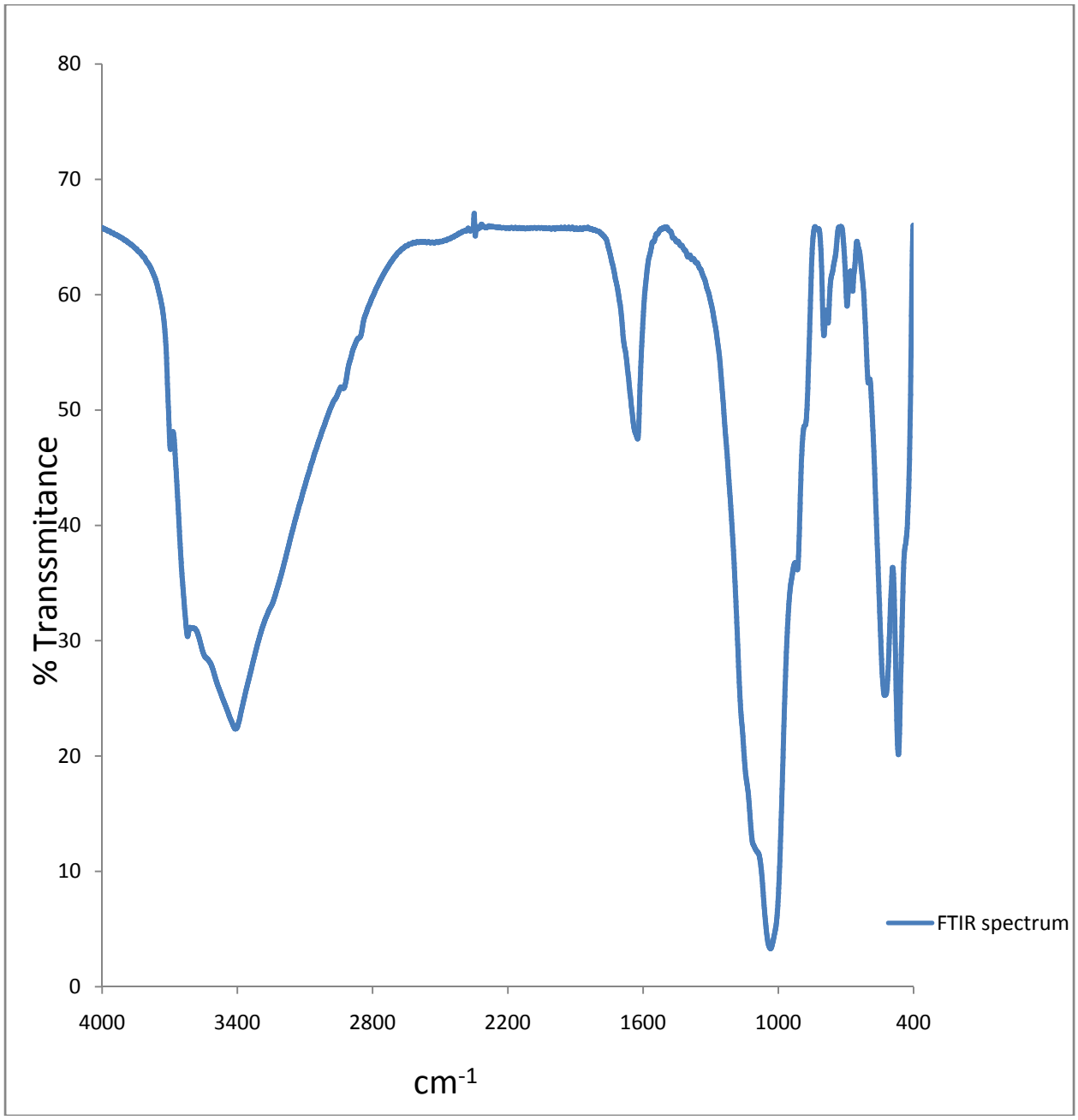


Figure B-2: FTIR Spectrum for acid Activated Clay Soil.

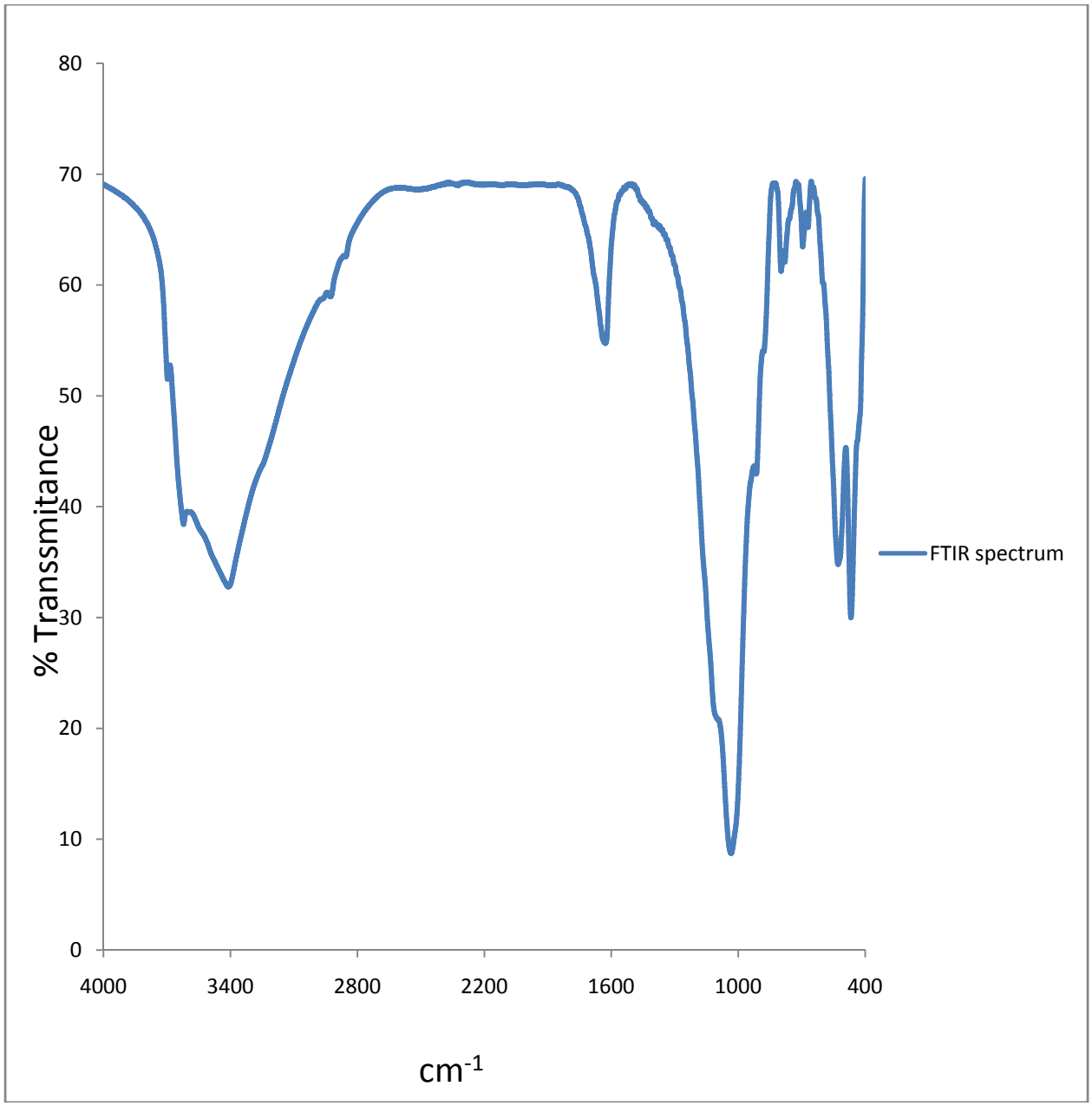


Figure B-3: FTIR spectrum for acid activated Clay Soil after Adsorption.

Appendix C: Results from the statically analysis

Table C-1: The experimental design matrix

			Factor 1	Factor 2	Factor 3	Factor 4	Response 1
Std	Run	Block	A:pH	B:conc	C:dose	D:time	percent removal
25	1	Block 1	2.75	60	4.6875	127.5	71.09
5	2	Block 1	1.5	40	7	75	91.82
24	3	Block 1	2.75	60	4.6875	232.5	60.97
14	4	Block 1	4	40	7	180	65.37
15	5	Block 1	1.5	80	7	180	87.73
28	6	Block 1	2.75	60	4.6875	127.5	71.09
13	7	Block 1	1.5	40	7	180	98.99
17	8	Block 1	0.25	60	4.6875	127.5	97.22
6	9	Block 1	4	40	7	75	57.9
11	10	Block 1	1.5	80	2.375	180	63.97
10	11	Block 1	4	40	2.375	180	48.45
23	12	Block 1	2.75	60	4.6875	22.5	48.23
27	13	Block 1	2.75	60	4.6875	127.5	71.09
2	14	Block 1	4	40	2.375	75	42.32
12	15	Block 1	4	80	2.375	180	29.63
4	16	Block 1	4	80	2.375	75	24.2
3	17	Block 1	1.5	80	2.375	75	53.14
8	18	Block 1	4	80	7	75	47.22
16	19	Block 1	4	80	7	180	50.6
20	20	Block 1	2.75	100	4.6875	127.5	44.43
19	21	Block 1	2.75	20	4.6875	127.5	76.14
9	22	Block 1	1.5	40	2.375	180	85
21	23	Block 1	2.75	60	0.0625	127.5	48.23
26	24	Block 1	2.75	60	4.6875	127.5	71.09
30	25	Block 1	2.75	60	4.6875	127.5	71.09
22	26	Block 1	2.75	60	9.3125	127.5	90.23
1	27	Block 1	1.5	40	2.375	75	70.14
7	28	Block 1	1.5	80	7	75	77.9
29	29	Block 1	2.75	60	4.6875	127.5	71.09
18	30	Block 1	5.25	60	4.6875	127.5	33.1

Table C-2: Diagnostics case statistics

Standard Order	Actual Value	Predicted Value	Residual	Leverage	Internally Studentized Residual	Externally Studentized Residual	Influence on Fitted Value DFFITS	Run Order
1	70.14	71.265	-1.125	0.583333	-1.5817385	-1.67408172	-1.980800198	27
2	42.32	42.05667	0.263333	0.583333	0.37024398	0.359335364	0.425171336	14
3	53.14	53.13833	0.001667	0.583333	0.00234332	0.002263859	0.002678634	17
4	24.2	24.135	0.065	0.583333	0.09138934	0.088315077	0.104495809	16
5	91.82	90.75	1.07	0.583333	1.50440908	1.577250209	1.866227615	2
6	57.9	59.61667	-1.71667	0.583333	-2.4136158	-2.98154888	* -3.53	9
7	77.9	78.70833	-0.80833	0.583333	-1.1365084	-1.14853465	-1.358964528	28
8	47.22	47.78	-0.56	0.583333	-0.7873543	-0.7768795	-0.919216224	18
9	85	83.29333	1.706667	0.583333	2.39955591	2.953308538	* 3.49	22
10	48.45	49.015	-0.565	0.583333	-0.7943842	-0.78411915	-0.92778229	11
11	63.97	63.62667	0.343333	0.583333	0.48272316	0.470019998	0.556135161	10
12	29.63	29.55333	0.076667	0.583333	0.10779255	0.104177854	0.123264899	15
13	98.99	100.4283	-1.43833	0.583333	-2.022282	-2.29079317	* -2.71	7
14	65.37	64.225	1.145	0.583333	1.60985831	1.709993838	* 2.02	4
15	87.73	86.84667	0.883333	0.583333	1.24195765	1.266741344	1.498828571	5
16	50.6	50.84833	-0.24833	0.583333	-0.3491541	-0.33869407	-0.400748227	19
17	97.22	97.65	-0.43	0.583333	-0.6045756	-0.59132449	-0.699664577	8
18	33.1	32.44333	0.656667	0.583333	0.92326663	0.918438534	1.086711129	30
19	76.14	75.92333	0.216667	0.583333	0.30463112	0.295216243	0.34930457	21
20	44.43	44.42	0.01	0.583333	0.0140599	0.013583241	0.016071908	20
21	48.23	48.72667	-0.49667	0.583333	-0.6983083	-0.68587045	-0.811532864	23
22	90.23	89.50667	0.723333	0.583333	1.01699928	1.018246946	1.204806034	26
23	48.23	46.93833	1.291667	0.583333	1.81607015	1.98640887	* 2.35	12
24	60.97	62.035	-1.065	0.583333	-1.4973791	-1.568581	-1.855970064	3
25	71.09	71.09	0	0.166667	0	0	0	1
26	71.09	71.09	0	0.166667	0	0	0	24
27	71.09	71.09	0	0.166667	0	0	0	13
28	71.09	71.09	0	0.166667	0	0	0	6
29	71.09	71.09	0	0.166667	0	0	0	29
30	71.09	71.09	0	0.166667	0	0	0	25

* Exceeds limits

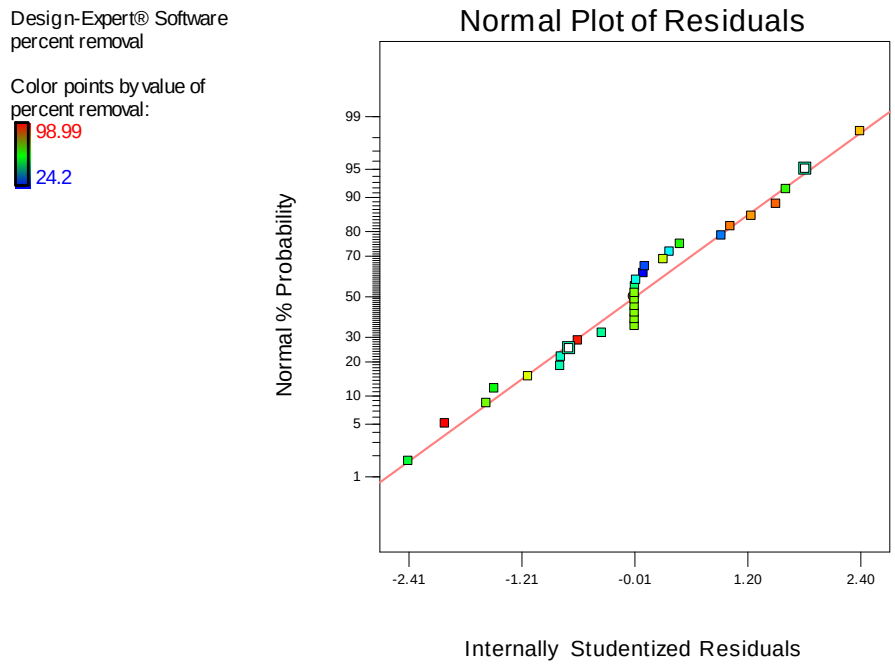


Figure C- 1: Normal plots of residuals.

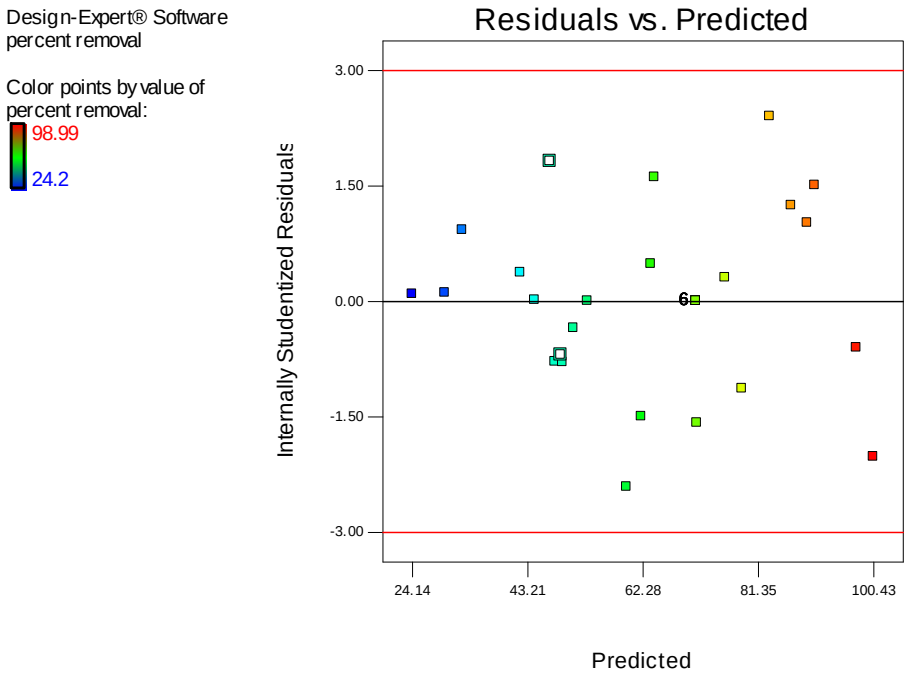


Figure C- 2: Residual vs. Predicted values.

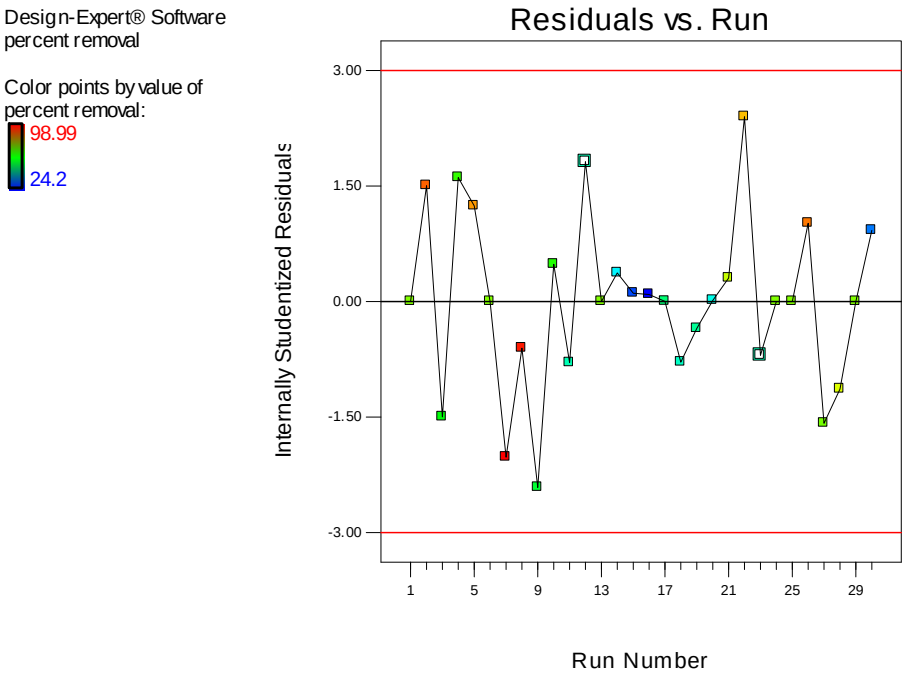


Figure C- 3: Plot of residual Vs. Run.

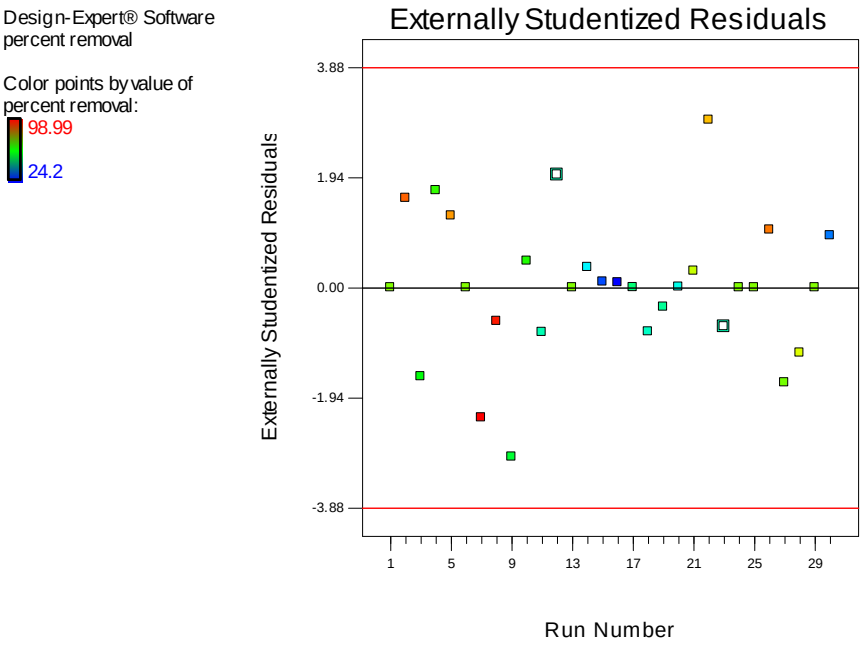


Figure C- 4: Plot of Externally studentized residuals.