ADDIS ABABA UNIVERSITY
ADDIS ABABA INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL AND BIOENGINEERING

# Modification of Bentonite Clay for Adsorption Enhancement for Congo Red Dye Removal from Textile Waste Water

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**A Thesis Submitted to Addis Ababa Institute of Technology, School of Chemical and Bio Engineering in Partial Fulfillment of the Requirements for the Degree of Masters of Science in Process Engineering.**

November, 2017
Addis Ababa, Ethiopia

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School Of Chemical and Bio Engineering

This is to certify that the thesis prepared by Kiros Fisseha, entitled: *"Modification of Bentonite Clay for Adsorption Enhancement for Congo Red Dye Removal from Textile Waste Water"* and submitted in partial fulfillment of the requirements for the degree of Master of Science in process engineering complies with the regulations of the university and meets the accepted standard with respect to originality and quality.

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# Declaration

I declare that, this thesis "Modification of Bentonite Clay for Adsorption Enhancement for Congo Red Dye Removal from Textile Waste Water" for M.Sc. Degree at Addis Ababa University Institute of Technology, hereby submitted by me, is my original work and it hasn't been submitted previously for the degree at this or any other university, and that all resources of materials used in this thesis have been duly acknowledged.

*Kiros Fisseha*

*Signature:* ______________________

*Date of Submission*: ______________

This thesis has been submitted for examination with my approval as University Advisor by *Dr. Beteley T. (Asst. Prof.)*

*Signature:* ___________________

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# *Abstract*

*Bentonite clays are considered as low cost adsorbents due to their local and abundant availability, non-toxicity, and potential for ion exchange and can easily undergo modification to increase their surface area and adsorption capacity.*

*The present study includes the preparation, characterization and performance testing of a set of adsorbents, prepared by the acid activation of bentonite clay obtained from Gewane, Afar regional state of Ethiopia. The acid activation experiments were carried out by sulfuric acid solutions of various concentrations in the range of (0.05-0.5 M) at different temperatures (30, 60, 90 $^{o}$C) for 3hours.The result revealed that bentonite activated with 0.1M sulfuric acid at 30 $^{o}$C showed a higher efficiency in removing congo red dye from aqueous solution and was selected for further investigation.*

*The raw and acid activated bentonite materials were characterized using several techniques such as wet-chemical /complete silicate analysis , Scanning electron microscopy (SEM with EDS), Fourier-transform infrared spectroscopy (FTIR) and XRD. The results of the analysis by complete silicate analysis and Energy Dispersive Spectroscopy (EDS), showed that the presence of silica and alumina as major constituents with a very small amount of iron, calcium, magnesium, sodium, potassium, and titanium as a form of impurities. The results of the XRD showed that the raw bentonite was composed of montmorillonite, quartz, hematite, feldspar, and cristobalite. The microscopic images obtained through SEM showed that the structure of the activated bentonite was different from the raw bentonite clay indicating the formation of perforation /vacant sites.*

*A general full factorial experimental design was employed to correlate the effect of key operational parameters, such as contact time, initial dye concentration and, pH on the adsorption of congo red dye onto bentonite activated with 0.1 M sulfuric acid were experimentally studied using a batch adsorption process. The result showed that the optimum condition for the percentage dye removal was 95.74% at the time of 6 hr. a dye concentration100.58 mg/l and pH 5.03 .The isotherm data for adsorption of congo red dye on AA bentonite were analyzed using Langmuir and Freundlich adsorption isotherms. Freundlich isotherm model was found more representative. Further to understand the adsorption kinetics the adsorption data were analyzed by pseudo first-order and pseudo second-order kinetics. The results revealed that adsorption kinetics was adequately described by pseudo second-order kinetics.*

***Key words: Raw bentonite, Acid activation, congo red dye, Adsorption***

# List of Acronyms

| | |
|---|---|
| AA | Acid Activation |
| AC | Activated Carbon |
| CR | Congo Red |
| DRI | Direct Reduction Iron |
| EU | Europian Union |
| FTIR | Fourier Transform Infra Red Spectroscopy |
| RB | Raw Bentonite |
| SEM | Scanning Electron Microscopy |
| XRD | X-ray Diffraction |

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# 1. INTRODUCTION

## 1.1. Background

Clay minerals belong to the family of phyllosilicate or sheet silicate family of minerals, which are distinguished by layered structures composed of polymeric sheets of $SiO_4$ tetrahedral linked into sheets of (Al, Mg, Fe) $(O, OH)_6$ octahedral. Clay minerals are layer-type aluminosilicates that are formed as products of chemical weathering of other silicate minerals at the earth's surface (Sposito et al. 1999). These minerals have a platy morphology because of the arrangement of atoms in the structure. Clays and clay minerals are very important industrial minerals; they have been in use as raw materials for hundreds of industrial applications due to its abundant availability and inexpensive. Clays are utilized in agricultural applications, in engineering and construction applications, in environmental remediation, in geology, pharmaceuticals, food processing, and many other industrial applications (Murray 2007).

Bentonite is a term that was first used to designate particular, highly colloidal, plastic clay found near Fort Benton in the Cretaceous beds of Wyoming, USA, which possesses unique characteristic of swelling to several times its original volume when placed in water and that forms thixotropic gels. Bentonites can be classified as sodium (Na), calcium (Ca), potassium (K) and aluminum (Al) depending on the dominant element in each. Of these elements, Na and Ca bentonites possess some physical properties, which make them valuable to a great variety of industries (Olugbenga et al., 2013). Na bentonite clay has extensive water absorption properties, accompanied by swelling and ability to remain suspended in water for long periods of time. Ca bentonite clays do not show swelling properties (Kutlic et al., 2012) and forms colloidal suspensions very quickly (Basim, 2011).

The effective application of raw bentonite clay materials in adsorption application for removal of dyes from aqueous solution is limited due to small surface area and presence of net negative surface charge, leading to low adsorption capacity. All these factors have led to the need for research and development in the field of modification of clay surfaces to enhance their adsorptive properties. Surface modified clays have high potential to provide an alternative to most widely used activated carbon. Therefore, in order to ameliorate the adsorption properties and range of applicability, a number of physical and chemical methods have been investigated to modify the clays, including heat treatment (Al-Asheh et al., 2003), acid activation (Motlagh et al., 2011; Lian et al., 2009; Ozcan and Ozcan, 2004 Christides et al. 1997; Foletto et al., 2011), treating the cationic surfactants (Yıldız et al, 2005; Wang and Wang, 2008), and polymer modification (Chen et al., 2008; Liu, 2007). Among these, acid activation is one of the most commonly used modification techniques because it is a simple and low-cost process (Toor, 2012). The acid activation of clay minerals is normally done by treating them with HCl, $H_2SO_4$, or $HNO_3$. The modification of bentonite by acid activation is a famous technique, in other words, most of the time the activation process is conducted at high acid concentrations and high temperatures. The acid activation of bentonites at a low temperature and a low acid concentration is still rarely studied.

According to Ethiopian Geological survey, Ethiopia has a huge amount of Bentonite clay deposits/ resources which are found in the Afar and Oromia regions. The main occurrences in afar are located at Ledi, Gewane, Hadar, and Warseiso. For this study, Gewane bentonite has used an adsorbent ( Mesfin ,2012).

## 1.2. Problem Statement

Dye pollutants generated from different industries are the sources of environmental pollution. Most industries such as textile, paper use dyes and pigments to color their products. The discharge of dyes from those industries into the aquatic environment has been of great concern due to their toxic nature and complex molecular structure that can affect light penetrations and upsetting of biological processes within a stream (Gomez et al., 2007). Congo red is a diazo dye which is known to be carcinogenic and due to its complex aromatic structure makes it difficult to biodegrade and photodegrade (Meroufel et al., 2013; Vimonses et al., 2009). Therefore, it is necessary to remove these contaminants from waste waters by an appropriate technique before discharging them into the environment.

Many industries use activated carbon as an adsorbent for dye removal because it has excellent adsorption capacity and high surface area. However, its widespread application is limited due to high cost and regeneration problems. Cost plays a vital role in selecting adsorbents. Therefore, if one would like to use an adsorbent for effluent treatment, then one would need to find low cost adsorbents. Nowadays, there are many alternative low cost adsorbents which have been proposed by several researchers such as agricultural by-products, natural clays (example bentonite clay), industrial by-products etc. for dye removal. However, due to abundant availability, inexpensive and easy capability to undergo modification bentonite clay is acquiring relative importance as low cost adsorbent. Therefore, development of low cost adsorbent material in the form of modified bentonite clay is as an alternative to activated carbon is another motivation for this study.

Currently, activation of bentonite by inorganic acid is a common method. In many research papers, the activation process was conducted at high acid concentration and high temperature ranges. In other words, the acid activation of bentonites at a low temperature and a low acid concentration is still rarely studied. Therefore, this thesis was focused on activation of bentonite at low acid concentration, temperature and testing its performance for congo red dye removal from aqueous solution.

## 1.3. Objectives

### 1.3.1. General Objective

The overall objective of this thesis was to study the adsorption performance of acid activated Bentonite clay for the removal of Congo red from aqueous solution.

### 1.3.2. Specific Objectives

The specific objectives of this thesis are:

- To characterize the physio-chemical properties of Ethiopian raw bentonite from Gewane (Afar region).
- To prepare and characterize acid activated bentonite adsorbent.
- To test the adsorption performances of raw and acid activated bentonite for removal of Congo red from aqueous solution (model solution).
- To study the main and interaction effects (initial dye concentration, pH, and time on adsorption performance of activated bentonite).
- To study the adsorption isotherm and kinetics of congo red by modified bentonite.
- To find the optimum process parameters on congo red adsorption using response surface methodology.

## 1.4. Significance of the Current Study

- To find an alternative cost effective and naturally available clay based adsorbent in the removal of dye from aqueous solution. This study was used to utilize raw and acid treated bentonite in the removal of Congo red dye effectively.
- It Reduces toxic substances released to the environment because that substance can cause serious problems on the environment such as air pollution, water pollution, soil pollution and several health problems to human and animals.
- The developed bentonite adsorbent may also use full for removal of other organic / inorganic effluents from industrial waste water and it provides quality water for different industrial applications and irrigation purposes.

# 2. LITERATURE REVIEW

## 2.1. Clay minerals

The term “clay mineral” refers to phyllosilicate minerals and to minerals which impart plasticity to clay and which harden upon drying or firing. Clay minerals are layer silicates that are formed usually as products of chemical weathering of other silicate minerals at the earth's surface.

### 2.1.1. Bentonite

Bentonite is smectite clay formed from the alteration of siliceous, glass-rich volcanic rocks such as tuffs and ash deposits (Nadežda et al., 2011). It is a term that was first used to designate particular, highly colloidal, plastic clay found near Fort Benton in the Cretaceous beds of Wyoming, USA, which possesses unique characteristic of swelling to several times its original volume when placed in water and that forms thixotropic gels. Later the term is used to describe plastic clays, generated by alteration of volcanic tuff and ash, with the dominant content of smectite minerals, usually montmorillonite, named after the deposits in Montmorillon, France (Kutlic et al., 2012). Later the term was used to describe every plastic clay generated by the alteration of organic ash or material emitted from volcanoes (Nadežda et al., 2011; Basim 2011; Kutlic et al., 2012).

The major mineral in bentonite is montmorillonite, a hydrated sodium, calcium, magnesium, aluminum silicate. The main constituent, which is the determinant factor in the clay’s properties, is the clay mineral montmorillonite. The sodium, calcium, and magnesium cations are interchangeable giving the montmorillonite a high ion exchange capacity. Smectites are clay minerals, i.e. they consist of individual crystallites the majority of which are < 2μm in the largest dimension. Smectite crystallites themselves are three-layer clay minerals. They consist of two tetrahedral layers and one octahedral layer (EUBA, 2011). As it is well known, the clay minerals are hydrous aluminum silicate and are classified as phyllosilicates.

## 2.2. Structure and Chemical Composition of Bentonite Clay

The structure of bentonite clay consists of two types of sheets; Tetrahedral sheets (Fig. 2-1) consist of corner-linked tetrahedral with oxygens in the corners and cations (T) in the center. The dominant cation is $Si^{4+}$, but $Al^{3+}$ is substituted for it frequently, up to half of the Si. $Fe^{3+}$ is substituted for $Si^{4+}$ occasionally; the tetrahedral rest on a triangular face and share all three oxygens with three other tetrahedral. The sheet of linked tetrahedral has hexagonal symmetry.

Octahedral sheets consist of edge-linked octahedral with OH in the corners and cations (R) in the center. The cations are usually $Al^{3+}$, $Mg^{2+}$, $Fe^{2+}$ or $Fe^{3+}$, but all other transition elements and Li are possible. The octahedral sheets can be described as composed of two planes of closest-packed hydroxyls with cations occupying the octahedral sites between the two planes.

The structure of bentonite is characterized by one Al octahedral sheet placed between two Si tetrahedral sheets (Fig. 2.1). The isomorphous substitution of $Al^{3+}$ for $Si^{4+}$ in the tetrahedral layer and $Mg^{2+}$ for $Al^{3+}$ in the octahedral layer results in a net negative surface charge on the bentonite (Özcan et al., 2004). These imbalanced charges in the interlayer space are balanced/equalized by the dominant cations, typically $Na^{+}$, $K^{+}$, $Mg^{2+}$, and $Ca^{2+}$. These cations are exchangeable due to their loose binding and this leads to a high cation exchange capacity of bentonite. (Vimonses et al., 2009).

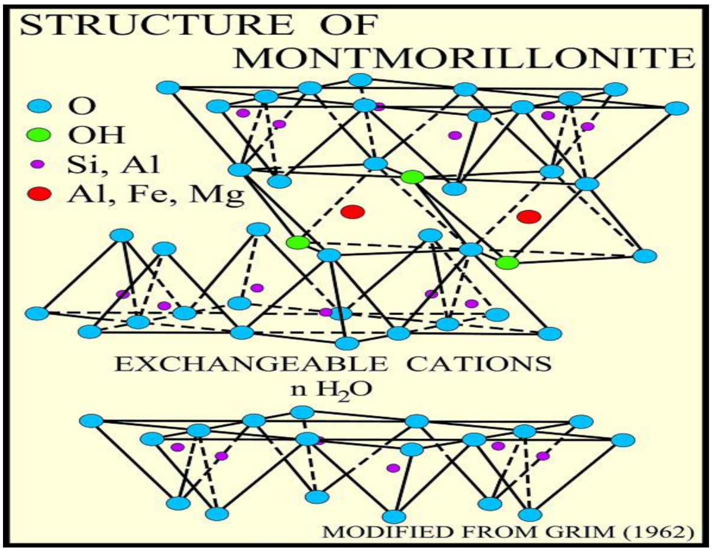


Figure 2. 1 Structure of montmorillonite (Grim, 1962)

Calcium montmorillonite and sodium montmorillonite are the most important clay minerals in smectite group. The main structural difference between calcium and sodium montmorillonite is at the water layer, calcium montmorillonite possesses two water layers in the interlayer position while for sodium montmorillonite only have one water layer (Murray 2007). With only one water layer in the interlayer position, sodium montmorillonite has significantly different properties with calcium-bentonite. Sodium montmorillonite has the much higher swelling capacity and viscosity than calcium montmorillonite**.** Neaman et al. (2003) gives the following general formula for montmorillonite:

$$\underset{\text{Exchangeble}}{Na_{0.18}Ca_{0.10}}\underset{\text{Tetrahedral}}{(Si_{3.98}Al_{0.02})}\underset{\text{Octahedral site}}{(\mathrm{Fe}^{3+}{}_{0.09}Fe^{2+}{}_{0.08}Mg_{0.28})}\underset{\mathrm{H_2O^+}}{O_{10}(OH)_2}\cdot \underset{H_2O^-}{nH_2O} \qquad (2\text{-}1)$$

Depending on the nature of their genesis, bentonites contain a variety of accessory minerals in addition to montmorillonite. These minerals may include quartz, feldspar, calcite, and gypsum. The presence of these minerals could impact the industrial value of the deposit, reducing or increasing its value depending on the application. Bentonite presents strong colloidal properties and its volume increases several times when coming into contact with water, creating a gelatinous and viscous fluid.

The special properties of bentonite (hydration, swelling, water absorption, viscosity, and thixotropy) make it a valuable material for a wide range of uses and applications. (EUBA, 2011).

### 2.2.1. Bentonite Occurrences in Ethiopia

Bentonite clay resources are found in the Afar and Oromia regions of Ethiopia. They are easily accessible, as they are located near the main road. The main occurrences in Afar are located at Ledi, Gewane, Hadar, and Warseiso. The total resource in the Afar region is estimated to be 170 million ton. The bentonite beds are well exposed and the overburden consists of loamy gravel and sandy clay. Tests conducted so far confirm that some beds could be used for the preparation of drilling mud and iron ore pelletization, and if upgraded, may have foundry application as well ( Mesfin ,2012).

## 2.3. Industrial Use of Bentonite Clay

### 2.3.1. Foundry

Bentonite is used as a bonding material in the preparation of moulding sand for the production of iron, steel, and non-ferrous casting. The unique proper ties of Bentonite yield green sand moulds with good flow ability, compactability and thermal stability for the production of high quality castings (EUBA, 2011).

### 2.3.2. Pelletizing

Bentonite is used as a binding agent in the production of iron ore pellets. Through this process, iron ore fines are converted into spherical pellets, suitable as feed material in blast furnaces for pig iron production, or in the production of direct reduction iron (DRI) (EUBA, 2011).

### 2.3.3. Construction and Civil Engineering

Bentonite in civil engineering applications is traditionally used as a thixotropic, support and lubricant agent in diaphragm walls and foundations, in tunneling, in horizontal directional drilling (HDD). Bentonite, due to its viscosity and plasticity, is also used in Portland cement and mortars (EUBA, 2011).

### 2.3.4. Environmental Markets

Bentonite's adsorption /absorption properties are very useful for wastewater purification.EU directives recommend low permeability soils, which naturally should contain Bentonite, as a sealing material in the construction and rehabilitation of landfills to ensure the protection of groundwater from the pollutants. Bentonite is the active protective layer of the Geosynthetic Clay Liners (EUBA, 2011).

### 2.3.5. Drilling

Another conventional use of Bentonite is as a mud constituent for oil- and water- well drilling. Its role is mainly to seal the borehole walls, to remove drill cuttings and to lubricate the cutting head (EUBA, 2011).

### 2.3.6. Oils / Food Markets

Bentonite is utilized for the removal of impurities in oils where its adsorptive properties are crucial in the processing edible oils and fats (Soya / palm / canola oil). In drinks such as beer, wine, and mineral water and in products like sugar or honey, Bentonite is used as a clarification agent (EUBA, 2011). Mineral oils such as lubricating oils and other hydrocarbons are refined by treatment with activated bleaching clays. A wider temperature range is used for these oils, some being bleached at 40 $^{o}$ C whilst others require temperatures of the order of 200-250 $^{o}$ C. At these higher temperatures it is necessary to maintain an inert atmosphere above the oil to prevent oxidation (Hartwell, 1965).

### 2.3.7. Agriculture

Bentonite is used as an animal feed supplement, as a pelletizing aid in the production of the animal feed pellets, as well as a flow ability aid for unconsolidated feed ingredients such as soy meal. It is also used as an ion exchanger for improvement and conditioning of the soil. When thermally treated, it can be used as a porous ceramic carrier for various herbicides and pesticides (EUBA, 2011).

### 2.3.8. Pharmaceuticals, Cosmetics and Medical Markets

Bentonite is used as filler in pharmaceuticals and due to absorption/adsorption functions, allows paste formation. Such applications include industrial protective creams, calamine lotion, wet compresses, and anti-irritants for eczema. In medicine, Bentonite is used as an antidote in heavy metal poisoning. Personal care products such as mud packs, sunburn paint, baby and face powders, and face creams may all contain Bentonite (EUBA, 2011).

### 2.3.9. Detergents

Laundry detergents and liquid hand cleansers/soaps rely on the inclusion of Bentonite, in order to remove the impurities in solvents and to soften the fabrics (EUBA, 2011).

### 2.3.10. Paints, Dyes, and Polishes

Due to its thixotropic properties, Bentonite and organoclays function as a thickening and/or suspension agent in varnishes, and in water and solvent paints. Its adsorption properties are appreciated for the finishing of indigo dying cloth and in dyes (lacquers for paints & wallpapers) (EUBA, 2011).

### 2.3.11. Cat Litter

Bentonite is used for cat litter due to its advantage of absorbing refuse by forming clumps (which can be easily removed) leaving the remaining product intact for further use (EUBA, 2011).

### 2.3.12. Paper

Bentonite is crucial to paper making, where it is used in pitch control, i.e. absorption of wood resins that tend to obstruct the machines and to improve the efficiency of the conversion of pulp into the paper as well as to improve the quality of the paper. Bentonite also offers useful de-inking proper ties for paper recycling. In addition, acid activated Bentonite is used as the active component in the manufacture of carbonless copy paper (EUBA, 2011).

### 2.3.13. Catalysts

Activated montmorillonites are used to catalyze various chemical reactions, for example, catalytic cracking of petroleum. This process, which is used for increasing the yield and quality of gasoline from petroleum, involves splitting the heavier molecular weight hydrocarbons into lighter ones with lower boiling points. Present uses of activated clays are as alkylation catalysts, particularly for the alkylation of phenols. These alkylated phenols have many uses and are intermediaries in the formation of detergents. Clays are also used to promote polymerization, dehydration and various other chemical reactions. In addition, the activated clays are used as delicate pH adjusters where the last traces of alkalinity have to be removed from organic liquids (Hartwell, 1965). Vijayakumar et al., (2009) have reported high efficient catalyst for esterification of various carboxylic acids with phenol alcohols made from acid activated Indian Bentonite.

### 2.3.14. Waste water treatment

Waste water generated from different industries can be treated by chemical precipitation, ion exchange, adsorption, membrane filtration. Among these methods, adsorption is an alternative technology for metal separation & dye removal from waste water. Activated clay is used in the removal of heavy metals and dyes from wastewater (Hajjaji and El Arfaoui 2009; Bhattacharyya and Gupta 2011; Chen et al., 2011; Toor and Jin 2012)

## 2.4. Activation Methods of Clay Mineral

Generally, activation is a chemical or physical treatment applied to certain types of clays to improve the capacity to adsorb coloring matter and other impurities in oils and solutions (Farihahusnah et al., 2011).

### 2.4.1. Intercalation/pillaring

Pillaring is a type of modification methods which alters the properties of bleaching earth by using a combination of chemical and physical treatment. Pillaring is defined as a process by which a layered compound is transformed in a thermally stable micro and/or mesoporous material with retention of the layer structure. Pillared clay minerals have attracted increasing attention, particularly from the industry since the 1970s, because of their micro porous nature and catalytic potential. However, pillared clay minerals have not been used as commercial adsorbents and catalysts. This is because the treatment was developed in the laboratory; it is difficult to extend to an industrial scale (Farihahusnah et al., 2011).

### 2.4.2. Polymer modified clays

Polymerically modified clays are among the most promising organically modified clays because of their easily tuned surface properties using a variety of functional polymers (Chen et al., 2008). There are two main approaches for the surface modification of clay minerals with polymers. One is physical adsorption, and the second is chemical grafting of functional polymers to the surfaces of the clay minerals. The physical adsorption can alter the nature of the clay mineral surfaces and improve their surface physical and chemical properties.

The advantage of physical attachment is that the structure of the clay mineral is not altered. The main disadvantage is that the forces between the adsorbed molecules and the clay mineral might be weak. Grafting of functional polymers to the surface of clay minerals can improve the interaction (Liu, 2007). Yue et al. (2007) studied Formation and characteristics of cationic-polymer/bentonite complexes as adsorbents for dyes. The study is carried out to adsorb disperse and reactive dye namely yellow SE-6GRL (DY SE-6GRL), disperse Red S-R (DR S-R), reactive Reddish Violet K2-BP (RRV K2-BP) and reactive Jade Blue K-GL (RJB K-GL) on epicholorohyrin-dimethylamine polyamine (EPIDMA).

The XRD analysis indicates that the intercalated EPI-DMA molecules expand the layer space of bentonite and the TGA and corresponding DSC plots show EPI-DMA/bentonite was more hydrophobic than natural bentonite and the zeta potential studies display EPI-DMA/bentonite complexes developed a positively charged surface at a relatively high loading of the polymer. These characteristics should make EPI-DMA/bentonite complexes capable of removing anionic pollutants from solution, such as anionic dye wastewater. The results of the dye adsorption experiments demonstrated that removal of dyes from water with EPI-DMA/bentonite complex is viable.

### 2.4.3. Thermal Activation

Thermal activation of clay mineral is a physical treatment which involves calcination of clays at high temperatures. It is done to remove any impurities or moisture attached to clay particles (Ajemba, 2012). The actual temperatures at which changes occur vary greatly from one clay mineral group to another, and depend on the particle size and on the heating regime. (Beragaya et al., 2006). Sennour et al. (2009) have mentioned that the adsorption potential of activated montmorillonite was determined by adsorption of chlorobenzene from aqueous solution.

Montmorillonite modified by thermal activation showed a higher adsorption potential than chemically activated montmorillonite (acid and hydrogen peroxide treatment).

Chaari et al. (2008) studied the adsorption of lead on thermal activated Tunisian smectitic clay at different temperatures ranging from 100-600$^{o}$C. The result showed that adsorption of lead from aqueous solution on smectitic clay increases with increasing activation temperature i.e. due to loss of physisorbed water, whereas the decrease of adsorption with further increase in temperature beyond 200 $^{o}$C because of the decrease in surface area.

Toor and Jin (2012) studied the adsorption of Congo red on Na-bentonite. The activation was conducted by thermal, acid and a combination of thermal and acid treatments. The thermal activation of raw bentonite was carried out over a temperature range from 50$^{o}$C to 500$^{o}$C for a period of 20min. The results reveal that surface area increased with an increase in the temperature up to 100$^{o}$C and then gradually decreased beyond 100$^{o}$C. The increase in surface area with increasing temperature is due to the removal of adsorbed and hydrated water and other impurities attached to the surface of raw bentonite. The adsorption capacity of natural bentonite was19.5 mg/g and this was increased to 54.64 mg/g after thermal activation. Aytas et al. (2009) also studied the adsorption of Uranium (VI) on thermal activated bentonite. The activation was carried out over a temperature range from 150$^{o}$C to 900 $^{o}$C for 1h.

## 2.4.4. Acid Activation

One of the most common chemical modifications of clays, used for both industrial and scientific purposes, is their acid activation. The acid activation of clay minerals is normally done by treating them with HCl, $H_2SO_4$, or $HNO_3$. Acid activation alters the physical properties, such as enhancing the surface area and average pore volume. It also changes the chemical properties such as cation exchange capacity and the surface acidity of the clays (Ajemba, 2012). The physical changes during the activation process depend on the acid strength, time of treatment, and temperature. (Doulia et al., 2009).

### 2.4.4.1. Mechanism of Acid Activation

The acid activation of the clays is a two-step procedure. In the first step, the exchangeable cations are replaced by protons ($H^+$). The second step involves the leaching of octahedral cations such as $Al^{3+}$, $Mg^{2+}$ and $Fe^{3+}$from the octahedral and the tetrahedral sheets, but the SiO4 groups of the tetrahedral sheet stay largely intact (Farihahusnah et al., 2011, Steudel et al., 2009). When clays are activated by acid, the octahedral $Al^{3+}$ cations are easier leached than tetrahedral $Si^{4+}$cations. However, to prevent the excessive leaching of $Al^{3+}$ at high concentration, which results in rupture of the lattice structure (Dai and Huang, 1999) and decrease in the surface area of the clay (Díaz and De Souza Santozs, 2001), it is essential to use the appropriate amount of acid. Hajjaji and El-Arfaoui (2009) investigated the adsorption of Methylene blue and zinc ions on raw and acid activated Bentonite. The acid activation of bentonite was carried out by treating it with 6.7N HCl at boiling temperature for 3h. The adsorption capability can decrease after acid activation using certain acid at a high concentration. The reduced adsorption was associated with the partial collapse of the montmorillonite particles and the formation of amorphous silica. Jovanović and Jonaćković (1991) activated Bentonite with HCl over a concentration range of 0.5-4M for 4h. The results showed that with the increase of the concentration of acid solution the total pore volume increased, while the maximum value of specific surface area was attained by the sample treated with 2 M HCl. Changes observed after treatment with 0.5 to 2 M HCI were caused by cation exchange and removal of impurities from Bentonite. Differences in pore structure and adsorption properties after treatment with 2 to 4 M HCl were caused by structural changes and partial decomposition of the samples. The results suggest that chemical treatment of the Bentonite with 2 M HCI produced an adsorbent with optimal porosity and other adsorption properties.

Bhattacharyya et al. (2013) activated kaolinite and montmorillonite by acid activation with 0.25 and 0.5M $H_2SO_4$ for 3hr  adsorption of Congo red. The acid-treated clay minerals showed better adsorption capacity of the dye.

Benguella and Yacouta-Nour (2009) studied the adsorption of Bezanyl Red and Nylomine Green from aqueous solutions by natural and acid-activated Bentonite. The activation of natural bentonite is carried out using 0.1M $H_2SO_4$ for 4h. The surface area of acid activated Bentonite was 23 m2/g. This surface area increased to56 $m^2$/g. Özcan and Özcan (2004) have been adsorbed acidic dyes, namely Acid red 57 (AR57) and Acid blue 294 (AB294), on H2SO4 acid activated Bentonite. The capacity of acid-activated bentonite to adsorb AR57 and AB294 dyes normally used in the textile industry is very high (416.3 mg/ g for AR57 and 119.1 mg /g for AB294) at 20 ◦C.

Yildiz et al. (2004) examined the effect of acid activation on the changes of thermal and surface properties of bentonite. Acid activation was conducted by treating bentonite with $H_2SO_4$ (0.5M – 4M). Surface area measurements showed that the total surface area was increased as H2SO4 acid concentration increased. The maximum value of the specific surface area (240.9 $m^2$/g) was attained by the sample activated with 2M $H_2SO_4$. Activation beyond 2M acid concentrations i.e. (3–4 M) caused a decrease in the surface area. Christides et al. (1997) have activated Milos and Chios bentonites with HCl over a concentration range of (0.5-8N). The mineralogical and physicochemical properties of the activation products were examined and their capacity to decolorize crude rapeseed oil was also evaluated. They found that although the acid-activated bentonites have increased surface area, the maximum bleaching capacity of all the materials tested was not associated with the maximum surface area. Lian et al. (2009) have been studied the adsorption of Congo red from aqueous solution on to Ca-bentonite. They found that 0.2 g of Ca-bentonite could remove more than 90.0% of the dye from 100mg/L Congo red dye solution. The amount of dye adsorbed per unit weight of Ca-bentonite increased from 23.25 to 85.29mg/g with increasing concentration from 50 to 200mg/L. Toor and Jin (2012) studied the adsorption of Congo red on Na-bentonite. The activation was conducted by thermal, acid and a combination of thermal and acid treatments. The acid activation of raw bentonite was carried out over a concentration range from (0.05-0.5) for a period of 3h.the maximum adsorption capacity was attained at 0.5 M HCL and the adsorption capacity of natural bentonite was 19.5 mg/g, and this was increased to 69.44 mg/g after acid activation.

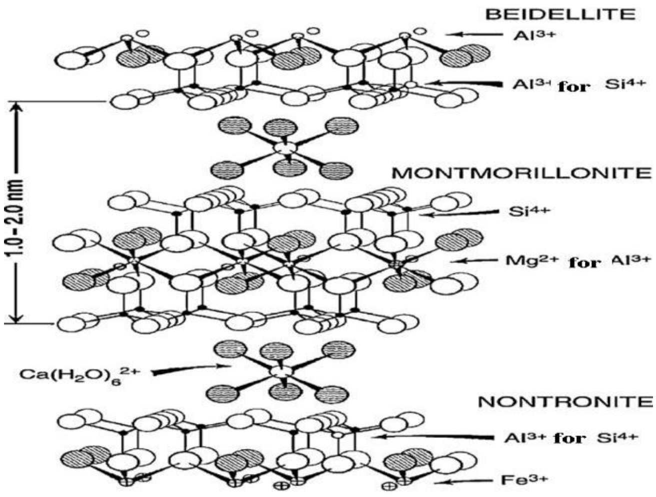


Figure 2. 2 Structure of 2:1 phyllosilicate minerals (Farihahusnah et al., 2011).

#### 2.4.4.2. Parameters affecting acid activation process

Acid activation is mostly affected by the following factors (Farihahusnah et al., 2011):

- Nature of the natural clay
- Contact time
- Temperature
- Acid concentration and Type of acid used for activation

- Solid/liquid ratio

## 2.5. The Source of Color in Dyes

Dye is an organic compound that imparts color to substances such as leather, plastic materials, food, hair, wax and textile fiber (Zollinger et al 1991) Dyes have been derived from natural plants in the ancient times. Nowadays, almost all the dyes, even the naturally occurring dyes are synthesized chemically.

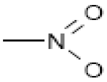
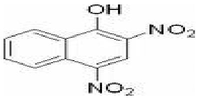
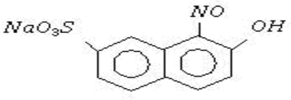
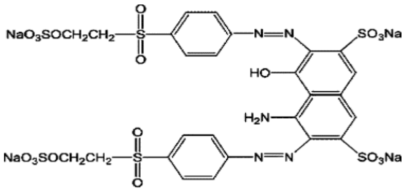
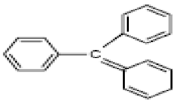
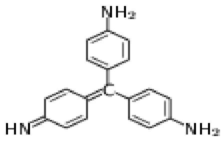
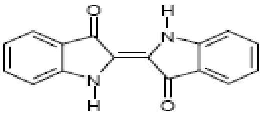
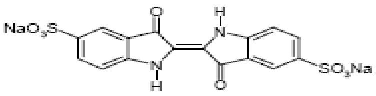
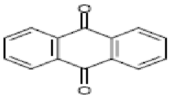
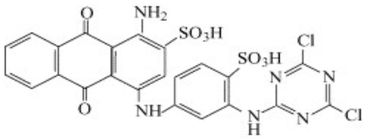
### 2.5.1. Classification of Dyes

Dyes can be classified in to two groups either according to the chemical structure or by their usage/ application.

➢ **Chemical Classification:** The most appropriate system for the classification of dyes is by chemical structure, which has many advantages. First, it readily identifies dyes as belonging to a group that has characteristic properties, for example, azo dyes (strong, good all-round properties, cost-effective) and anthroquinone dyes (weak, expensive). Second, there are a manageable number of chemical groups (about a dozen). However, due to the complexities of the color nomenclature from the chemical structure system, the classification based on application is often favorable (Gupta, 2009).

➢ **Usage Classification:** It is advantageous to consider the classification of dyes by use or method of the application before considering chemical structures in detail because of the dye nomenclature and jargon that arises from this system. Classification by usage or application is the principal system adopted by the Color Index. Because the most important textile fibers are cotton and polyester, the most important dye types are those used for dyeing these two fibers, including polyester-cotton blends (Hunger, 2007).

Table 2. 1 Classification of dyes based on the chromophore adopted from (Ali, 2010)

| Class | chromophore | Example |
|---|---|---|
| Nitro dyes |  | <br>Acid Yellow 24 |
| Nitroso dyes | $-N=O$ | <br>Acid green1 |
| Azo dyes | $-N=N-$ | <br>Reactive Black 5 |
| Triphenylmethane |  | <br>Basic Red 9 |
| Dyes Phthalein dyes | | |
| Indigo dyes |  | <br>Acid Blue 71 |
| Anthroquinone dyes |  | <br>Reactive Blue 4 |

## 2.6. Toxicity Effects of Dyes

Basic dyes have high intensity of colors and are greatly visible even in very little concentration (Clarke and Anliker, 1980, Banat et al., 1996, Mittal and Gupta, 1996, Fu and Viraraghavan, 2001, Chu and Chen, 2002, Fu and Viraraghavan, 2002c) Table 2.4 shows the disadvantages according to different dye class

Table 2. 2 Disadvantages of different dye class (Robinson et al., 2001)

| Dye class | Disadvantages |
|---|---|
| Basic dye | It has high brilliance and intensity of colors and is highly visible even in a low concentration. |
| Azo groups | Their reductive cleavage of azo linkages is responsible for the formation of toxic amines in the effluent. |
| Anthraquinone-based<br>Dyes | It is most resistant to degradation due to their fused aromatic ring structure and thus remains colored for a longer time in wastewater. |

## 2.7. Current Dye Removal Techniques

### 2.7.1. Microbiological decomposition of synthetic dyes

Biological treatment is often the most economical alternative when compared with other physical and chemical processes. Biodegradation methods such as fungal decolorization, microbial degradation, adsorption by (living or dead) microbial biomass and bioremediation systems are commonly applied to the treatment of industrial effluents because many microorganisms such as bacteria, yeasts, algae, and fungi are able to accumulate and degrade different pollutants(crini.,2006). The application of microorganisms for the biodegradation of synthetic dyes is an attractive and simple method for the operation. However, the biological mechanisms can be complex (Forgacs et al., 2004).

The use of microorganisms for the removal of synthetic dyes from industrial effluents offers considerable advantages. The process is relatively inexpensive, running costs are low and end products of complete mineralization are not toxic (Stoltz, 2001).

### 2.7.1.1. Aerobic Degradation

White-rot Fungi White-rot fungi are those organisms that are able to degrade lignin, the structural polymer found in woody plants (Robinson et al., 2001). The most widely studied white-rot fungus, in regards to xenobiotic degradation, is Phanerochaete chrysosporium.

White-rot fungi are able to degrade dyes using enzymes, such as lignin peroxidases (LiP), manganese dependent peroxidases (MnP). Other enzymes used for this purpose include $H_2O_2$-producing enzymes, such as glucose-1-oxidase and glucose-2-oxidase, along with laccase, and a phenol oxidase enzyme. Because of its high enzyme production, the white rot fungus, P. chrysosporium has been frequently employed for the biodegradation of synthetic dyes. It was applied to the decoloration of Orange II, Tropaeolin 0, Congo red and Azure B under aerobic conditions. Decolorization was achieved in 6–9 days (Forgacs et al., 2004).

Table 2. 3 Adsorption capacities of various fungi for dyes (adapted from Banat et al., 1996)

| culture | Dye | Conc. mg/l | Removal time | Mechanism | %Removal | Reference |
|---|---|---|---|---|---|---|
| Aspergillus sojae B-10 | Amaranth | 10 | 5dayes | Not reported | 97.8 | Ryu & Weon (1992) |
| | Sudan III | 10 | | | 97.4 | |
| | Congo Red | 10 | | | 93 | |
| Myrothecum verrucaria | Orange II | 200 | 5hour | Adsorption | 70 | Brahimi-Horn et al. (1992) |
| | 10B (Blue) RS (Red) | 200 | | | 86 | |
| | | 200 | | | 95 | |
| Myrothecum sp. | Orange II | 100 | | Adsorption | 25-91 | Mou et al. (1991) |

| | | | | | | |
|---|---|---|---|---|---|---|
| | 10B (Blue) | 100 | 24 hour | | 58-98 | |
| | RS (Red) | 100 | | | 81-98 | |
| Neurospora crassa | Vermelho Reanil P8B | 16-32 | 24hour | Adsorption | 89-91 | Corso et al.,(1981) |
| Pycnoporus cinnabarins | Pigment plant effluent | Unknown | 3days | extracellulr oxidases | 90 | Schliephe etal.(199) |
| Trichoderma sp. | Hardwood extraction effluent | Unknown | 3days | ligninolytic enzymes | 85 | Prasad & Joyce (1991) |
| Candida sp. | Procyon Black | 100 | 2hour | Adsorption | 93.8 | De Angelis & Rodrigues (1987) |
| | Procyon Blue | 100 | | | 96.8 | |
| | Procyon Red | 100 | | | 98.9 | |
| | Procyon orange | 100 | | | 96.8 | |

### 2.7.1.2. Anaerobic Degradation

The investigations on anaerobic decolorization of azo dyes have been studied since1970s (Rai et al., 2005). The anaerobic degradation of azo dyes has been studied by various researchers (Carliell et al., 1996; Banat et al. 1996; Baughman and Weber, 1994). Azo dyes are soluble in solution and are not removed via conventional biological treatments (Robinson et al., 2001). It has been presumed that the biodegradation of azo dyes occurs by an oxidation-reduction mechanism with hydrogen rather than free molecular oxygen in aerobic systems. Typically, anaerobic breakdown yields methane and hydrogen sulphide (Carliell et al., 1996). The presences of salts influence the biodegradation process. The effect of salts on the removal of azo dye Reactive Red 141 in the presence of sulfates and nitrates under anaerobic conditions showed that decomposition was delayed in the presence of nitrates, on the other hand, the degradation process remained unaffected in the presence of sulfates (Carliell et al., 1998). The decolorization of reactive water-soluble azo dyes was achieved under anaerobic conditions using glucose as a carbon source. A major advantage of this anaerobic system, apart from the decolorization of soluble dyes, is the production of biogas. Biogas can be reused to provide heat and power and will reduce energy costs (Robinson et al., 2001).

#### 2.7.1.3. Living/Dead Microbial Biomass

Dead bacteria, yeast, and fungi also have been used for degradation dyes. The removal capacity of microorganism depends on the affinity of the dye for binding with microorganisms (Robinson et al., 2001). Biological treatment process only is not enough for treating dye effluent. It requires some degree of involvement of physical, chemical or physico-chemical processes as pretreatment. Furthermore, complete mineralization of the dye is still unsuccessful. Thus, it is necessary to identify that the biodegradation products are not causing any harm to the environment (Rai et al., 2005).

The interaction of textile dyes with micro-organisms depend on the chemistry of a particular dye and the specific chemistry of the microbial biomass. The thermal tolerance of microorganisms used for microbial degradation of dyes is not yet known. Currently, the textile effluent has to be cooled for biological degradation which also adds to the cost of operation (Banat et al., 1996). The microbiological decomposition of dyes is a relatively new field and requires the isolation of new strains (Forgacs et al., 2004).

### 2.7.2. Electrochemical Methods

#### 2.7.2.1. Electrocoagulation

Physico-chemical treatment of phase separation for the decontamination of dyes wastewaters before discharge to the environment is coagulation. It consists in the addition of coagulating agents such as $Fe^{3+}$or $Al^{3+}$ ions, usually in the form of chlorides, for dyes precipitation and this technique uses a current to dissolve Fe (or steel) or Al. The removal of the dyes in electrocoagulation is affected by the type of anode used for the production of the coagulating agents (Martínez-Hutile and Brillas 2009).

Generally, three main processes occur during electrocoagulation: (a) electrolytic reactions at electrode surfaces; (b) formation of coagulants in the aqueous phase; (c) adsorption of soluble or colloidal pollutants on coagulants and removal by sedimentation or flotation (Can et al., 2003). Can et al. (2003) studied on decolorization of Reactive Dye Solutions by electrocoagulation Using Aluminum Electrodes and the result indicated that about 97% of the dye was removed. Daneshvar et al. (2007) studied removal of Acid Yellow 23 by electrocoagulation process and the result showed that almost 98% color and 69% chemical oxygen demand (COD) were removed.

#### 2.7.2.2. Electrochemical Reduction

The study on the removal of dyes by electrochemical reduction is limited and is generally recognized to be less effective than electrochemical oxidation. Jain et al. (2003) investigated the adsorption of reactofix golden Yellow 3 RFN from industrial wastes. The result revealed that COD of the solutions showed a decrease from 1416 to 352 mg/L.

#### 2.7.2.3. Electrochemical Oxidation

Over the years, electrochemical oxidation of refractory effluents has received a great deal of attention due to its attractive characteristics of versatility, energy efficiency, amenability of automation and environmental compatibility, because of the main reagent, the electron is a clean reagent. In direct electro-oxidation, the pollutants are oxidized after adsorption on the anode surface without the involvement of any substances other than the electron (Panizza and Cerisola, 2007).

### 2.7.3. Chemical Methods

#### 2.7.3.1. Oxidative processes

Because of its simple handling, oxidation is the most commonly used chemical decoloration process. In most cases, the oxidizing agent is hydrogen peroxide, which, due to its stability in pure form, needs to be activated. Decolorization methods differ in the way in which hydrogen peroxide is activated. $H_2O_2$-Fe (II) salts (Fenton's reagent).

Fenton's reagent [hydrogen per-oxide, activated with Fe (I1) salts] is very suitable for the oxidation of waste-waters which inhibit biological treatment are poisonous. Besides offering advantages in COD, color and toxicity reduction, this process also has dis-advantages. Since the mechanism involves flocculation, impurities are transferred from the wastewater to the sludge, which still needs ecologically questionable land-deposition. To avoid this problem, Peroxid-Chemie GmbH developed the FSR process (Fenton Sludge Recycling System), in which Fe(III)-sludge deposition is eliminated (Slokar & Majcen Le Marechal, 1998).

Other dyes that have been successfully removed by hydrogen peroxide are Reactive red 120, Direct blue 160 and Acid blue 40 (Forgacs et al., 2004). The efficacy of the oxidation process is a function of the ability of the dye molecules to coagulate on the application of oxidizing agents. The removal of dyes by oxidation using hydrogen peroxide as an oxidant has a major drawback of sludge disposal (Robinson et al., 2001).

- **The activation of Fenton's reagent, $H_2O_2$**: - is also performed by application of UV radiations and is known as the photo-Fenton process. The activation of $H_2O_2$ by UV radiation is carried out to enhance the generation of hydroxyl radicals. The rate of dye removal is influenced by the intensity of the UV radiation, pH, dye structure and the dye bath composition (Slokar and Le Marechal, 1997).

- **Sodium hypochlorite** (NaOCl): - Chemical oxidation of colored wastewaters is also possible with Cl-compounds. The electrophilic attack at the amino group by Cl+ initiates and accelerates the subsequent azo bridge cleavage. Treatment of reactive dyes required longer times, while solutions of metal-complex dyes remained partially colored. Disperse dyes do not decolorize with NaOCl. Decoloration rate increases with increasing chlorine concentration and decreasing pH of the medium (Slokar and Le Marechal, 1997). According to Omura (1994) dyes containing amino or substituted amino groups on the naphthalene ring, i.e. dyes derived from aminonaphthol- and naphthylamine sulphonic acids) are most susceptible to chlorine decoloration.

- **Ozonation: -** Ozonation, as an effective oxidation process, has found application in the decolorization of synthetic dyes. The technique employed in the decoloration of Orange II. Oxalate. Formate and benzene sulfonate ions were the most important decomposition products. Ozone effectively decomposed azo dyes in textile wastewater. The decomposition rate was considerably higher at acidic pH (Forgacs et al., 2004). Khadhraoui et al. (2009) investigated the removal of Congo red by ozone treatment and concluded that, though the effective removal of Congo red was attained there was an only small reduction in chemical oxygen demand. Moreover, the efficient mineralization of the dye was not obtained.

The drawback in use of ozone for wastewater treatment is its short half-life in water. It decomposes in about 20min. Furthermore, the time can be significantly shortened if compounds like dyes are present. Its stability is affected by the presence of salts, pH and temperature. If alkaline salts are present, the solubility of ozone is reduced, while neutral salts may increase its solubility. Under alkaline conditions ozone decomposes more rapidly than under acidic conditions. With increasing temperature, ozone solubility decreases. If ozone is used as a hydrogen peroxide activator, the rate of decoloration is increased, but additional pollution of wastewater occurs (Slokar and Le Marechal, 1997).

## 2.7.4. Physicochemical Methods

### 2.7.4.1. Coagulation

Coagulation is a popular physico-chemical method used for the treatment of wastewater. It involves the addition of coagulating agents/coagulants such as $Fe^{3+}$ or $Al3^{+}$ ions, usually in the form of chlorides, to increase the tendency of the smaller particles to aggregate/ to form precipitation (Martínez-Hutile and Brillas, 2009).

### 2.7.4.2. Filtration

Filtration is usually employed to remove any particulate matter present in the wastewater. Membrane filtration has a high affinity towards the treatment of dye effluent. Most importantly membrane filtration can be used for the continuous removal of dyes from the dye effluent (Xu and Lebrun, 1999). It has some special features greater than any 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 are its disadvantages (Robinson et al., 2001).

### 2.7.4.3. Ion exchange

Ion exchange is the process of removing cations and anions present in the wastewater. Synthetic resins are normally used for ion exchange. Ion exchange finds extensive application for the softening of hard water. However, the use of ion exchange is limited for the treatment of dye effluents, mainly due to the opinion that ion exchangers cannot accommodate a wide range of dyes (Slokar and Le Marechal, 1997). Advantages of this method include no loss of adsorbent on regeneration, reclamation of the solvent after use and the removal of soluble dyes. A major drawback the ion exchange is high cost and Organic solvents are expensive (Robinson et al., 2001).

### 2.7.4.4. Adsorption

The term adsorption refers to the accumulation of substances at the interface between two phases such as solid and liquid or solid and gas. The substance that accumulates at the interface is called adsorbate and the solid on which adsorption occurs is adsorbent. Adsorption can be classified in to two types; chemical sorption and physical sorption. Chemical adsorption or chemisorption is formed due to the formation of strong chemical interaction/forces between the molecules of adsorbate and adsorbent surface whereas, physical adsorption/physisorption is characterized by the weak van der Waals forces between adsorbent and adsorbent (Dabrowski, 2001).

Adsorption techniques have gained favor 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 (Choy et al., 1999, Allen and Koumanova, 2005). For water re-use adsorption has been found to be superior to other techniques in terms of flexibility and simplicity of design, initial cost, insensitivity to toxic pollutants and ease of operation. Adsorption also does not produce the harmful substances (Crini, 2006). Adsorption process occurred through the following steps:

i. Mass transfer:
ii. Intra-particle diffusion:
iii. Physical and/or chemical adsorption:

Factors that influence the adsorption efficiency include adsorbate adsorbent interaction, adsorbent surface area, adsorbent to adsorbate ratio, adsorbent particle size, temperature, pH and contact time (Allen and Koumanova, 2005, Crini, 2006) etc.

### ➢ Advantages of adsorption

Adsorption is a well- known equilibrium separation process and an effective method for water decontamination applications and this is because of low initial cost, flexibility, and simplicity of design, ease of operation and insensitivity to toxic pollutants. Adsorption also does not generate harmful substances (Crini, 2006). Adsorption produces a high quality product and is a process which is economically feasible (Choy et al., 1999).

Table 2. 4 Current dye removal methods: advantages and disadvantages (adapted from Robinson et al., 2001 and Crini, 2006)

| Method of dye removal | Advantages | Disadvantages |
|---|---|---|
| **Biodegradation** | Economically feasible, publicly acceptable treatment | Slow process, necessary to create an optimal favorable environment, maintenance and nutrition requirements |
| **Electrochemical** | Breakdown compounds are non-hazardous | High cost of electricity |
| **Chemical** | | |
| Fenton's reagent | Effective in removing of both soluble and insoluble dyes | Sludge creation |
| Sodium-hypochlorite | Initiates and accelerates azo-bond cleavage | Release of aromatic amines |
| Ozonation | Applied in gaseous state: no alteration of volume | Short half-life (20 min) |
| Photocatalysis | No sludge formation | Generation of hazardous by-Products |
| **Physicochemical** | | |
| Coagulation | Simple, economically feasible | High sludge production, handling and disposal problems |
| Filtration | Capable of treating all dyes, produce a high-quality treated effluent | Concentrated sludge production |
| Ion exchange | No loss of sorbent on regeneration, effective | Economic constraints,<br>Not effective for all dyes |
| Adsorption | Effective, suitable for all types of dyes, treated effluent is of high-quality. Availability low-cost adsorbents | High cost of adsorbent (activated carbon) and low surface area of some low-cost adsorbents |

## 2.8. Different Adsorbents for Removal of Dyes

### 2.8.1. Activated Carbon

Adsorption techniques employing solid sorbents are widely used to remove certain classes of chemical pollutants from waters, especially those that are practically unaffected by conventional biological wastewater treatments. However, amongst all the sorbent materials proposed, activated carbon is the most popular for the removal of pollutants from wastewater. Because of their great capacity to adsorb dyes, CAC is the most effective adsorbents. This capacity is mainly due to their structural characteristics and their porous texture which gives them a large surface area, and their chemical nature which can be easily modified by chemical treatment in order to increase their properties. Commercially available activated carbons (AC) are usually derived from natural materials such as wood, coconut shell, lignite or coal, but almost any carbonaceous material may be used as a precursor for the preparation of carbon adsorbents. Because of its availability and cheapness, coal is the most commonly used raw material for AC production. However, activated carbon has several disadvantages it is highly expensive, not feasible and effective for removal of disperse and vat dyes (Crini et al., 2006). The carbon also has to be reactivated otherwise disposal of the concentrates has to be considered. Reactivation results in 10-15% loss of the sorbent (Robinson et al., 2001). This problem leads many researchers to find /develop low-cost adsorbents.

### 2.8.2. Low-Cost Adsorbents

The low cost adsorbent is a sorbent requires little processing, abundant in nature, or is a by-product or waste material from another industry, (Bailey et al., 1999, Crini, 2006). Gupta and Suhas (2009) also have been defined low cost adsorbents as natural materials or the wastes/by-products of industries or synthetically prepared materials, which cost less and can be used as such or after some minor treatment as adsorbents are generally called low-cost adsorbents (LCAs). In general, a sorbent said to be “low-cost” if ti requires little processing, abundant in nature, or waste/byproduct from industry and environmental friendly. Conversion of these materials in to adsorbents helps to reduce the cost of waste disposal and gives an option to commercial activated carbon. The low-cost adsorbents can be classified in two ways; (i) depending on their availability i.e., (a) Natural materials such as natural and modified clays, wood, peat, coal, lignite etc. (b) Industrial/Agricultural/ Domestic wastes or by-products such as slag, sludge, fly ash, bagasse fly ash, red mud etc and (c) Synthesized products; (ii) depending on their nature, i.e., (a) Inorganic and (b) Organic. For instance, an excellent review on the removal of metals by low-cost adsorbents has been presented by Bailey et al. (1999), an overview of low-cost adsorbents for heavy metal removal has been presented by Babel and Kurniawan (2003) and also a nice review has been discussed by Crini (2006) regarding the feasibility of various non-conventional low-cost adsorbents for removal of dyes. Natural materials generally used as LCAs are the one existing in nature and used as such or with minor treatment. Some of the materials used are:

#### 2.8.2.1. Agricultural Wastes

Agricultural materials have high sorption capacity, particularly those material's containing hemicellulose, lignin, lipids, proteins, simple sugars, water, hydrocarbons, and starch. This is due to abundance, eco-friendly, low-cost and this helps for production of agricultural waste based activated carbon that is why a promising adsorbent to solve environmental problems. Agricultural productions are available in large quantities around the world; thus the big amount of wastes rejected (Bhatnagara, and Sillanpää .,2010 , Salleh, *et al 2011*).

#### 2.8.2.2. Industrial By-Product

Industrial activities generate huge amount of solid wastes as by-products and are found free of cost and causes major disposal problem such as metal hydroxide sludge, fly ash, red mud, (Bhatnagara, and Sillanpää, 2010 Netpradit et al., 2003, Acemioğlu, 2004, Namasivayam and Arasi, 1997,) are classified as low-cost adsorbents. A number of industrial wastes have been investigated with or without treatment as adsorbents for the removal of pollutants from wastewaters. Some of them are discussed here.

**Metal hydroxide sludge:** Metal hydroxide sludge is one industrial by-product to remove azo dyes. The sludge is a dried waste from the electroplating industry, which is produced by precipitation of metal ions in wastewater with calcium hydroxide. It contains insoluble metal hydroxides and other salts. (Netpradit et al., 2003) studied reactive dyes removal by electroplating industry hydroxide sludge and they found that the maximum adsorption capacities of 45.87 and 61.73 mg/g for Reactive Red 120 and Reactive Red 2 respectively at 30 °C and at pH 8–9.

**Fly ash** is a major solid waste by product from thermal power plants and mainly used in the construction of roads, bricks, cement, etc. the high percentage of silica and alumina found in fly ash makes it good and low cost adsorbents (Bhatnagara, and Sillanpää .,2010). The estimated global production of fly ash was 67.5 million tons per year in 2010 (Ali et al., 2012).

Khan *et al* (2009) studied removal of methylene blue, malachite green and rhodamine B dyes from Textile Wastewater using fly ash and they observed that the removal of methylene blue, malachite green and rhodamine B varied from 0.228 to 0.814, 0.219 to 0.644, and 0.184 to 0.618 mgg$^{-1}$ respectively when the initial dye concentration was raised from 5 to 20 mgL$^{-1}$. The amount of dye adsorbed (mgg$^{-1}$) was found to increase with an increase in the contact time; with 80 minutes for malachite green and rhodamine B and 100 minutes for methylene blue.

Acemioğlu (2004) studied the adsorption of Congo red from aqueous solution on to calcium rich fly ash and observed that the amount of dye adsorbed per unit weight of fly ash increases with increasing concentration and temperature, it decreases slightly with increasing pH. The adsorption was between 93 and 98% under the conditions studied.

**Red mud (aluminum industry waste)** is a waste material formed during the production of alumina when the bauxite ore is subjected to caustic leaching (Namasivayam and Arasi, 1997, Ali *et al*,2012). Namasivayam and Arasi (1997) studied the adsorption of Congo red on to waste red mud. They found that the adsorption capacity of red mud was 4.05mg/g. Adsorption was found to be nearly at pH 2.0. Effect of pH and desorption studies suggest that the mechanism of adsorption is mostly ion exchange.

Tor and Cengeloglu (2006) investigated the adsorption of Congo red (CR) from wastewater by using HCl acid activated red mud and this helps to increase the surface area. They investigated that the adsorption capacity was 7.08 mg/g. They also analyzed that equilibrium adsorption using both Langmuir, the Freundlich, and the three parameter Redlich–Peterson isotherms. The Langmuir isotherm was the best-fit adsorption isotherm model. Gupta et al (2004) studied that the adsorption of methylene blue, fast green, and rhodamine B from wastewater using red mud. The percentage removal was 75, 94, 92.5 respectively and the adsorption process followed both the Langmuir and Freundlich models.

**Steel Industry Waste:** the steel industry produces a large amount of wastes such as blast furnace slag, dust and sludge which have been considered as low cost adsorbents The utilization of acid treated basic oxygen furnace slag (BOF slag) was successfully carried out to remove three synthetic textile dyes Reactive Blue 19, Reactive Black 5 and Reactive Red 120 by adsorption from aqueous solutions by Xue et al (2009).the maximum removal capacities of Reactive Blue 19, Reactive Black 5 and Reactive Red 120 at 500mg/l dye concentration were 76, 60, 55 mg/g at respectively.

#### 2.8.2.3. Biosorbents

The accumulation and concentration of pollutants from aqueous solutions by the use of biological materials are termed biosorption. In this instance, biological materials, such as chitin, chitosan, peat, yeasts, fungi or bacterial biomass, are used as chelating in order to concentrate and to remove dyes from solutions.

**Chitin and chitosan: -** The sorption of dyes using biopolymers such as chitin and chitosan is one of the emerging biosorption methods for the removal of dyes, even at low concentration (ppm or ppb levels) because they are abundant, renewable and biodegradable resources and has been found in a wide range of natural sources such as crustaceans, fungi, insects, annelids, and molluscs. However, chitin and chitosan are only commercially extracted from crustaceans (crab, krill, crayfish) primarily because a large amount of the crustacean’s exoskeleton is available as a by-product of food processing (Crini, 2006). Chatterjee et al. (2009) investigated that Congo red adsorption from aqueous solutions by using chitosan hydrogel beads impregnated with a nonionic or anionic surfactant, Therefore, adsorption of Congo red by Chitosan beads could be enhanced by surfactant impregnation at a very small dosage, even with an anionic surfactant.

Table 2. 5 Adsorption capacities qm (mg/g) for chitosan and chitosan-based Biosorbents (adapted from Crini, 2006)

| Biosorbents | Dye | $q_m$ |
|---|---|---|
| Crosslinked chitosan bead | Reactive blue 2 | 2498 |
| Crosslinked chitosan bead | Reactive red 2 | 2422 |
| Crosslinked chitosan bead | Direct red 81 | 2383 |
| Crosslinked chitosan bead | Reactive red 189 | 1936 |
| Crosslinked chitosan bead | Reactive yellow 86 | 1911 |
| Chitosan bead | Reactive red 189 | 1189 |
| Chitosan (bead, crab) | Reactive red 222 | 1106 |
| Chitosan (bead, lobster) | Reactive red 222 | 1037 |
| Chitosan | Acid orange 12 | 973.3 |
| Chitosan | Acid orange 10 | 922.9 |
| Chitosan | Acid red 73 | 728.2 |
| Chitosan | Acid red 18 | 693.2 |
| Chitosan | Acid green 25 | 645.1 |
| Chitosan (flake, lobster) | Reactive red 222 | 398 |
| Chitosan (flake, crab) | Reactive red 222 | 293 |

### 2.8.2.4. Natural materials as adsorbent

**Clays**

Natural clay minerals are well known and familiar to mankind. Because of their low cost, abundance in most continents of the world, high sorption properties and potential for ion exchange, clay materials are strong candidates as adsorbents. They are classified by the differences in their layered structures. There are several classes of clays such as smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pylophyllite (talc), vermiculite and sepiolite. The adsorption capabilities result from a net negative charge on the structure of minerals and their high surface area and high porosity. This negative charge gives clay the capability to adsorb positively charged species. Montmorillonite clay has the largest surface area and the highest cation exchange capacity (Crini, 2006).

There are a large number of clays which are widely used for the removal of dyes from wastewater, such as kaolin (Nandi et al. 2009; Unuabonah et al., 2008), montmorillonite (Damardji et al., 2009; Yan et al., 2007) Bentonite (Oscan et al., 2007; Vimonses et al., 2009), smectite (Díaz and De Souza Santozs, 2001), sepiolite (Kara et al., 2003) and zeolite (Vimonses et al., 2009).

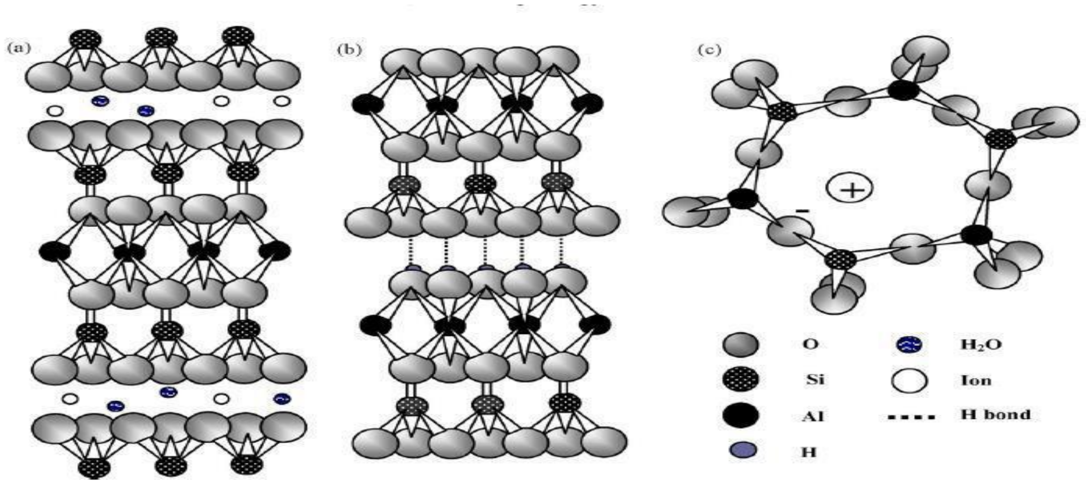
**Kaolin: -** Kaolin or china clay is commonly referred to as clay that consists mainly of kaolinite. It has 1:1 clay as its structure presents a tetrahedral silica sheet alternating with an octahedral alumina sheet (Fig. 2.3b). These sheets are arranged so that the end of the silica tetrahedrons and the adjacent layers of the octahedral sheets form a layer. The layer consists of octahedral and tetrahedral groups, in which two-thirds of the oxygen atoms are allocated by the silicon and aluminum, becoming O instead of OH. The charges within the structure unit are balanced, and there is very little substitution in the interlayer space. The bond held between two adjacent layers is a weak hydrogen bond, but the sum of many hydrogen bonds between units creates a strong and stable force which is nearly impossible to separate. The structure is fixed and no expansion occurs between layers when the clay is wetted. Thereby, kaolinite is defined as a nonexpanding phyllosilicate mineral (Vimonses et al., 2009). Unuabonah et al. (2008) evaluated the adsorption of aniline blue on kaolinite and sodium tetraborate (NTB) modified kaolinite. The specific surface area for NTB-modified Kaolinite was $15.84 m^2\, g^{-1}$ while that of the unmodified was $10.56 m^2\, g^{-1}$.

**Zeolite: -** The chemical formula of natural zeolite mineral, clinoptilolite, is given as $Na_6[(AlO_2)_6\ (SiO_2)_{30}].24H2O$. Three-dimensional crystal structure of zeolite contains two dimensional channels which embody/contains some ion exchangeable cations such as Na, K, Ca and Mg (Fig. 2.3c). These cations can be exchanged between organic and inorganic cations (Benkli et al., 2005).

Its molecular is structured by a three-dimensional framework formed by fully connected SiO4 and AlO4 tetrahedral linked by coordinating oxygen atoms (Fig. 2c). An imbalance charge between $Al3^+$ and four negative charges of surrounding oxygen atoms generates a negative excess charge within the lattice. This negative charge can be compensated by certain exchangeable ions in solutions, providing zeolites high ion exchange capacity. Differing from clays, the zeolite is categorized as a tectosilicate (framework silicates) with micro-porous channels, of which their pore space is filled in a volumetric manner rather than a layer-by-layer pattern in clays. One of the most important features of zeolites is their silicon and aluminum (Si/Al) ratio. If the Si/Al ratio is high, the zeolite is strongly hydrophilic in nature but this ratio can be changed through acid treatment to make the material surface hydrophobic (Vimonses et al., 2009). Vimonses et al (2009) studied the adsorption of Congo red on zeolite, kaolin, and bentonite. Among the three clay minerals, zeolite showed the least adsorption of Congo red.

**Bentonite: -** Bentonite is known as 2:1 type aluminosilicate, highly colloidal and plastic clay consisting mostly of montmorillonite. Special properties of bentonite are its ability to absorb large quantities of water and form thixotrophic gels (Vimonses et al., 2009).

The structure of bentonite is characterized by one Al octahedral sheet placed between two Si tetrahedral sheets (Fig. 2.3a). The isomorphous substitution of $Al^{3+}$ for $Si^{4+}$ in the tetrahedral layer and $Mg^{2+}$ for $Al^{3+}$ in the octahedral layer results in a net negative surface charge on the bentonite (Özcan et al., 2004). These imbalanced charges in the interlayer space are balanced/equalized by the dominant cations, typically $Na^+$, $K^+$, $Mg^{2+,}$ and $Ca^{2+}$. These cations are exchangeable due to their loose binding and this leads to a high cation exchange capacity of bentonite. (Vimonses et al., 2009).



(a) (b) (c)

Figure 2. 3 Structure of (a) Bentonite, (b) Kaolin (c) Zeolite (adapted from Vimonses et al., 2009)

# 3. MATERIALS AND METHODS

## 3.1. Materials

### 3.1.1. Collection and Pretreatment of Adsorbent (Bentonite)

The bentonite used in the study was obtained locally from Gewane, Afar regional state of Ethiopia. It was crushed, ground, and sieved through a 150 μm and washed several times with distilled water to remove impurities and then dried in an oven at 105 $^{O}$C for 24 hours. Dried bentonite was ground by using jaw crusher and attrition mill. The powder was sieved through 200 mesh size (74 μm) and packed in plastic bags and finally prepared for modification/activation. All chemicals used were of analytical grade.

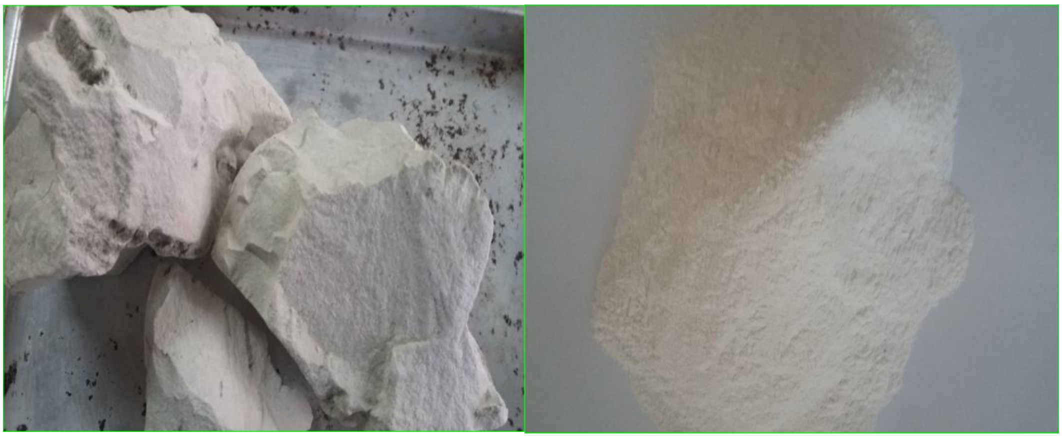


Figure 3. 1 Raw bentonite

### 3.1.2. Modification of Raw Bentonite Clay via acid treatment

Acid activation of raw bentonite was conducted in an incubator shaker (EXCELLA, E24R) in the Addis ababa Institute of Technology, school of chemical and Bioengineering (food engineering laboratory). Raw bentonite was activated using $H_2SO_4$ at different acid concentrations (0.05, 0.075, 0.1, 0.25, 0.5 M) and at different activation temperatures (30, 60, 90 $^{O}$C). A stock solution of 18.4M $H_2SO_4$ was prepared, this stock solution was diluted to different acid concentration mentioned above. The adsorbent was prepared by mixing10g of bentonite with 100ml of known sulfuric acid concentration solution (i.e. the ratio of the mass of clay to the volume of acid solution was fixed at1:10). Agitation was conducted in an incubator shaker with a constant speed of 180 rpm, and the reaction was carried out for 3h (Bhattacharyya et al., 2013). After 3h the reaction is stopped and the solution was filtered and repeatedly washed with distilled water and centrifuged in blue force MSE080.Cx3 model at 4500 rpm for 20 min. The washing was continued until the supernatant was free of sulfate ion ($SO_4^{-2}$) and until it reaches pH of 5.3-5.6. The washed clay was then oven dried at 55 °C for 12h (Benguella and Yacouta-Nour 2009), ground (200 mesh), and then stored in plastic bags for further use.

Figure 3. 2 Acid activated bentonite powder

### 3.1.3. Preparation of Adsorbate

Congo red (CR), a diazo dye was used as a model adsorbate to evaluate the adsorption capacity of bentonite in this study. The chemical formula of CR is $C_{32}H_{22}N_6Na_2O_6S_2$ with Color Index 22120 and molecular weight of 696.663g.mol$^{-1}$ (Meroufel et al., 2013). The IUPAC name of Congo red is [1-napthalene sulfonic acid, 3,3´ - (4,4´ - biphenylenebis (azo)) bis (4-amino) disodium salt]. Congo red contains $NH_2$ and $SO_3$ functional groups. The chemical structure of Congo red is shown in Figure 3.1.

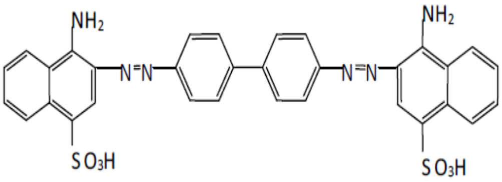


Figure 3. 3 Chemical structure of Congo red

The Congo red was obtained from Micron international trading plc. Addis Ababa, Ethiopia and has an analytical grade. It was used without further purification. The color of CR changes from red to blue in the presence of inorganic acids. The change of color is due to the resonance between charged canonical structures (Meroufel et al., 2013). The red color is stable in the pH range of 5-10. The dye stock solution was prepared by dissolving 1g of Congo red in 1000ml of distilled water. The experimental solutions were obtained by diluting the stock solution with distilled water to give appropriate experimental solutions. The maximum absorbance of Congo red on a UV-vis spectrophotometer is recorded at 496.5nm (Vimonses et al., 2009).

## 3.2. Characterization of Raw and Modified Adsorbent

### 3.2.1. Moisture Content

The moisture content of raw bentonite clay was determined by drying approximately 1g of Bentonite clay at 105 °C in an oven until the mass became constant. Then after cooling in a desiccator, the moisture content was determined using the equation below.

$$W(\%) = \frac{W_1 - W_2}{W_1} * 100 \qquad (3\text{-}1)$$

Where: -

W (%): percentage of moisture in the sample

$W_1$: weight of wet sample (grams)

$W_2$: weight of dry sample (grams)

### 3.2.2. pH determination

pH of natural Bentonite was determined by soaking 5g±0.025g of clay in 50 ml of distilled water for twelve hours. The mixture was stirred vigorously, the pH of the clay suspension was measured using pH-meter.

### 3.2.3. Swell Index (ASTM D5890-95)

The Swell Index or Free Swell test is used to determine the general swelling characteristics of sodium bentonite clay. Bentonite was grinded to pass 100% a100 mesh standard sieve and minimum of 65% passing 200 mesh using mortar and pestle. The ground bentonite clay was then dried in an oven at 105$^{O}$C until the mass is constant. 2g of the dried sample was weighed on to weighing paper.90ml reagent/distilled water was added in to a cleaned 100ml graduated cylinder. Remove not more than a 0.1g increment 0f the clay mineral with a spoon from weighing paper and carefully dust it over the entire surface of the water in the graduated cylinder over a period of approximately 30s. A minimum of 10 minutes must pass between additions to allow for full hydration and settlement of the clay to the bottom of the cylinder.

These steps were followed until the entire 2g sample has been added to the cylinder. After the final addition of the clay distilled water was added until it reached 100ml.The sample is then covered and protected from disturbances for a period of 24 hours, at which time the level of the settled and swollen clay is recorded.

### 3.2.4. Apparent bulk density

The sieved raw bentonite clay was put into 10ml of a graduated cylinder of known weight and avoiding compression. The cylinder was tapped vigorously on the horizontal surface to constant clay volume. The volume of the packed clay was taken and apparent bulk density (AB) was calculated as follows:

$$AB = \frac{Wa - W_b}{V} \qquad (3\text{-}2)$$

Where AB is apparent bulk density ($g/cm3$)

Wa: weight of the cylinder plus clay;

Wb: weight of the empty cylinder;

V: total weight of clay used after compression.

## 3.3. Characterization of Bentonite surface properties using spectroscopic and microscopic techniques

The effect of the modification of surface properties of the adsorbent was determined using different characterization tools such as XRD, Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). A detailed description of these tools was discussed below.

### 3.3.1. Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectroscopy is used to obtain the functional groups/ to analyze the effect of acid attack and the change that has taken place in the structure of bentonite due to acid activation. The spectra were recorded in the range from 4000-400cm$^{-1}$ using 65 FT-IR (PerkinElmer). Solid bentonite was mixed with KBr. The mixture was ground to a very fine powder using mortar and pestle. The fine powder was pressed under 15kpa pressure in to a Pellet. The Infrared spectra were obtained from the pellet. KBr helps to make the sample transparent.

### 3.3.2. Scanning Electron Microscopy

The surface morphology of both raw and modified bentonite was examined using a JSM-IT300 (LA) SEM at accelerating voltage of 20 kV, beam size 3.0, working distance 12.1 and magnification of 2500. Microscope images were taken to compare surface properties of raw and modified bentonite samples.

### 3.3.3. X-Ray Diffractograms (XRD)

XRD is used to determine the mineralogical composition of raw bentonite. X–ray diffraction (XRD) patterns of the sample raw and modified were determined with D8 Avance XRD of Brucker powder diffractometer with Cu-Kα (λ=1.540593-1.544414 Å, 40 KV, and 15 mA) radiation having a continuous scanning mode with speed of 10 deg/min. the XRD patterns were acquired in the range from $10^o$ to $70^o$.

## 3.4. Adsorption performance analysis - Experimental Procedure

Adsorption of Congo red on bentonite was carried out by batch experiments. The batch system was selected due to simplicity. A specific amount of adsorbent (bentonite) was added to 50ml of aqueous Congo red solutions of a known concentration in a series of 250ml conical glass flasks. The pH was adjusted with 0.1M $HNO_3$ and 0.1 NaOH. The mixture was shaken at 150 rpm in an incubator shaker (EXCELLA, E24R) a constant temperature of $30^oC$ at different time intervals. At the predestined time the bottles were withdrawn from the shaker and centrifuged in (universal 320 R) centrifuge at 6000rpm for 15 min to separate the Congo red solution from the adsorbent and then measuring the absorbance of the supernatant at the wave length of 496.5nm. Dye concentration in the reaction mixture was calculated from the calibration carve. The pH of the solution can be adjusted with 0.1M of $HNO_3$ or NaOH. Adsorption experiments were conducted by varying initial solution pH, contact time, initial Congo red dye concentration. The amount of adsorbed CR at any time t $q_t$ (mg/g) was calculated using the equation below:

$$q_t = \frac{(C_o - C_t)\,V}{m} \tag{3-3}$$

Where:

$C_0$ and $C_t$ are the initial and liquid-phase concentrations at any time t of dye solution (mg/L), respectively

V is the volume of dye solution (L) which is constant and

m is the mass (g) of the adsorbent used.

The removal efficiency, R (%) of the system was calculated using equation 3.4

$$R = \frac{(C_o - C_t)}{C_o} * 100 \tag{3-4}$$

## 3.5. Adsorption kinetics

The kinetics of adsorption of Congo red on modified bentonite were examined by pseudo-first-order kinetics, pseudo-second-order kinetics and intraparticle diffusion to understand the dynamics of adsorption process (Lagergren, 1898; Ho and McKay, 1999; Weber and Morris, 1963).

### 3.5.1. Pseudo-first order model

The Lagergren pseudo-first-order model for adsorption kinetic data which is the earliest known equation describing the adsorption rate based on the adsorption capacity. The differential equation is generally expressed as (Lagergren, 1898):

$$\frac{dq}{dt} = k1(qe - qt) \tag{3-5}$$

Here qe and qt 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. (3.5) at the boundary conditions t = 0 to t = t and qt = 0 to qt = qt, gives i.e. The linearized integral form of the Pseudo-first-order Model generally expressed as (Nandi et al., 2009b, Santhi et al., 2009):

$$\log(qe - qt) = \log qe - \frac{k1}{2.303} t \tag{3-6}$$

The values of log (qe −qt) will linearly correlate with t. The plot of log (qe −qt) vs. t should give a linear relationship from which k1 can be determined from the slope. To plot log (qe −qt) versus t give a linear relationship from which $k_1$ and predicted qe can be determined from the slope and intercept of the plot respectively.

### 3.5.2. Pseudo-second order model

The adsorption kinetics may also be described by the pseudo-second-order model. The differential equation is generally given as (Ho and McKay, 1999):

$$\frac{dqt}{dt} = k2(qe - qt)2 \tag{3-7}$$

Where; $k_2$ (g (mg min)$^{-1}$) is the second-order rate constant of adsorption. Integrating Eq. (3.8) is simplified and linearized to get

$$\frac{t}{qt} = \frac{1}{k2qe2} + \frac{1}{qe}t \tag{3-8}$$

The plot of t/qt versus t shows a linear relationship. Values of $k_2$ and equilibrium adsorption capacity qe were calculated from the intercept and slope of the plot of t/qt versus t according to Eq. (3.8).

### 3.5.3. Intra-particle diffusion model

The adsorption proceeds in several steps involving transport of solute molecules from the bulk aqueous phase to the surface of the adsorbent particles followed by integration of the molecules into the interior of the solids pores. According to Weber and Morrs (1963) for most adsorption process, the amount of adsorption varies almost proportionally with $t^{½}$ and can be expressed as:

$$q_t = k_{id}t^{0.5} + \mathrm{c} \tag{3-9}$$

Where qt 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 passes through the origin for intra-particle diffusion controlled adsorption process. The value of k can be calculated from the slope of such plot. The values of the constant illustrate the effect of the boundary layer on the rate of adsorption.

## 3.6. Adsorption Isotherms

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. Langmuir and Freundlich models are the most widely used to describe adsorption isotherms.

### 3.6.1. Langmuir Adsorption Isotherm

The Langmuir adsorption isotherm model depends on the assumption that adsorption occurs at the specific homogeneous surface within the adsorbent (Langmuir, 1918).It is assumed that once the dye molecule occupies a site, no further adsorption can take place at that site. The Langmuir equation is expressed by the following relation:

$$qe = \frac{q_m k_a C_e}{1 + k_a C_e} \qquad (3\text{-}10)$$

Where qe is the amount of dye adsorbed at equilibrium time (mg/g), C is equilibrium concentration of dye in solution (mg/ L), q is maximum adsorption capacity (mg/g) and Ka is isotherm constants for Langmuir (L /mg).

The linearized form of Langmuir can be written as two different forms;

**a. Langmuir-1**

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{k_a q_m} \qquad (3\text{-}11)$$

**b. Langmuir-2**

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{k_a q_m}\frac{1}{C_e} \qquad (3\text{-}12)$$

The separation factor, $R_l$ can be determined from Langmuir plot as per the following relation

$$RL = \frac{1}{1+KaCo}$$

### 3.6.2. Freundlich Adsorption Isotherm

The Freundlich adsorption isotherm model considers a heterogeneous adsorption surface that has unequal available sites with different energies of adsorption. The Freundlich adsorption isotherm model is represented as follows (Freundlich, 1906):

$$q_e = kfCe\frac{1}{n} \qquad (3\text{-}13)$$

The linearized form of Freundlich can be expressed as;

$$\ln qe = \ln k_f + \frac{1}{n}\ln c_e \qquad (3\text{-}14)$$

Where qe is the amount of dye adsorbed at equilibrium time (mg/g), Ce is equilibrium concentration of dye in solution (mg $L^{-1}$). $K_f$ is the capacity of the adsorbent and n is the intensity of adsorption constant for Freundlich. The plot of lnqe versus lnCe is employed to determine the $K_f$ and n from intercept and slope respectively.

## 3.7. Experimental Design and Data Analysis

The experimental design selected for this study was general factorial design i.e. a complete $3^3$ with a total of 27 experiments and the response variable was removal capacity. Design-Expert 6.0.8 software was used to determine the effect of time, initial dye concentration and pH on the percentage removal capacity. The analysis of general factorial design for three variable factors, each with three level was given in table (3.1). This software also used to identify which factor significantly affects the experiment, to develop mathematical models that describe the main and interaction effects on the response and to conduct optimization processes.

Table 3. 1 Experimental factors and levels to conduct adsorption performance

| Factors | Low level | Medium level | High level |
|---|---|---|---|
| Time (hr) | 2 | 4 | 6 |
| Dye concentration(mg/l) | 100 | 500 | 900 |
| pH | 5 | 7 | 9 |

# 4. RESULTS AND DISCUSSION

## 4.1. Proximate analysis and physicochemical characterization of raw bentonite

Table 4. 1 Proximate analysis and physicochemical characterization of raw bentonite

| Parameters | Result |
|---|---|
| Moisture content (%) | 10.1 |
| Bulk density(g/cm$^3$) | 1.04 |
| Swell index (ml/2g) | 18.12 |
| pH | 8.1 |

Moisture content is one of the properties that determine the adsorption properties of bentonite clay. According to Farihahusnah et al (2011) bentonite clay normally contains between 10% and 18% free moisture. Therefore, removal of the moisture content from the clay increases in void space. From table 4.1 the moisture content of raw bentonite clay was conducted in triplicates and the average moisture content was taken as 10.1%. Similar results have been observed by Toor (2012).

Bulk density is an important parameter for consideration in the design of adsorption towers for use either in pilot plant or large commercial applications. It affects the overall performance of adsorption process. Bulk density proportional to the particle size. Bulk density is defined as the mass of particles of the material divided by the total volume they occupy. Higher bulk density provides greater volume activity i.e. if density is high adsorption capacity of the clay also high. Therefore, from the table (4.1) the bulk density of raw bentonite clay was 1.04g/cm$^3$.

The Swell Index or Free Swell test is used to determine the general swelling characteristics of bentonite clay.it also helps us to identify the type of bentonite. The result the table (4.1) demonstrated that the bentonite was classified as a swelling type of bentonite/sodium bentonite with an average swell index of 18.12 ml/2g.

### 4.1.1. Chemical composition of raw and acid activated bentonite

Chemical composition and loss on ignition (L.O.I) of raw bentonite was shown in table 4.2

Table 4. 2 Chemical composition of raw bentonite in wt (%)

| Component | Composition (%) |
|---|---|
| $SiO_2$ | 60.24 |
| $Al_2O_3$ | 14.94 |
| $Fe_2O_3$ | 1.88 |
| CaO | 1.24 |
| MgO | 3.84 |
| $Na_2O$ | 2.06 |
| $K_2O$ | 0.22 |
| MnO | 0.02 |
| $P_2O_5$ | 0.06 |
| $TiO_2$ | 0.09 |
| $H_2O$ | 8.80 |
| LOI | 7.17 |

Table 4. 3 Elemental analysis for raw and acid activated (0.1MH2SO4 T=30OC) bentonites

| Elements (%) | CK | O K | Na K | MgK | Al K | Si K | K K | Ca K | Ti K | FeK |
|---|---|---|---|---|---|---|---|---|---|---|
| Raw bentonite | 6.34 | 50.82 | 1.78 | 2.48 | 8.54 | 26.81 | 0.86 | 0.74 | 0.18 | 1.45 |
| Activated bentonite | 6.1 | 53.33 | 0.32 | 2.23 | 7.88 | 27.77 | 0.15 | 0.58 | 0.19 | 1.44 |

Table (4.2) shows the chemical composition of natural/ raw bentonite clay and indicates that the presence of silica and alumina as major constituents with a very small amount of iron, calcium, magnesium, sodium, potassium, titanium and phosphors oxides in the form of impurities. Chemical analysis is a good indicator of quality. From table (4.2) the ratio of $Na_2O$

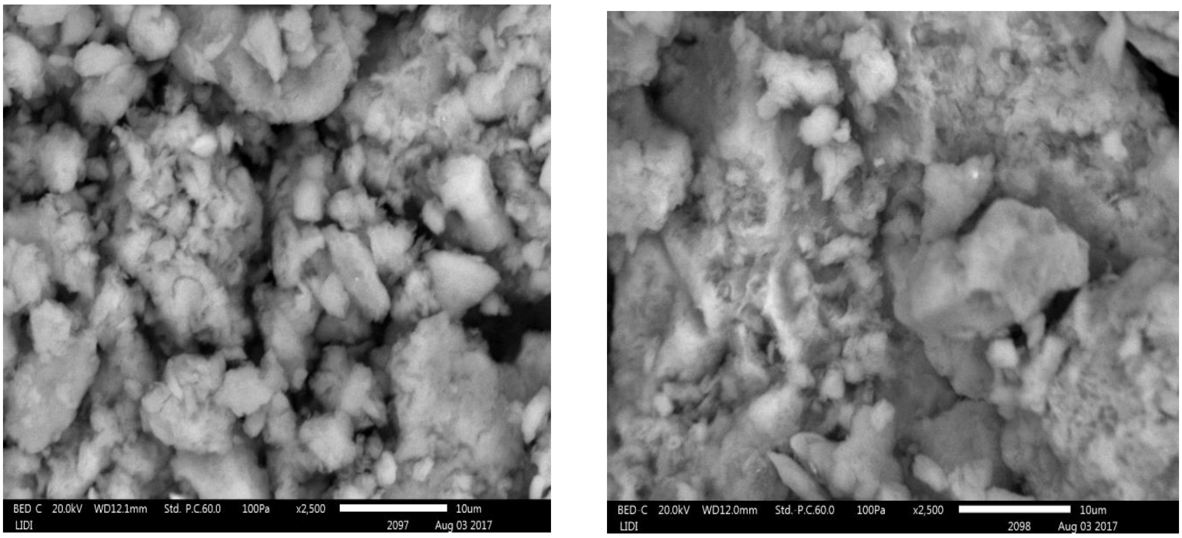
to CaO is 1.67, a value in the range of 1-2 which indicates the bentonite has a tolerable quality requiring further processing (kultic et al., 2012). In Addition, the ratio 1.67 was a value greater than 1 which indicates the presence of a swelling type of bentonite (Basim, 2011, Taha et al., 2011). Therefore, the clay was classified as sodium bentonite.

Acid activation modifies the structure of bentonite as indicated above table (4.3) by changing chemical composition. The composition of $SiO_2$ was increased from 26.8 to 27.8% as a result of acid activation, whereas the composition of other components decreased after activation. Almost similar results were reported by Usman et al., (2012) and Taha et al., (2011). It is expected that the exchangeable cations such as $Ca^{+2}$, $K^{+}$, and $Na^{+}$ were removed during the acid activation of bentonite and replacement of exchangeable cations (K+, Na+, Ca2+) with hydrogen ions and leaching of Al3+, Fe3+, and Mg2+ from the octahedral and tetrahedral sites in bentonite. This leads to creating vacant sites on the surface of the clay as consequences the adsorptive capacity was increased. Even though, traces amount of these elements remains in the activated bentonite due to due to the presence of impurities, mainly, feldspar that has calcium, sodium, and potassium, and is resistant to acid attack (Motlagh et al.,2011).

## 4.2. Characterization of Raw and Acid Modified Bentonite Clay

### 4.2.1. Morphology Study of Raw and Modified Bentonite Clay

Raw and modified bentonite surface was examined by scanning electron microscopy (SEM) which describes the information of surface morphology. The SEM of raw and acid activated bentonite clay was shown in in fig 4.1(a-b) respectively.



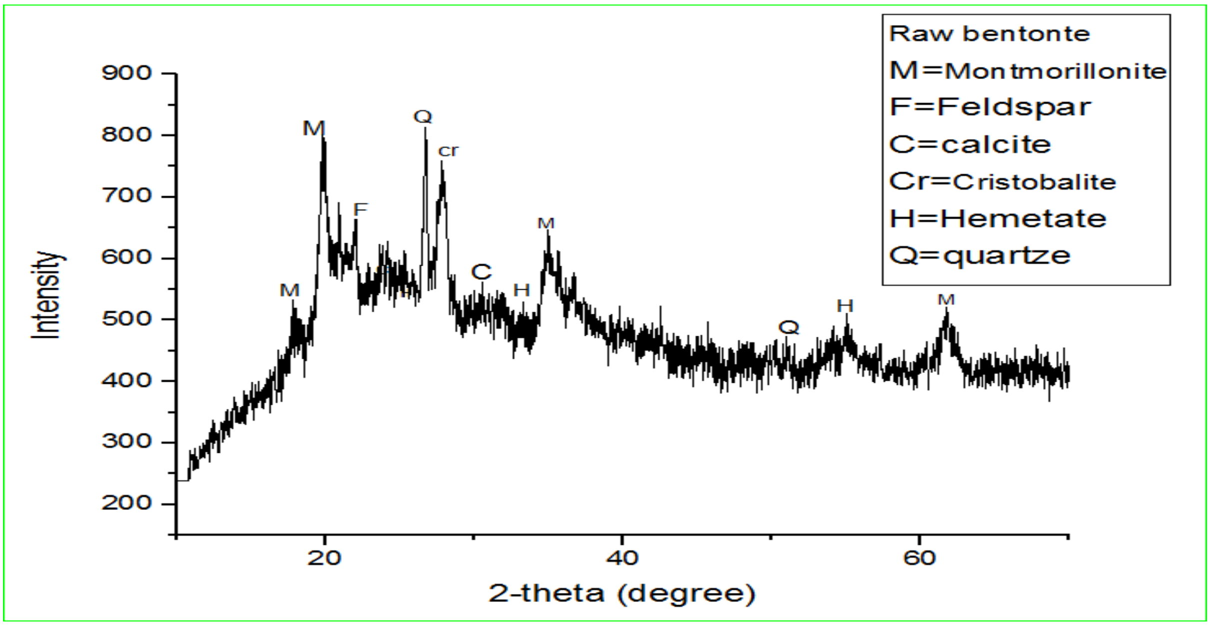
(a) (b)

Figure 4. 1 SEM image of Raw Bentonite (a) Modified Bentonite (0.1M@30oC) (b)

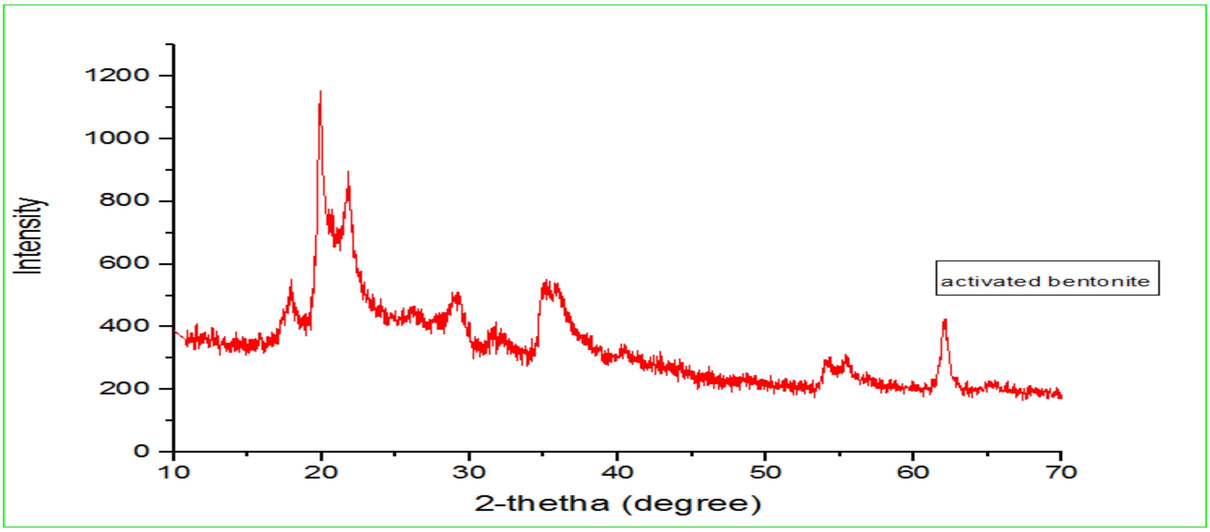
From the above figure, the surface morphology of raw Bentonite is different from the modified ones which means the treatment may alter the physico-chemical and porosity of the material. The treatment with sulfuric acid was expected to partially remove exchangeable cations making the clay surface as what can observe in figure (4.1b). Figure 4.1b also shows the appearance of perforation probably due to leaching of structural materials that might have exposed the active sites on modified bentonite. Moreover, the appearance of the agglomerated surface is observed due to acid treatment. This result was also found by (Toor, 2014) in the modification of raw bentonite using HCl.

### 4.2.2. XRD Study of Raw and Modified Bentonite Clay

The XRD patterns of the natural and acid–activated samples are given in Fig. 4.2. The natural bentonite contains montmorillonite (M) as the dominant clay mineral. Montmorillonite seems well crystallized in the sample. Other accessory minerals were found to be quartz, cristobalite ($SiO_2$), calcite, and feldspar (alumina and silica ($SiO_2$)) (Motlagh, 2011; Bulut, 2008). The most pronounced modification occurs in the montmorillonite peak (the peak appearing at 2thetha angle about 35, 61.72 $^oC$) which shows a reduction in intensity as a result of the acid attack. The reduction in intensity indicate that the crystallinity of the montmorillonite considerably affected by acid activation. This means that the process favors the production of amorphous phase by decomposing montmorillonite structure. Other accessory minerals such as cristobalite, and calcite also showed a reduction in intensity. On the other hand, since the montmorillonite peak is still present after acid treatment, we may assume that the structure has been partially destroyed.



(a)



(b)

Figure 4. 2 X-ray diffraction patterns for raw (a) and activated bentonite (b)

### 4.2.3. FTIR Study of Raw and Modified Bentonite Clay

One important characteristic properties of raw bentonite are surface function groups present that are largely characterized by the FTIR spectroscopy method. In other words, FTIR of the activated bentonites helps the identification of the minerals present in the bentonite. The FTIR spectra of raw and acid activated samples were performed in the range from 4000 to 400 cm$^{-1}$ to investigate the effect of activation on the chemical composition of the bentonite.

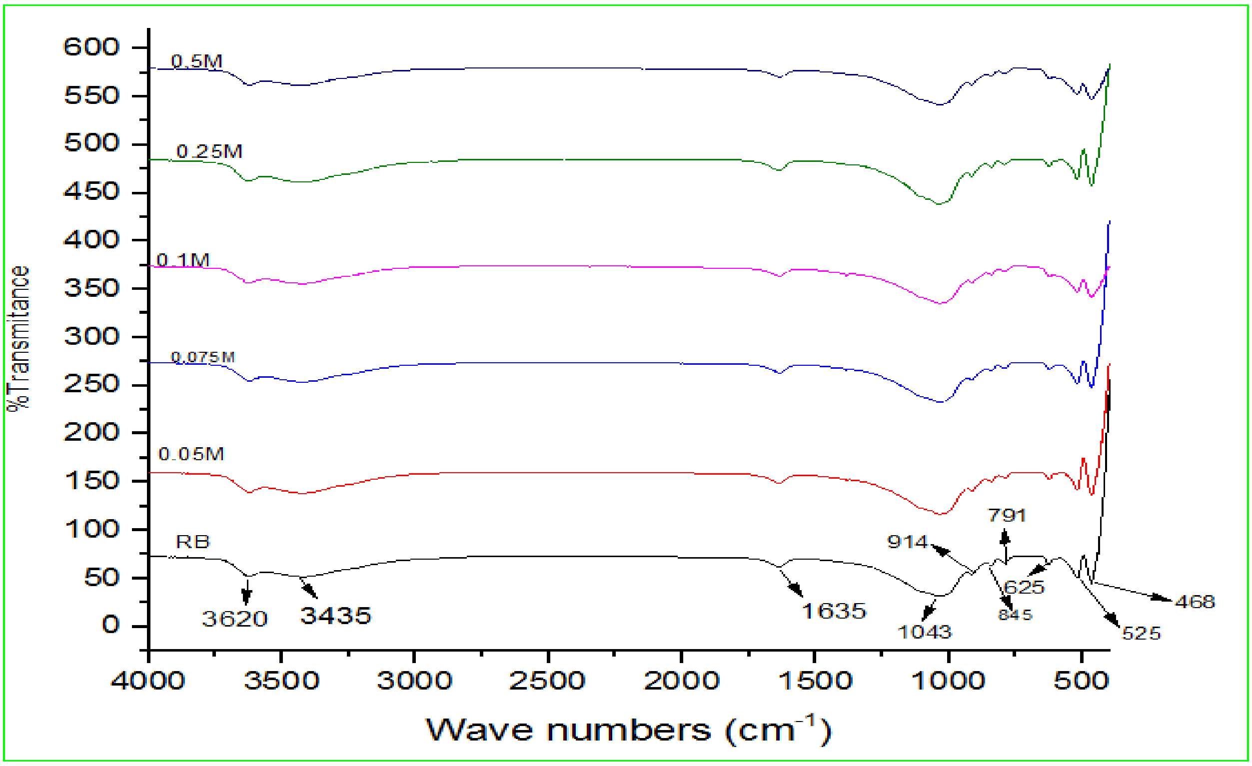


Figure 4. 3 FTIR spectra RB and bentonite modified by AA at different acid concentrations

The IR spectrum of raw bentonite indicates that montmorillonite is the dominant mineral phase in this bentonite (Figure 4. 3). The absorption band at 3620 cm$^{-1}$ is due to stretching vibrations of structural OH groups of montmorillonite. The natural bentonite has characteristic montmorillonite with a single sharp band at 3620 cm$^{-1}$ and a broad band at 3435 cm$^{-1}$ of the OH stretching vibration of structural hydroxyl groups and water coordinated to octahedralAl$^{3+}$ Cations respectively. In the lower frequency region, montmorillonite had a strong band at 1043 cm$^{-1}$ ponding to the Si–O stretching (in-plane) vibration of bentonite mineral. The absorption band at 1635 cm$^{-1}$ was attributed to the OH deformation mode of water. IR peaks at 914 and 845 cm$^{-1}$ was attributed the OH bending vibrations (A1MgOH), and ($A1_2OH$) respectively (Komadel et al, .1990, and Christidis et al. 1997). The clay spectrum also contains a band at 791 cm-1 which indicated the presence of cristobalite/quartz (Motlagh, 2011), and the bands at 525 and 468 cm-1 correspond to Si–O–Al (octahedral) and Si–O–Si bending vibrations respectively.

## 4.3. Effect of acid activation

The changes in the functional groups provide the indication of the modifications that occurred during the activation process. During the acid-leaching of the clay samples, the protons from the acid medium penetrate into the clay structures attacking the OH groups thereby causing the alteration in the adsorption bands attributed to the OH vibrations and octahedral cations. The A-O-R vibration at 625 cm-1(with R = Al, Mg, Fe (Li)) and the Al-O-Si vibration at 525 $cm^{-1}$ decrease after $H_2SO_4$ treatments. This shows the decrease of the relative amounts of octahedral Al and Mg in H2SO4 treated samples since a part of the octahedral sheets has been dissolved by the acid. The intensity of the band at 468 cm $^{-1}$ (Si-O-A1 and Si-O-Mg coupled by OH vibrations or Si-O bending vibrations) is essentially unchanged this is due to high resistance of the bands to acid attack. Generally, no important changes were observed.

### 4.3.1. Adsorption of Congo red on Acid Activated Bentonite

The adsorption performance of differently modified bentonite adsorbents for percent removal of congo red was studied at 30°C. The effect of acid concentration on adsorption performance was investigated with an initial dye concentration of 100mg/L clay dosage for 2 hours is shown in Figure 4.4.

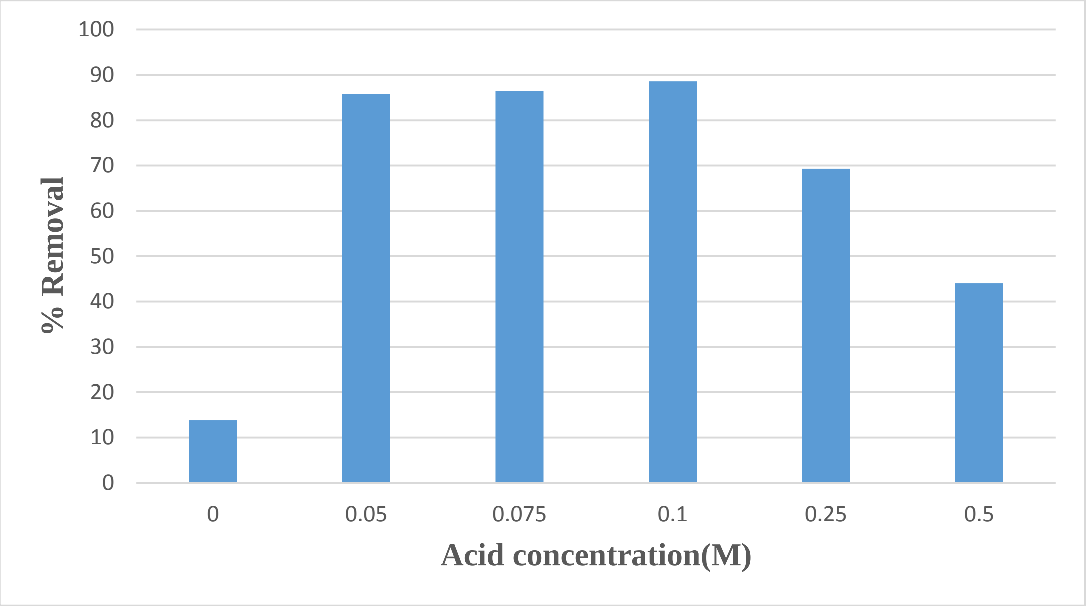


Figure 4. 4 Effect of acid activation on the adsorption of CR on bentonite modified by AA at different acid concentration (initial dye concentration 100mg/L, adsorbent dosage 1g, pH=5.5)

As shown in figure 4.4, the removal capacity of raw bentonite is 13.8%. Modified bentonite treated at 0.05, 0.075, 0.1, 0.25 and 0.5M concentration of acid resulted in dye removal capacity of 85.78%, 86.4%, 88.6%, 69.27% and 44% respectively. All bentonite samples modified at different acid concentration showed superior removal efficiency than raw. This could be due to increase in surface area and pore volume of treated bentonite.

Moreover, the removal capacity of Congo red slightly increased with acid concentration until it reaches 0.1 $H_2SO_4$.The reason for increasing the adsorption capacity/removal capacity is due to increasing of surface area. However, increasing the acid concentration to 0.5 resulted in the decrement of adsorption performance to 44%. This decrease could be associated with to the collapse of structure and decrease in surface area, as a result of excessive leaching of cations, and agglomeration

### 4.3.2. Effect of Activation Temperature on Adsorption of Congo red

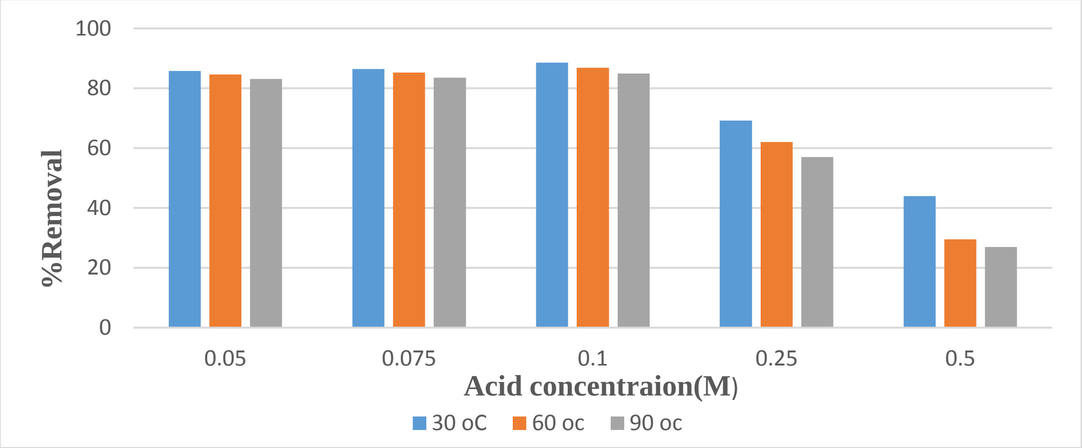


Figure 4. 5 Effect of activation temperature on the adsorption of CR on bentonite modified by AA at different acid concentration (initial dye concentration 100mg/L, adsorbent dosage 1g, pH=5.5)

It is evident from Figure 4.6 that as the acid concentration increases the amount of congo red removal increased at all temperatures. However, the percent of dye removal was decreased as the temperature was increased keeping the time constant. The decreasing of dye removal is due to deeper penetration of the acid molecules which results in the collapse of the structure.

## 4.4. Adsorption Performance and Kinetics of Modified Bentonite

### 4.4.1. Statistical Analysis of adsorption Process

A general full factorial design method of Response Surface Methodology with a total of 27 experiments was done to determine the individual and interaction effects of the selected variables on the adsorption of congo red dye. The single dependent output response of percentage removal (% R) was obtained from the independent input variables. The linear effects of three independent variables initial dye concentration, time, solution pH, each with three levels were chosen as independent variables with designated factors as A, B, and C, respectively.

Table 4. 4 Summary of statistical analysis using ANOVA

| | ***Sum of squares*** | ***DF*** | ***Mean square*** | ***F-Value*** | ***Prob >F*** | |
|---|---|---|---|---|---|---|
| Model | 1241.65 | 9 | 137.96 | 73.11 | < 0.0001 | Significant |
| A | 250.21 | 1 | 250.21 | 132.59 | < 0.0001 | |
| B | 705.75 | 1 | 705.75 | 374.00 | < 0.0001 | |
| C | 172.55 | 1 | 172.55 | 91.44 | < 0.0001 | |
| $A^2$ | 5.40 | 1 | 5.40 | 2.86 | 0.1091 | |
| $B^2$ | 103.75 | 1 | 103.75 | 54.98 | < 0.0001 | |
| $C^2$ | 0.25 | 1 | 0.25 | 0.13 | 0.7192 | |
| AB | 2.96 | 1 | 2.96 | 1.57 | 0.2274 | |
| AC | 0.17 | 1 | 0.17 | 0.088 | 0.7706 | |
| BC | 0.62 | 1 | 0.62 | 0.33 | 0.5737 | |
| Residual | 32.08 | 17 | 1.89 | | | |
| Cor Total | 1273.73 | 26 | | | | |

From table (4.4) the Model F-value of 73.11 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case, A B, C, $B^2$, are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. In this case time, initial dye concentration and pH are significant model terms.

Table 4. 5 Measure of significance using $R^2$ and adequate precision

| | | | |
|---|---|---|---|
| Std. Dev. | 1.37 | R-Squared | 0.9748 |
| Mean | 81.34 | Adj R-Squared | 0.9615 |
| C.V. | 1.69 | Pred R-Squared | 0.9338 |
| Press | 84.37 | Adeq Precision | 31.306 |

The goodness of the model was checked by the determination coefficient (R) as shown in the Table (4.5). The regression coefficient ($R^2$) quantitatively evaluates the correlation between the experimental data and the predicted responses. The R value is always between 0 and 1. The closer the $R^2$ value is to 1, the stronger the model is and the better it predicts the response. In this case, the value of the determination coefficient (R =0.9748) indicates that 97.48 % of the variability in the response could be explained by the model. In addition, the response surface

Results of $R^2$= 0.9748 and Adj-$R^2$= 0.9615 obtained explicates that the predicted values were found to be in good agreement with experimental values. Since the $R^2$ value is closer to 1.0 it indicates that the regression line perfectly fits the data. Similar to that in this investigation, $R^2$ obtained was 0.9748, which was close to 1.

The "Pred R-Squared" of 0.9338 is in reasonable agreement with the "Adj R-Squared" of 0.9615."Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. In this study 31.306 indicates an adequate signal. This model can be used to navigate the design space.

### 4.4.2. Development of model equation

A model equation is a representative equation in which it represents the whole model with a single mathematical relation that helps to maximize response (in this case removal capacity) and the operating conditions. The mathematical relationship between dependent (response variable) and the independent variables such as time, pH, and initial dye concentration in terms of coded and actual factors can be determined from the design experiment. The model equation that relates the response to independent variables in terms of coded factors and actual factors was given below.

Table 4. 6 Model equation in coded and actual factors

| The final model equation in terms of coded factors: | Final model equation in terms of actual factors: |
|---|---|
| | capacity removal= |
| Dye remova(%) = | |
| +79.06 | +98.54271 |
| +3.73 * A | +3.24479*Time |
| -6.26 * B | -0.046118*dyeconcentration |
| -3.10 * C | -2.52524*pH |
| $-0.95* A^2$ | $-0.23708*\text{Time}^2$ |
| $+4.16* B^2$ | $+2.59896\text{E-00}*\text{dyeconcentration}^2$ |
| $+0.20 * C^2$ | $+0.051250*\text{pH}^2$ |
| +0.50 * A * B | +6.20833E-004* Time * dye concentration |
| +0.12 * A * C | +0.029375*Time*pH |
| +0.23 * B * C | +2.84375E-004 * dye concentration * pH |

From the regression model equation developed in terms of coded factors, the response removal capacity was affected by linear terms time, pH and initial dye concentration (B and C), the pure quadratic term ($B^2$). On the basis of the coefficients in equations, it was evident that the percentage of response removal capacity increases with the time (A) and decreased as the concentration (B), and pH (C) increased. Time, concentration and pH have a positive linear effect on capacity removal but concentration has a more great effect on removal capacity as compared to time and pH. Pure quadratic terms ($B^2$, and $C^2$) have positive effects and $A^2$ has a negative effect on the response /removal capacity.

## 4.4.3. Effect of Individual Factors on Removal capacity

### 4.4.3.1. Effect of Time

The effect of contact time on the amount of Congo red adsorbed on bentonite modified by AA has been experimentally investigated in CR solution at 100mgL$^{-1}$ initial dye concentration and pH 5. Figure 4.6 shows that the effect of time on percentage removal of CR on AA bentonite. It has been observed that the CR adsorption increased with an increase in time. A CR removal of 88.35% and 96.55% was obtained as the time increases from 2 to 6 hrs. It is observed that the maximum percent removal by AA bentonite is 97.58% i.e. the equilibrium was nearly reached after 12hr. The high removal of dye initially is attributed to the availability of a large number of vacant sites for adsorption of Congo red. Similar results have been reported by Lian et al., (2009) for the adsorption of Congo red on Ca-bentonite.

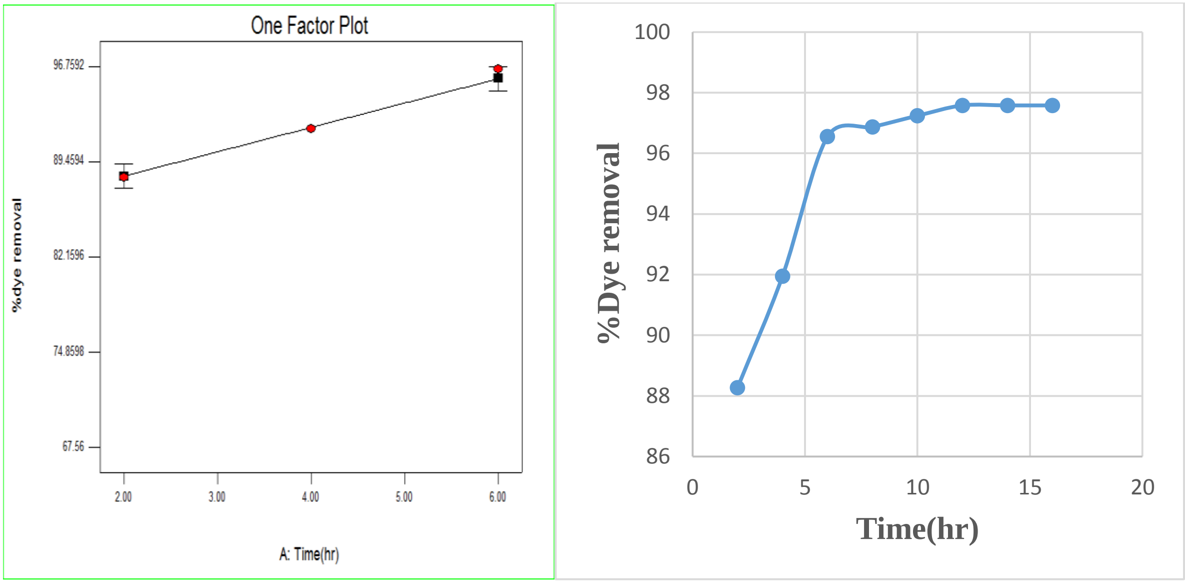


Figure 4. 6 Effect of time on CR adsorption

#### 4.4.3.2. Effect of Initial Dye Concentration

The adsorption of Congo red is influenced significantly by initial concentration. In this study, the initial concentration of Congo red was varied from 100 to 900 mg/l while maintaining other variable constant (adsorbent dose at 1 g, time at 6 hours and pH 5). Figure (4.5) show the effect of variation of the initial concentration on the percentage of congo red removal. It was evident that percentage removal of congo red decreased from 96.55 % to 82.5 % when the initial concentration increased from 100 to 900 mg/l. The reduction in the removal efficiency was probably due to increased concentration of the congo red in the solution for the same number of sites and surface of the adsorbent. In other words, this decrease in percentage removal may be attributed to lack of sufficient surface sites to accommodate much more congo red concentration present in the solution. At lower concentration, all dye molecules present in solution could interact with binding sites and thus percentage adsorption was higher than those at higher concentration. Similar results have been reported by Lian et al., (2009) for the adsorption of Congo red on Ca-bentonite and Toor, (2010).

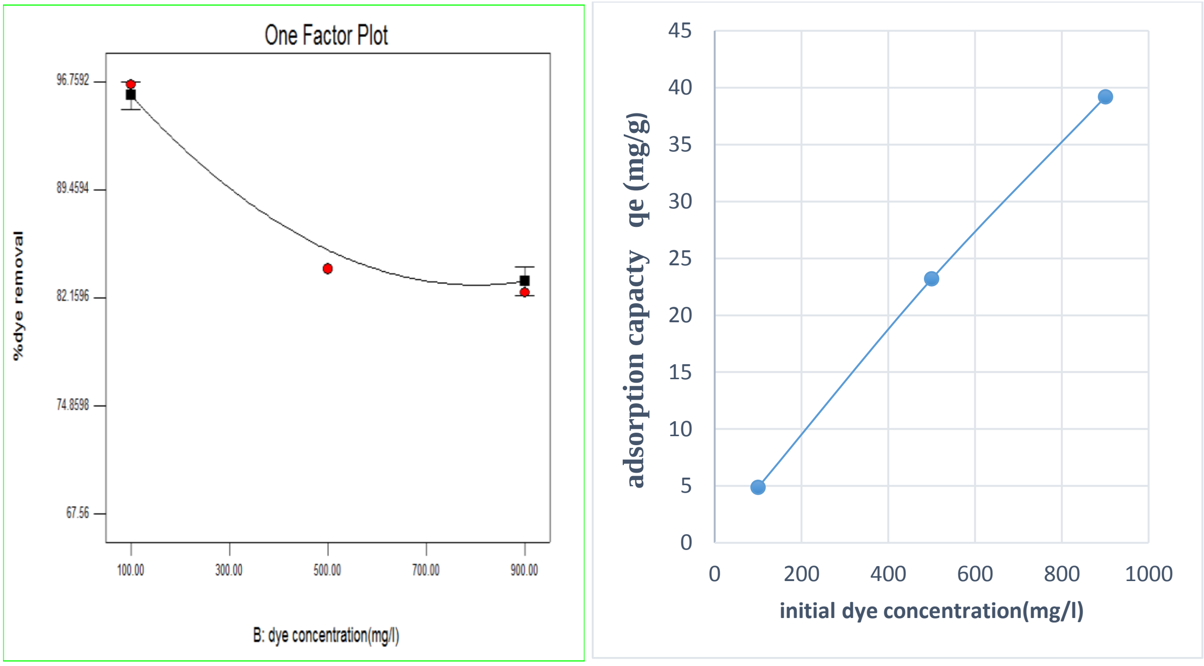


Figure 4. 7 Effect of initial dye concentration on adsorption efficiency and capacity

#### 4.4.3.3. Effect of pH

The initial pH of the dye solution is the important operational parameter which can significantly affect the adsorption mechanisms of the dye molecules and the adsorbent. The color of CR changes from red to blue in the presence of inorganic in pH range of 2 - 4 (Acemioğlu et al., 2004). Under a high alkaline condition, i.e. pH 10 – 12, the solution of CR remains red but the red color is different from the original color of the solution. Therefore, the red color is stable in the pH range of 5-10. In order to optimize the pH for maximum removal efficiency, adsorption experiment was conducted in the initial pH range from 5 to 9 with initial Congo red concentration of 100 mg/l and an adsorbent dose of 1 g, as shown in Figure (4.2). The maximum adsorption of Congo red was around 96.55 %, 93.4 % and 88.4 % at the pH 5, 7 and 9 were observed respectively. The value at pH 5 was the highest removal efficiency obtained as compared to the efficiencies obtained at other pH values. With an increase of pH from 5 to 9, Cong red removal efficiencies slightly decreased.

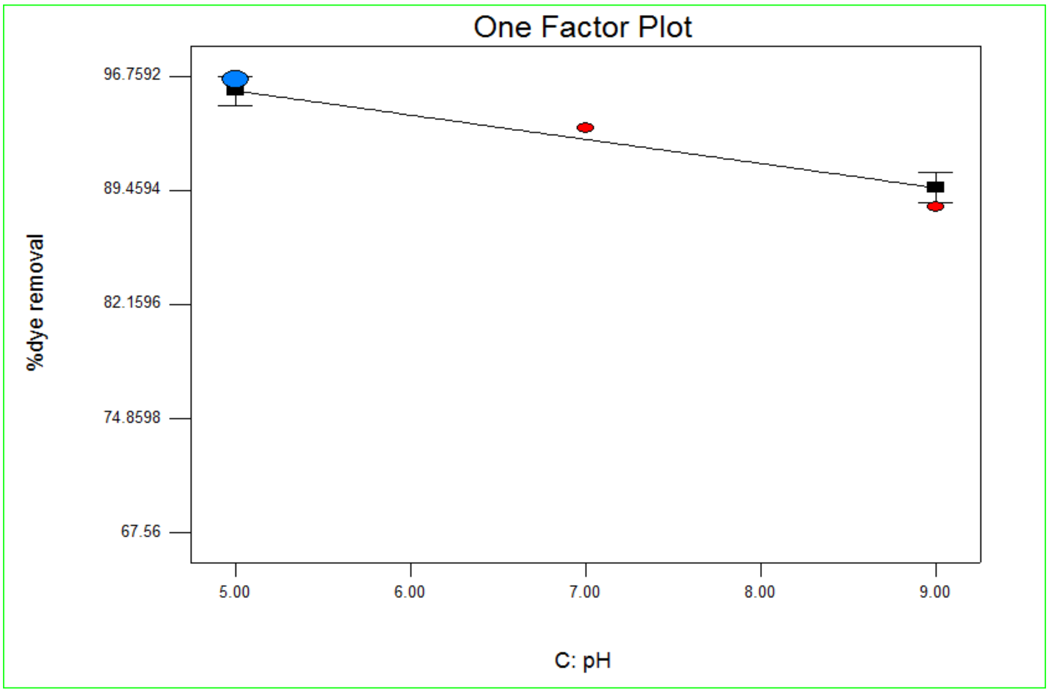


Figure 4. 8 Effect of pH on the adsorption of Congo red

This slight decrease in CR adsorption may be attributed to the repulsion between the anionic dye molecules and negatively charged clay particles (Lian et al., 2009). The results reveal that the effect of pH on the adsorption of CR is not significant especially when the concentration is increased to 500and 900 mg/l. This may be due to the alkaline nature of bentonite that neutralizes the acidic pH of the CR solution.

## 4.5. Adsorption Isotherms

Adsorptions isotherms are important to investigate the interaction of adsorbate molecules and adsorbent surface. Hence, two well-known isotherms were selected in this study, namely Langmuir, and Freundlich isotherms.

The applicability of the isotherm equation is compared by judging the correlation coefficients, $R^2$.

### 4.5.1. Langmuir Isotherm

A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the adsorbent (Lian et al., 2009)

Figures (4.9) showed Langmuir isotherm fittings for AA activated bentonite adsorbent with high linear regression. The maximum monolayer adsorption capacity AA activated bentonite, $q_m$, and constant related to the binding energy of the sorption system, Ka, is calculated from the slop and intercept of this plot. The maximum monolayer adsorption capacity $q_m$ was 47.62 mg/g and the constant related to the binding energy of the sorption system, Ka was 0.036.

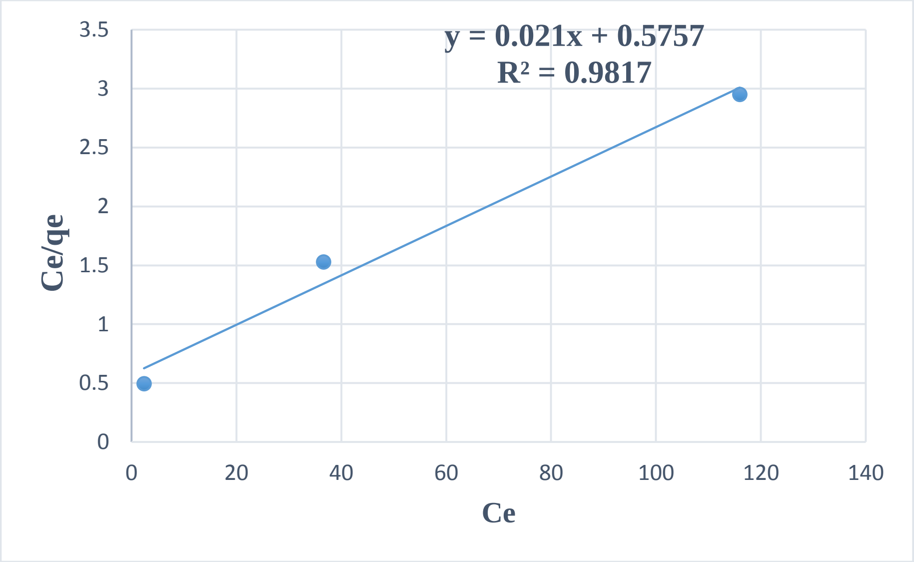


Figure 4. 9 Langmuir adsorption isotherms for CR adsorption (linear)

The favorability and feasibility of adsorption process can be determined by the separation factor $R_L$ in the analysis of data by Langmuir isotherm table (4.7).

Table 4. 7 Initial dye concentration and separation factor

| Number | $C_0$ (mg/g) | $RL = \frac{1}{1+KaCo}$ |
|---|---|---|
| 1 | 100 | 0.217 |
| 2 | 500 | 0.053 |
| 3 | 900 | 0.0299 |

The nature of the adsorption process to be either unfavorable (RL> 1), linear (RL= 1), favorable (0 < RL< 1) or irreversible (RL= 0). Here, RL values obtained are listed in Table (4.7). In the present study all the RL-values for the adsorption of Congo red onto AA bentonite lies between 0 and 1 shows that the adsorption process is favorable.

### 4.5.2. Freundlich Isotherm

The Freundlich model is applicable to heterogeneous systems and it involves the formation of multilayers. Figures (4.10) show Freundlich isotherm fittings AA bentonite clay adsorbent. Freundlich constants, i.e. adsorption capacity, $K_f$, and rate of adsorption, n, are calculated from the plots. The adsorption capacity, $K_f$ , and rate of adsorption, n, for AA bentonite clay are 3.09 and 1.83 respectively. The favorability and the nature of adsorption process can be identified from the value of n. In the present study, the value of n is greater than 1 in all cases indicating that the adsorption process is favorable. The comparison of the values of correlation coefficient ($R^2$=0.9817 for Langmuir) and value of correlation coefficient ($R^2$ = 0.997 for Freundlich isotherm) the value of correlation coefficient ($R^2$ = 0.997) is larger than the Langmuir isotherm value. The adsorption of CR dye on AA bentonite clay was better represented by the Freundlich isotherm model rather than the Langmuir isotherm model.

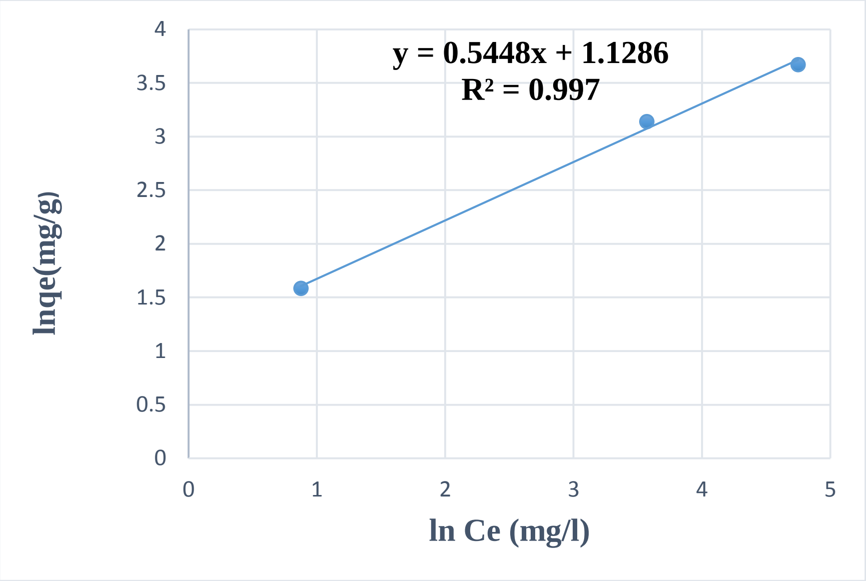


Figure 4. 10 Freundlich adsorption isotherms for CR adsorption (linear)

## 4.6. Adsorption Kinetics

Adsorption kinetics in wastewater treatment is significant because it gives valuable insights into the mechanism of the adsorption process, which is useful for absorber design. The best-fit model was selected based on the linear regression correlation coefficient $R^2$.

### 4.6.1. Pseudo first order kinetics model

Figure 4-11 showed the plot of log (qe-qt) gives a linear relationship from which k1 and qebe determined from the slope and intercept of the plot, respectively. The pseudo first order graphs showed that the values of Log (qe -qt) versus time decreased with time giving the dye ions more opportunity to be taken up by the adsorbent. The calculated values of *qe* as shown in Table 4.8 are much lower than the experimental values. The values of correlation coefficients of pseudo first order model are lower than pseudo second order model (shown below) indicating that the CR adsorption does not obey pseudo first order kinetic.

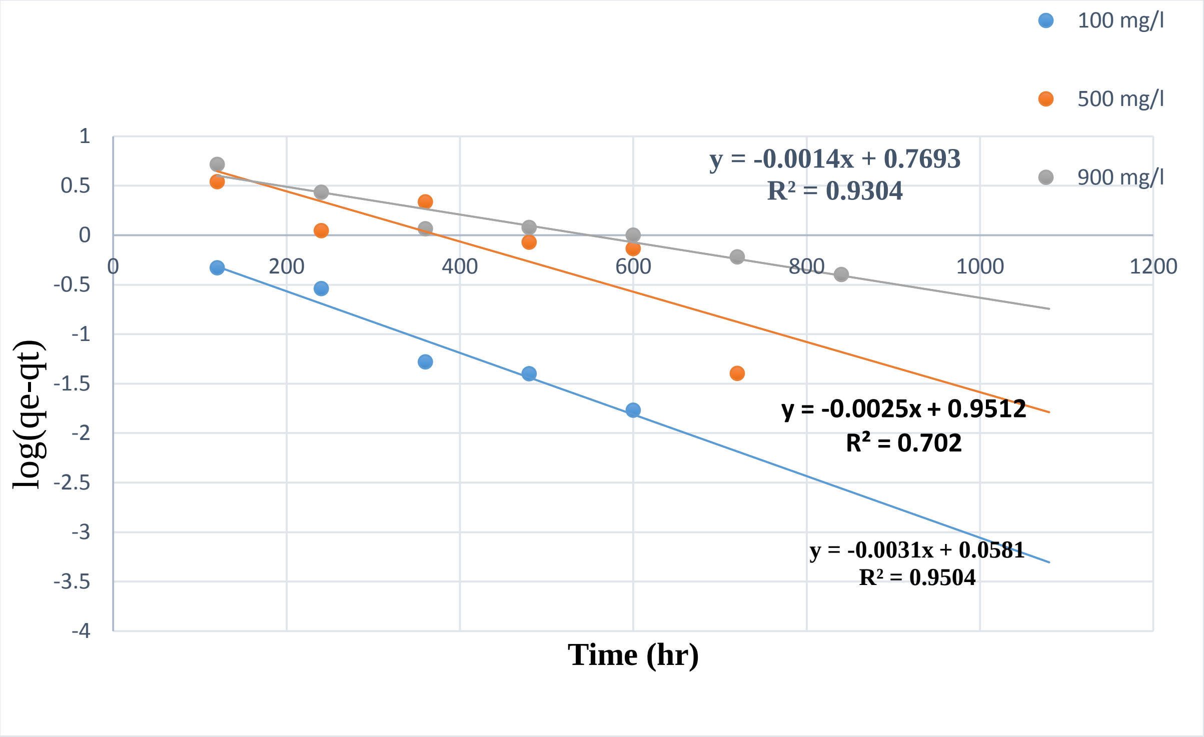


Figure 4. 11 Pseudo-first-order plot for the adsorption of CR onto AA bentonite clay

Table 4. 8 Pseudo first order constants

| Concentration(mg/l) | K1 | qe (experimental) | qe (calculated) | $R^2$ |
|---|---|---|---|---|
| 100 | $7.13 \times 10^{-3}$ | 4.88 | 1.43 | 0.9504 |
| 500 | $5.75 \times 10^{-3}$ | 23.2 | 8.94 | 0.702 |
| 900 | $3.22 \times 10^{-3}$ | 39.9 | 5.87 | 0.9304 |

### 4.6.2. Pseudo-Second Order Model

The pseudo second order model is based on the assumption that the rate limiting step may be chemisorption which involves valence forces by sharing or electron exchange between the adsorbent and the adsorbate (Wang et al., 2008). The maximum adsorption capacities *qe* calculated from the pseudo second order model are in accordance with the experimental values. This implies that the adsorption obeys a pseudo second order model. Similar results for the adsorption of acid dyes have also been reported by other researchers (Özcan and Özcan et al., 2009). The plot of *t/qt* versus *t* is linear showing that chemisorption is the main rate controlling step of the adsorption process.

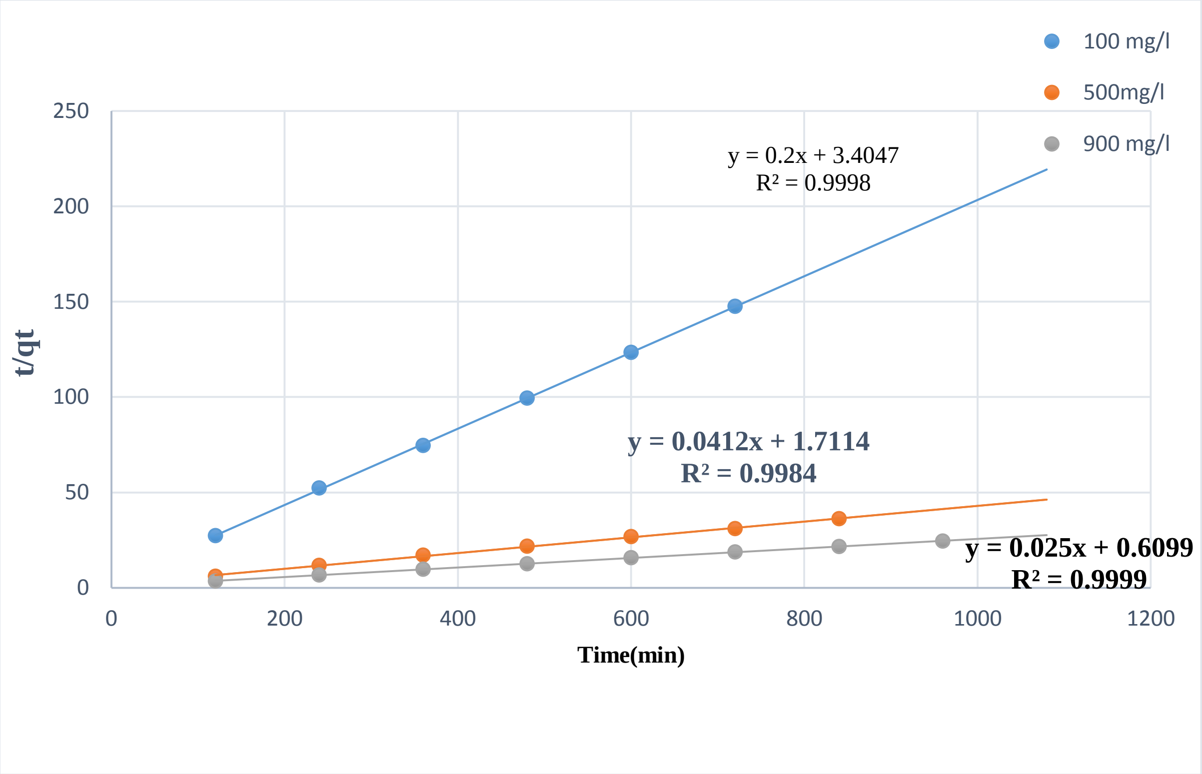


Figure 4. 12 Pseudo-second order plot for the adsorption of CR onto AA bentonite clay

Table 4. 9 Pseudo second order constants

| Concentration(mg/l) | K2 | qe (experimental) | qe (calculated) | $R^2$ |
|---|---|---|---|---|
| 100 | $11.75 \times 10^{-3}$ | 4.88 | 5 | 0.9998 |
| 500 | $992 \times 10^{-4}$ | 23.2 | 24.27 | 0.9984 |
| 900 | $1.025 \times 10^{-3}$ | 39.9 | 40 | 0.9999 |

### 4.6.3. Intraparticle Diffusion Model

A plot of qt versus t $^{0.5}$ should be a linear line which passes through the origin with a slope of Kid and intercepts C when the adsorption mechanism follows the intra-particle diffusion model. The plot of qt versus t $^{0.5}$ for the corresponding adsorbent is given in figure 4-13. The calculated values of Kid with the regression correlation coefficient are summarized in table 4-10.

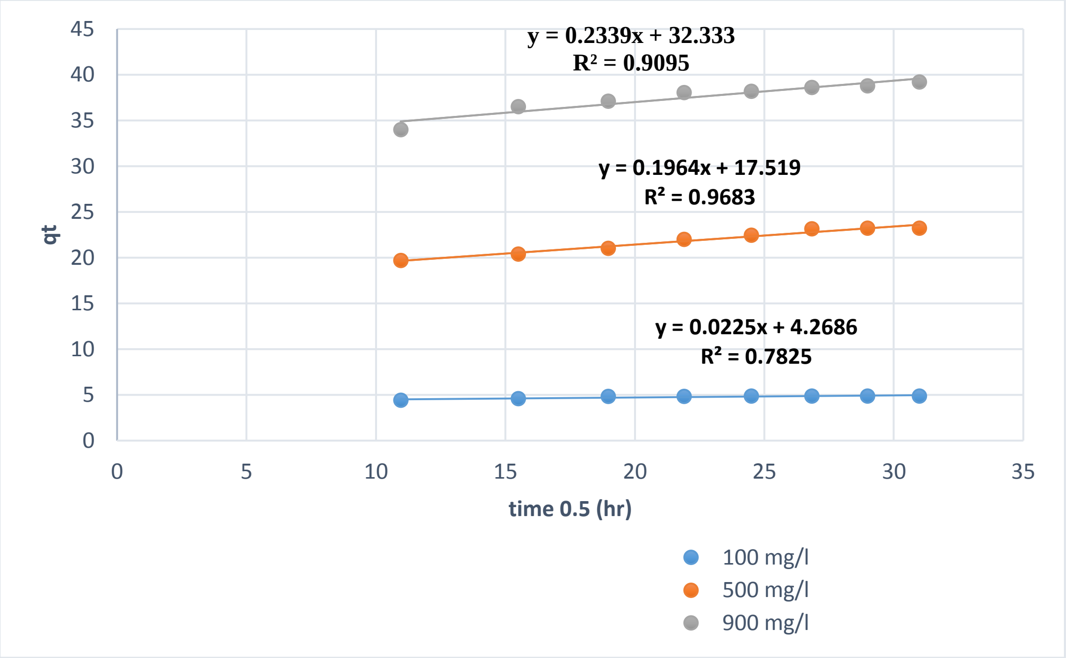


Figure 4. 13 Intra-particle diffusion model plot

Table 4. 10 Intraparticle diffusion constants

| Concentration(mg/l) | $K_{id}$ | $R^2$ |
|---|---|---|
| 100 | 0.0225 | 0.7825 |
| 500 | 0.1964 | 0.9683 |
| 900 | 0.2339 | 0.909 |

From the figure 4.13, it is clear that the graphs linear within a certain range, but the trend of the data did not pass through the origin. The calculated values of Kid and C were summarized in the table. The value of the intercept gives an idea about the thickness of boundary layer i.e. the larger the intercept the larger the boundary layer effect (Özcan et al., 2005). 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 Similar results have been reported by Vimonese et al., (2009) and Özcan et al., (2005).

## 4.7. Optimum conditions for Congo red removal

The objective of optimization is to determine optimum process variables and response for removal of congo red dye removal using bentonite clay. Here the interest is to maximize the removal efficiency of congo red dye using bentonite clay from aqueous solution as much as possible. Table (4.11) shows the working conditions (goals, high and low limits) of the factors and response. Therefore, the best solution chosen by the method of numerical optimization was the one with higher desirability. According to the software, the optimum conditions for the removal of Congo red from aqueous solution using AA bentonite clay were initial dye concentration 100.58 mg/l, pH 5.03, and time 6hr. At these conditions, the maximum removal of Congo red was found to be 95.7439 % t table (4.12).

Table 4. 11 Optimization Constraints for Congo red dye removal

| Name | Goal | Lower limit | Upper limit |
|---|---|---|---|
| Time | is in range | 2 | 6 |
| dye concentration | is in range | 100 | 900 |
| PH | is in range | 5 | 9 |
| capacity removal | maximize | 73.2 | 97.2 |

Table 4. 12 Different alternative optimization solutions for Congo red removal

| Nº | Time(hr) | Dye concentration(mg/l) | pH | %dye removal | Desirability | |
|---|---|---|---|---|---|---|
| 1 | 6.00 | 100.58 | 5.03 | 95.7439 | 0.972 | Selected |
| 2 | 6.00 | 100.00 | 5.24 | 95.4334 | 0.961 | |
| 3 | 5.78 | 100.00 | 5.00 | 95.3946 | 0.960 | |
| 4 | 5.97 | 100.00 | 5.32 | 95.267 | 0.956 | |
| 5 | 5.18 | 100.00 | 5.00 | 94.2827 | 0.922 | |
| 6 | 6.00 | 737.98 | 5.00 | 83.1365 | 0.537 | |
| 7 | 5.36 | 900.00 | 5.00 | 82.0877 | 0.501 | |

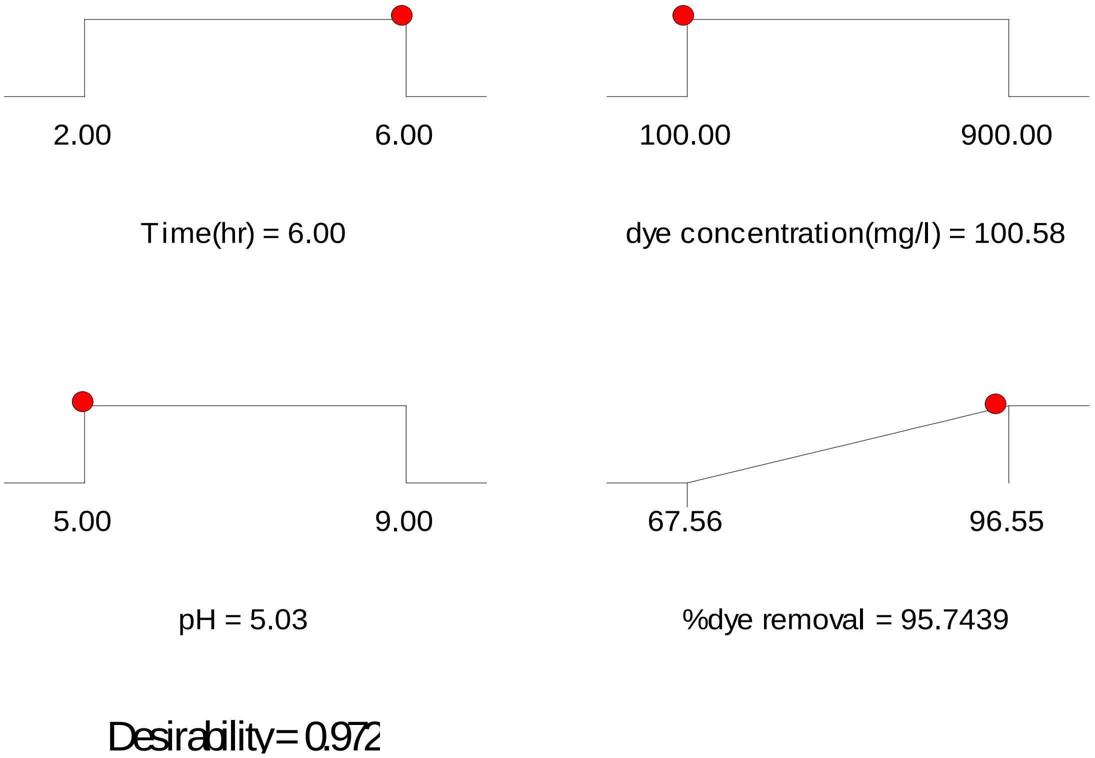


Figure 4. 14 Optimum solutions for congo red removal AA bentonite

# 5. CONCLUSIONS AND RECOMMENDATIONS

## 5.1. Conclusions

This thesis investigates the performance of acid activated bentonite as a low-cost adsorbent to remove CR dye contaminate from aqueous solution. In this study, raw bentonite was modified with a different concentration of the acid solution. The results indicated that the percentage congo red dye removal of bentonite increased initially with an increase in acid concentration until 0.1M $H_2SO_4$. Further increase in acid activation indicated that a decrease in percentage cong red dye removal. Similarly, an increase in activation temperature demonstrated a decrease in percentage congo red dye removal as the time and acid concentration was kept constant.

The effects of acid activation on clay structural properties were determined by XRD, FTIR, SEM, and EDS. From the results, it can be concluded that the acid treatment affected mainly the montmorillonite phases. The octahedral sheet was affected by acid activation resulting in the dissolution of cations ($Mg^{2+}$, $Fe^{2+}$, and $Al^{3+}$) and consequent decomposition of montmorillonite structure. Therefore, it can be concluded that more active sites are generated on the clay surface.

The adsorption capacity of an anionic dye, Congo red on AA bentonite clay was affected by different parameters, such as contact time, initial dye concentration, and pH. It has been evident from the results that the amount of CR dye uptake on AA bentonite clay was found to increase with an increase in initial dye concentration, contact time, but slightly decreased with increase in solution pH. In the batch study, the kinetic experiments revealed that adsorption of dyes was rapid at initial stage followed by a slower phase where equilibrium uptake was achieved. It was also observed that the adsorption was concentration dependent and the maximum adsorption of 39.9 mg/g occurred at an initial dye concentration of 900mg/l for pH of 5 and time of 6 hr.

The adsorption isotherm plays an important role to understand the mechanism of adsorption. The surface phase may be considered as a monolayer or multilayer. Langmuir and Freundlich models are the most widely used to describe adsorption isotherms. The adsorption data exhibited a better fit to Freundlich model. This confirms that the adsorbate does not form a monolayer on the adsorbent surface and rather adsorbs in multilayers. Adsorption kinetics were determined using pseudo first order and pseudo second order models and it was found that CR adsorption process followed pseudo-second-order kinetics models.

Optimal values of process variables which gave maximum percentage removal of CR were selected using full factorial numerical optimization of design expert. The result showed that the optimum condition for the percentage dye removal was 95.74% at the time of 6 hr. , dye concentration100.58 mg/l and pH 5.03 These values were selected from the 7 alternative optimal solutions set by design expert,

## 5.2. Recommendations

- In this study acid activated bentonite was applied to the removal of anionic dye CR. However, to assess the range of applicability of the modified bentonite other organic and inorganic pollutants which pose serious problems in wastewater treatment need to be tested.
- Real dye waste water always consists of more than one dye and could possibly be mixed with another type of dyes such as cationic and anionic. Therefore, much work is necessary to predict the performance of adsorption process for dye removal from real industrial effluents under a wide range of operating conditions.
- It is also evident from the literature review that most of the adsorption studies were based on batch adsorption experiments. The scale up of batch adsorption process of dyes by AA bentonite to a continuous process is very important on a commercial scale.
- In the present study activation time and clay to acid, ratio was kept constant, but these parameters have a great impact on the properties of the bentonite during activation. The activation of bentonite can also carry out with hydrochloric acid and nitric acid. It is also important to find out other activation methods such as thermal treatment and both acid and thermal treatments.
- Complete cost analysis should be important.

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# APPENDICES

## Appendix A: Experimental Data

Table A-1 Moisture content of raw bentonite

| Clay sample | Empty vial (g) | Vial+wet sample(g) | Wet sample(g) | Dry sample | Moisture Content (%) |
|---|---|---|---|---|---|
| 1 | 26.9108 | 27.964 | 1.0532 | 0.1011 | 9.599 |
| 2 | 44.632 | 45.6352 | 1.0032 | 0.1071 | 10.676 |
| 3 | 38.1014 | 39.2044 | 1.10300 | 0.1104 | 10.009 |
| | | | | | Average=10.09% |

Table A-3Swell index of raw bentonite

| Clay sample | initial volume$_1$(ml) | Final volume(ml) | Swell index (ml/2g) |
|---|---|---|---|
| 1 | 10 | 18.5 | |
| 2 | 9 | 17 | 1.0032 |
| 3 | 11 | 19 | 1.10300 |
| | | | Average=18.12 |

Table A-4 Apparent density of raw bentonite

| Clay sample | mass1(g) | mass2(g) | V(ml) | Bulk density(g/cm$^3$) |
|---|---|---|---|---|
| 1 | 17.967 | 25.1642 | 7 | 1.023 |
| 2 | 17.9656 | 25.5997 | 7.2 | 1.06 |
| 3 | 17.9668 | 25.4352 | 7.2 | 1.037 |
| | | | | Average= 1.04 |

Table A-4 pH of raw bentonite

| Clay sample | pH |
|---|---|
| 1 | 8.25 |
| 2 | 8.03 |
| 3 | 8.00 |
| average | 8.1 |

Table A-5: Data for Langmuir isotherm model parameters.

| Initial dye conc.(mg/l) | Final conc. Ce (mg/l) | Adsorption capacity qe(mg/g) | Ce/qe |
|---|---|---|---|
| 100 | 2.4 | 4.88 | 0.495 |
| 500 | 36.6 | 23.2 | 1.53 |
| 900 | 116 | 39.2 | 2.95 |

Table A- 6: Data for Freundlinch isotherm model parameters

| Initial dye conc.(mg/l) | Ln Ce (mg/l) | Adsorption capacity qe(mg/g) | Ln qe |
|---|---|---|---|
| 100 | 0.875 | 4.88 | 1.585 |
| 500 | 3.57 | 23.2 | 3.14 |
| 900 | 4.75 | 39.2 | 3.67 |

Table A- 7: Data for adsorption Kinetics on Adsorption of congo red dye.

| Time (min) | $t^{0.5}$ | qt(mg/g) | | | Log(qe-qt) | | | t/qt | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 100 | 500 | 900 | 100 | 500 | 900 | 100 | 500 | 900 |
| 120 | 10.95 | 4.41 | 19.91 | 34 | -0.33 | 0.542 | 0.716 | 27.2 | 6 | 3.53 |
| 240 | 15.49 | 4.59 | 20.4 | 36.5 | -0.539 | 0.0447 | 0.433 | 52.28 | 11.76 | 6.577 |
| 360 | 18.97 | 4.83 | 21.03 | 37.12 | -1.28 | 0.336 | 0.0644 | 74.58 | 17.12 | 9.69 |
| 480 | 21.9 | 4.84 | 22 | 38.04 | -1.4 | -0.072 | 0.079 | 99.44 | 21.8 | 12.6 |
| 600 | 24.49 | 4.86 | 23.16 | 38.2 | -1.769 | -0.1366 | 0 | 123.4 | 26.7 | 15.7 |
| 720 | 26.83 | 4.88 | 23.22 | 38.6 | | -1.398 | -0.22 | 147.57 | 31 | 18.65 |
| 840 | 28.98 | 4.88 | 23.22 | 38.8 | - | - | -0.397 | | 36.17 | 21.65 |
| 960 | 30.98 | | | 39.2 | - | - | - | - | - | 24.48 |
| 1080 | 32.86 | | | 39.2 | | | | | | |

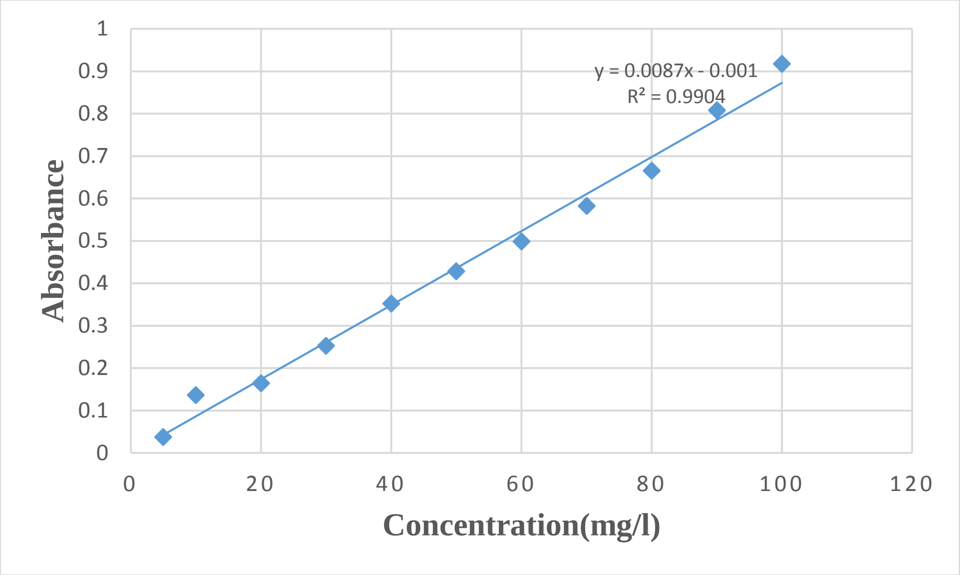
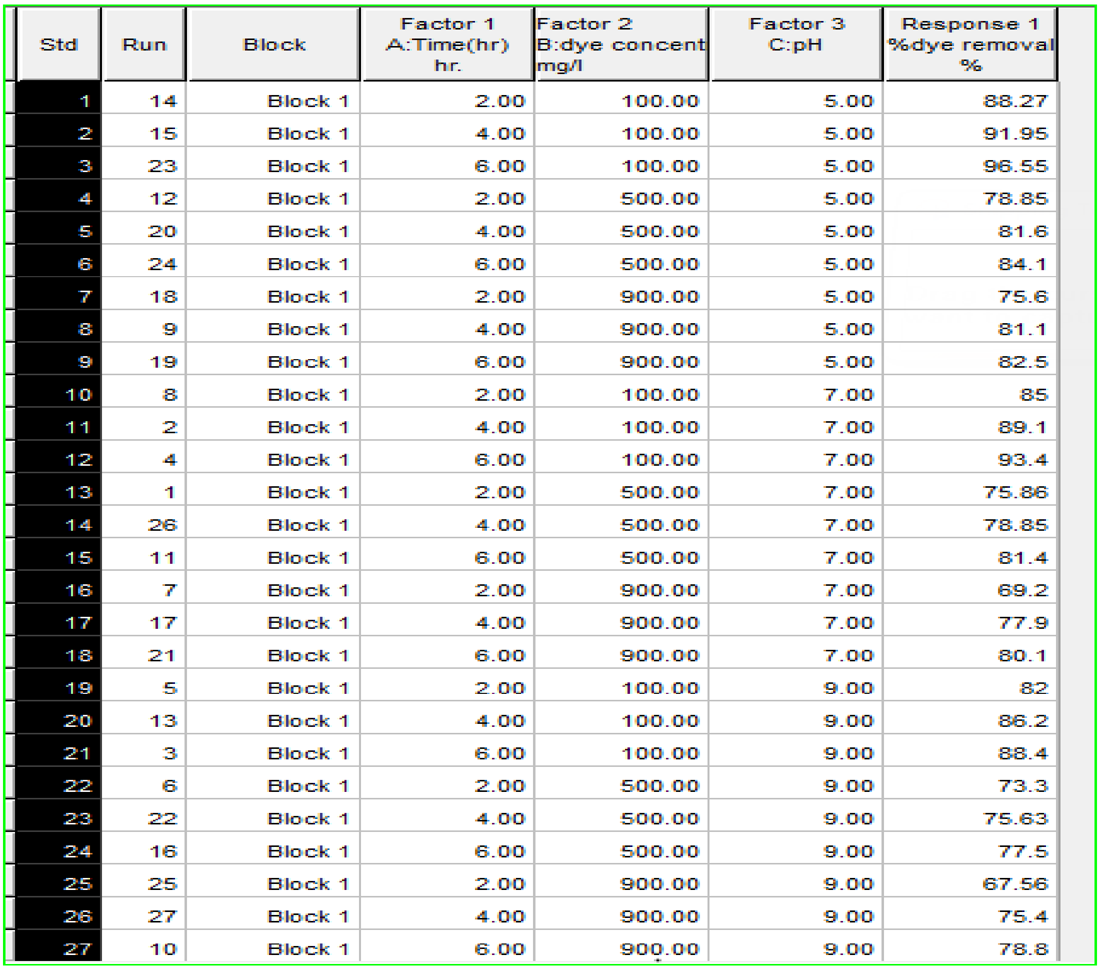


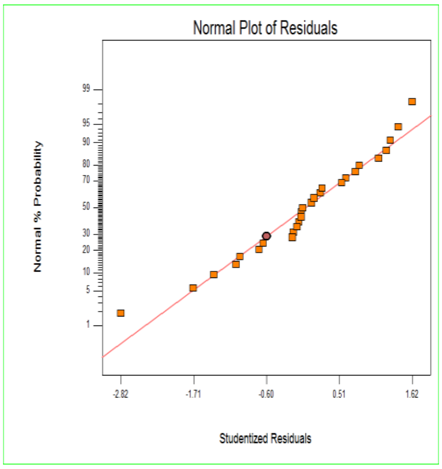
Figure A-7. Calibration graph for determination of dye concentration.

# Appendix B: Experimental Design Outputs

Table B-1: The experimental design matrix for congo red removal



| Std | Run | Block | Factor 1 A:Time(hr) hr. | Factor 2 B:dye concent mg/l | Factor 3 C:pH | Response 1 %dye removal % |
|---|---|---|---|---|---|---|
| 1 | 14 | Block 1 | 2.00 | 100.00 | 5.00 | 88.27 |
| 2 | 15 | Block 1 | 4.00 | 100.00 | 5.00 | 91.95 |
| 3 | 23 | Block 1 | 6.00 | 100.00 | 5.00 | 96.55 |
| 4 | 12 | Block 1 | 2.00 | 500.00 | 5.00 | 78.85 |
| 5 | 20 | Block 1 | 4.00 | 500.00 | 5.00 | 81.6 |
| 6 | 24 | Block 1 | 6.00 | 500.00 | 5.00 | 84.1 |
| 7 | 18 | Block 1 | 2.00 | 900.00 | 5.00 | 75.6 |
| 8 | 9 | Block 1 | 4.00 | 900.00 | 5.00 | 81.1 |
| 9 | 19 | Block 1 | 6.00 | 900.00 | 5.00 | 82.5 |
| 10 | 8 | Block 1 | 2.00 | 100.00 | 7.00 | 85 |
| 11 | 2 | Block 1 | 4.00 | 100.00 | 7.00 | 89.1 |
| 12 | 4 | Block 1 | 6.00 | 100.00 | 7.00 | 93.4 |
| 13 | 1 | Block 1 | 2.00 | 500.00 | 7.00 | 75.86 |
| 14 | 26 | Block 1 | 4.00 | 500.00 | 7.00 | 78.85 |
| 15 | 11 | Block 1 | 6.00 | 500.00 | 7.00 | 81.4 |
| 16 | 7 | Block 1 | 2.00 | 900.00 | 7.00 | 69.2 |
| 17 | 17 | Block 1 | 4.00 | 900.00 | 7.00 | 77.9 |
| 18 | 21 | Block 1 | 6.00 | 900.00 | 7.00 | 80.1 |
| 19 | 5 | Block 1 | 2.00 | 100.00 | 9.00 | 82 |
| 20 | 13 | Block 1 | 4.00 | 100.00 | 9.00 | 86.2 |
| 21 | 3 | Block 1 | 6.00 | 100.00 | 9.00 | 88.4 |
| 22 | 6 | Block 1 | 2.00 | 500.00 | 9.00 | 73.3 |
| 23 | 22 | Block 1 | 4.00 | 500.00 | 9.00 | 75.63 |
| 24 | 16 | Block 1 | 6.00 | 500.00 | 9.00 | 77.5 |
| 25 | 25 | Block 1 | 2.00 | 900.00 | 9.00 | 67.56 |
| 26 | 27 | Block 1 | 4.00 | 900.00 | 9.00 | 75.4 |
| 27 | 10 | Block 1 | 6.00 | 900.00 | 9.00 | 78.8 |



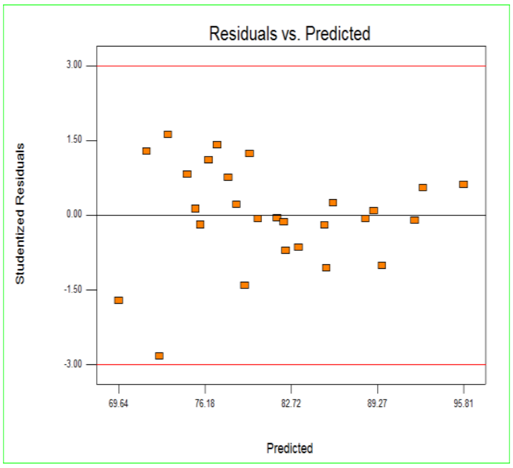


Figure B- 2: Normal plots of residuals    Figure B- 3: Residual vs. Predicted values

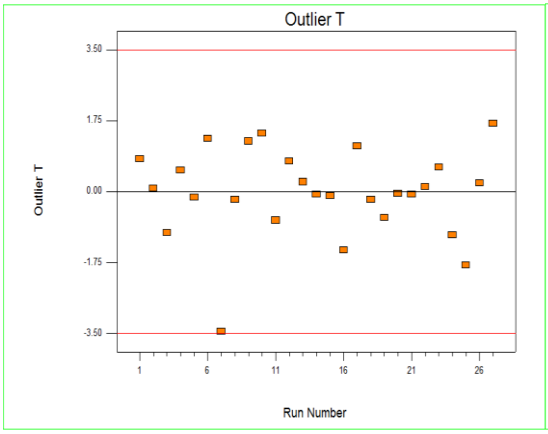


Figure B-4 Plot of outlier from normal distribution plots

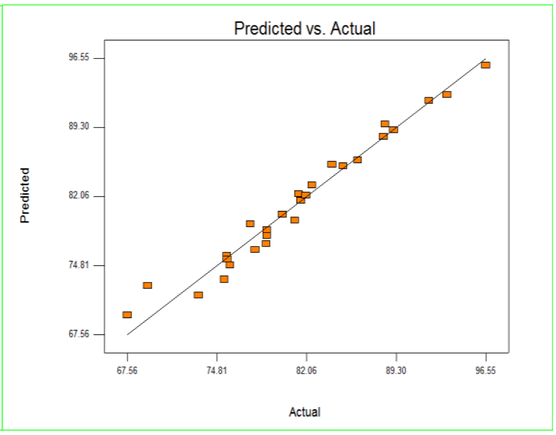
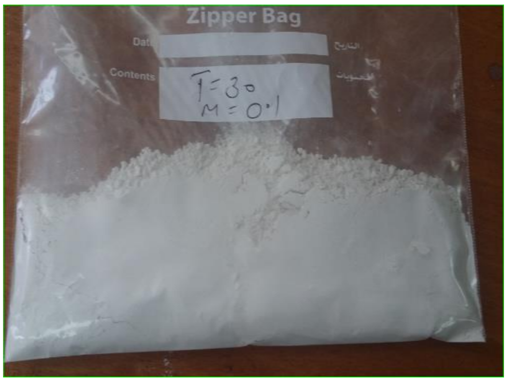


Figure B-5 Predicted vs. Actual

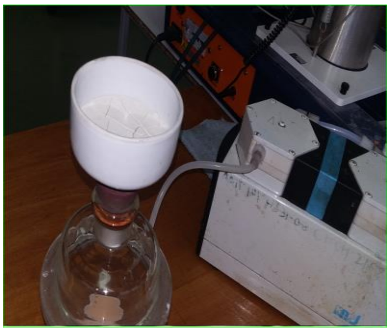
## Appendix C: Experimental Pictures

Raw bentonite



AA bentonite

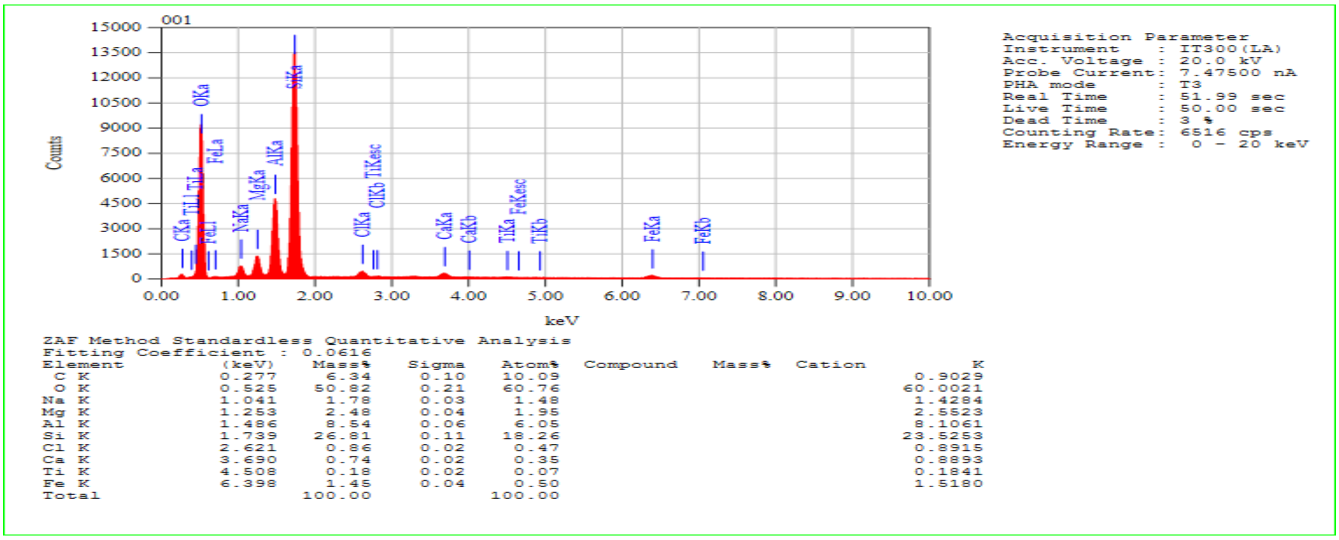
Acid Activation(30,60 and 90ºC)



Vacuum filter

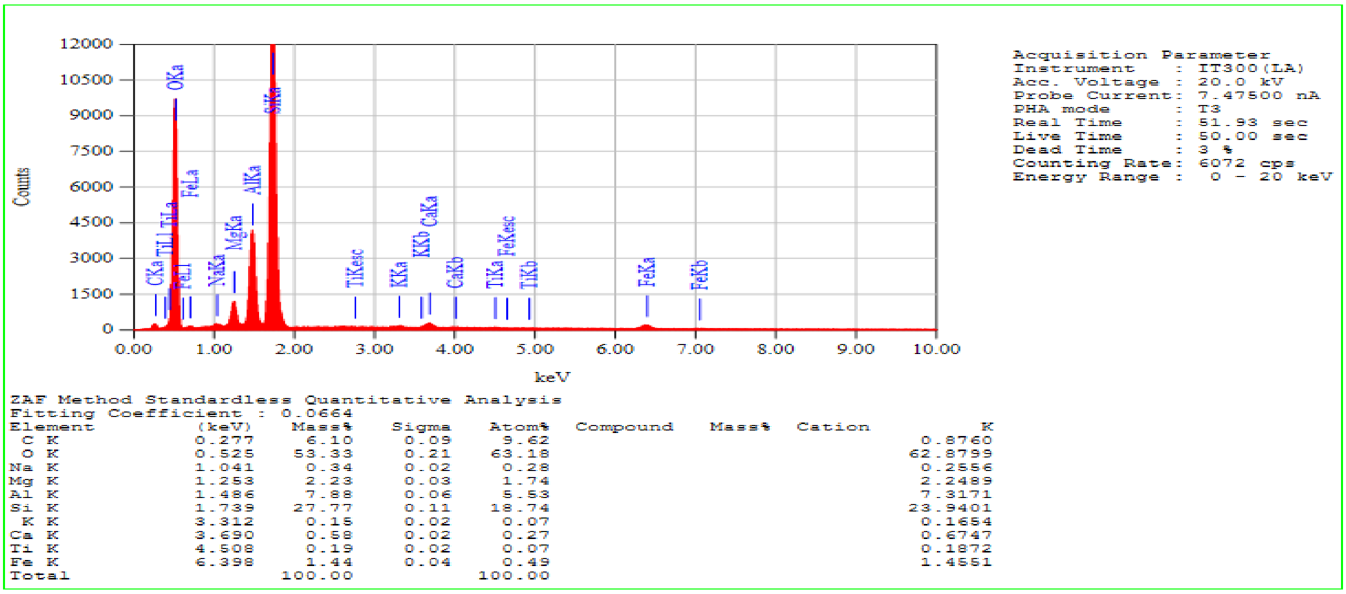
Color change after adsorption

Swell index



```
Acquisition Parameter
Instrument     : IT300(LA)
Acc. Voltage : 20.0 kV
Probe Current: 7.47500 nA
PHA mode       : T3
Real Time      : 51.99 sec
Live Time      : 50.00 sec
Dead Time      : 3 %
Counting Rate: 6516 cps
Energy Range :  0 - 20 keV
```

```
ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.0616
Element          (keV)    Mass%    Sigma    Atom%   Compound    Mass%  Cation          K
 C  K            0.277     6.34     0.10    10.09                                0.9029
 O  K            0.525    50.82     0.21    60.76                               60.0021
Na  K            1.041     1.78     0.03     1.48                                1.4284
Mg  K            1.253     2.48     0.04     1.95                                2.5523
Al  K            1.486     8.54     0.06     6.05                                8.1061
Si  K            1.739    26.81     0.11    18.26                               23.5253
Cl  K            2.621     0.86     0.02     0.47                                0.8915
Ca  K            3.690     0.74     0.02     0.35                                0.8893
Ti  K            4.508     0.18     0.02     0.07                                0.1841
Fe  K            6.398     1.45     0.04     0.50                                1.5180
Total                    100.00            100.00
```



```
Acquisition Parameter
Instrument     : IT300(LA)
Acc. Voltage : 20.0 kV
Probe Current: 7.47500 nA
PHA mode       : T3
Real Time      : 51.93 sec
Live Time      : 50.00 sec
Dead Time      : 3 %
Counting Rate: 6072 cps
Energy Range :  0 - 20 keV
```

```
ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.0664
Element          (keV)    Mass%    Sigma    Atom%   Compound    Mass%  Cation          K
 C  K            0.277     6.10     0.09     9.62                                0.8760
 O  K            0.525    53.33     0.21    63.18                               62.8799
Na  K            1.041     0.34     0.02     0.28                                0.2556
Mg  K            1.253     2.23     0.03     1.74                                2.2489
Al  K            1.486     7.88     0.06     5.53                                7.3171
Si  K            1.739    27.77     0.11    18.74                               23.9401
 K  K            3.312     0.15     0.02     0.07                                0.1654
Ca  K            3.690     0.58     0.02     0.27                                0.6747
Ti  K            4.508     0.19     0.02     0.07                                0.1872
Fe  K            6.398     1.44     0.04     0.49                                1.4551
Total                    100.00            100.00
```

EDS spectrum of raw and acid activated samples.