



# **Adsorptive Removal of Reactive Azo Dyes using Industrial Residue**

**A thesis presented to the School of Graduate Studies  
Addis Ababa University in the partial fulfillment of the  
requirement for the Degree of Masters of Science in  
Environmental Science**

**By**

**Admasu Adamu**

Feb., 2008

## Declaration

I the undersigned declare that this Thesis is my original work and has not been presented for any degree in any university and all the resource of materials used for the Thesis have been duly acknowledged.

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Environmental Science Program

Addis Ababa University

Feb., 2008

**ADDIS ABABA UNIVERSITY  
SCHOOL OF GRADUATE STUDIES  
ENVIRONMENTAL SCIENCE PROGRAM**

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## **Abstract**

The potential of waste residue obtained from alum manufacturing process to remove problematic reactive azo dye (Cibacron brilliant red 3B-A) was investigated. Batch adsorption experiments were carried out to find out the effects of contact times, adsorbent doses, initial dye concentrations, and final pH on the adsorption of the dye by both unmodified and neutralized adsorbents. The results of the experiment showed that from initial dye concentration of 50 mg/L, the adsorption of dye was rapid in the first 15 and 30 minutes of contact time and equilibrium is reached in about 90 and 120 minutes for both unmodified and neutralized adsorbents, respectively. About 92% the dye was removed by unmodified adsorbent at its equilibrium contact time and optimum dose of 12 g/L, however, only 68% removal efficiency was obtained for neutralized adsorbent at its equilibrium contact time and optimum dose of 15 g/L. The time required to reach equilibrium is independent of initial dye concentrations in the working range of this experiment. For the neutralized adsorbent, the percentage of dye removal is nearly constant in the initial pH range of 4-9, and the maximum removal of the dye was obtained at initial pH of 3. In the case of unmodified adsorbent, maximum removal of the dye was obtained at initial pH of 2. The equilibrium adsorption isotherms have been examined by applying the Langmuir, Freundlich, Dubinin-Rasdushkevich (D-R), and Temkin models. The experimental results can be best described by the D-R isotherm. Adsorption kinetics of was analyzed using the pseudo first and second order models and the regression results showed that the adsorption kinetics were more accurately described by a pseudo second-order model, moreover, the intra-particle diffusion was not the only rate limiting factor of adsorption of the dye.

*Key words: Cibacron brilliant red 3B-A, unmodified and neutralized adsorbents adsorption isotherm, adsorption kinetics, and intra-particle diffusion.*

# **1. Introduction**

## **1.1. Background of the Study**

Even though it appears to be in plentiful supply on the earth's surface, water is a rare and precious commodity, and only an extremely small part of the earth's water reserves constitutes the water resource, which is available for human activities. The growth of the world's population and industry has given rise to a constantly growing demand for water in proportion to the supply available, which remains constant. On the global level, the question of the supply of freshwater is becoming more acute every day (Allegre et al., 2006).

In Ethiopia, the textile industry is the largest manufacturing industry. There are more than fourteen state owned and private textile and garment factories. As compared to that of developed countries, the growth of the textile industry in Ethiopia is low. However, according to the current strategy, textile industry is given more attention and further expansion is expected. In almost all cases, the Ethiopian industries (textile, paper, plastic, leather, food, cosmetic, etc) release their untreated or partially treated wastewaters into municipal sewers or directly into nearby drains, rivers, stagnant, ponds, lagoons, or lakes. Such wastewater disposal may cause damage to the quality of the receiving water bodies, the aquatic ecosystem and the environment at large (UNESCO, 2004).

Large volumes of synthetic dyes are used by several industries including textile dyeing (60%), paper (10%), and plastic matter (10%). Some of the reports show that there are over 100,000 commercially available dyes with a production greater than  $7 \times 10^5$  metric tones per year, and out of which the textile industry uses about 10,000 different dyes (Guivarch, Trevin, Lahitte, 2003). Especially the dyeing industry effluents not only result in the need of treating the problematic wastewater with high chemical and biological oxygen demands, suspended solids and toxic compounds, but also color that is perceived by human eyes at very low concentration (Aksu, 2005). When dyes are discharged into receiving water bodies, they produce toxic amines through reductive cleavage of azo linkages, which

causes severe effects on human beings by damaging the vital organs such as the brain, liver, kidney, central nervous and reproductive systems. Moreover, synthetic dyes may adversely affect the photosynthetic activity of some aquatic life because of the presence of aromatics, metals, chlorides, etc. Hence their removal from aquatic environment is important and subject of many scientific researches (Bayramoglu, Africa, 2007 and Iscen, Kiran, Ilhan, 2007).

In the dyeing of textile materials, water is used in the form of steam to heat the treatment baths, and to enable the transfer of dyes to the fibers. Cotton, which is the world's most widely used fiber, requires large amount of water during processing. Dyeing of one kilogram of cotton with reactive dye demands from 70 to 150 L of water, 0.6 to 0.8 kg NaCl and from 30 to 60 g dyestuff. More than 80,000 tones of reactive dyes are produced and consumed each year, making it possible to estimate the total pollution caused by their use. After the dyeing is completed, the discharge stream is heavily colored and contains a substantial load of salt and organic substances (Allegre et al., 2006).

The wastewater produced by a reactive dye contains (Allegre et al., 2006):

- Hydrolyzed reactive dyes not fixed on the substrate, representing 20-30% of the reactive dyes applied (on average  $2 \text{ gL}^{-1}$ ). This residual amount is responsible for the coloration of the effluents and cannot be recycled,
- Dyed organic substances, which are non-recyclable and responsible for the high biological oxygen demand (BOD) and chemical oxygen demand (COD) of the effluents,
- Textile fibers,
- $60\text{-}100 \text{ gL}^{-1}$  electrolytes, essentially sodium chloride and sodium carbonate, which are responsible for the very high saline content of the wastewater.

In addition, these effluents exhibit a pH of 10-11 and high temperature ( $50\text{-}70 \text{ }^\circ\text{C}$ ). Due to the toxic nature of most dyes to plants and microorganisms, colored wastewater should not be discharged without adequate treatment. Even if they are non-toxic, such wastewater obstructs light penetration, therefore, decreases the efficiency of photosynthesis in aquatic

plants, and raises the chemical oxygen demand (Allegre et al., 2006, and Netpradist, Thiravetyan, Towprayoon, 2007).

Residual color is a problem with reactive dyes because, in current dyeing processes, as much as 50% of the dye is lost in the wastewater. These losses are due to the relatively low levels of dye-fiber fixation and the presence of unreacted hydrolyzed dye in the bath. Dye hydrolysis occurs when the dye molecule reacts with water rather than with the hydroxyl groups of the cellulose (Malik, Ramteke, Wate, 2006, and Stead, 1982). The reason behind this phenomenon is that in the process of dyeing cellulosic fibers with reactive dyes, the use of alkalis are required to promote formation of covalent bonds between the dye and cellulosic substitute. However, the uses of alkalis results in hydrolysis of reactive groups in the dye, and the reaction necessary to introduce the substitute on the fiber do not go to completion. Therefore, residual reactive hydrolyzed dyes remain in the process water. These problems are compounded by the high water solubility and characteristic brightness of the dyes (Al-Ghouti et al., 2003).

Emerging color problem and consents for discharges are based on the intensity of color. However, this does present the textile industry with a problem. Given that 1mg/L of color is still perceptible by the human eye, a typical padding application may still result in up to 340 mg/L or more dyestuff in the effluent. Even very efficient dyeing process can result in up to 60 mg/L of color in the aqueous effluent. It is recognized that public perception of water quality is greatly influenced by the color. The presence of unnatural color is aesthetically unpleasant and tends to be associated with contamination. It has been reported that up to 1.56 mg/L dye can be detected in receiving watercourses, although dye concentrations as low as 0.005 mg/L is visible in clear river water (Banat et al., 1996, and Robinson et al., 2001).

## 1.2. Types and Properties of Dyes

### 1.2.1. Types of dyes

Synthetic dyes have many structural varieties, such as, acidic, basic, disperse, azo, diazo, anthroquinone based and metal complex dyes, that fall into either the cationic, nonionic or anionic type. Anionic dyes include the direct, and the most problematic water-soluble acid and reactive dyes. Nonionic dyes refer to disperse dyes that do not ionize in aqueous medium and some of them have the ability of bioaccumulation. Whereas anthroquinone based dyes are the most resistant to degradation due to their fused aromatic ring structure (Robinson et al., 2001).

The color of dye is combined effects of chromophores, delocalized electron system with conjugated double bonds, and auxochrome – electron withdrawing or electron donating substituent that enhance the color of chromophore by changing the overall energy of electron system. Some of the important chromophores are  $-\text{N}=\text{N}-$ ,  $-\text{C}=\text{O}$ ,  $-\text{NO}_2$  and quinoid groups, and important auxochromes are  $-\text{NH}_2$ ,  $-\text{OH}$ ,  $-\text{SO}_3\text{H}$  and  $-\text{CO}_2\text{H}$ . Both chromophore and auxochrome increase the bathochromic effect – shifting adsorption bands to longer wavelength, on a conjugated system of dye. In addition to enhancing the chromophore in production of color, auxochromes are also responsible for the solubility of dye and increase its reactivity towards fibers (Dos Santos, 2005, Mutambanengwe, 2006, and Zee, 2002).

The chromophores in anionic and non-ionic dyes are mostly azo groups or anthroquinone type. Toxic amines result when azo groups undergo reductive cleavage. Reactive dyes are azo-based chromophores that contain different types of reactive groups such as vinyl sulfone, chlorotriazine, trichloropyrimidine, difluorochloropyrimidine. In contrast to other classes of dyes, they form covalent bonds to the textile fibers such as cotton. The uses of reactive dyes are highly favored in the textile industries owing to their bright color, water-fast, simple application techniques with low energy consumption and, thus reactive dyes are among the dyes most commonly in use today (Aksu, 2005).

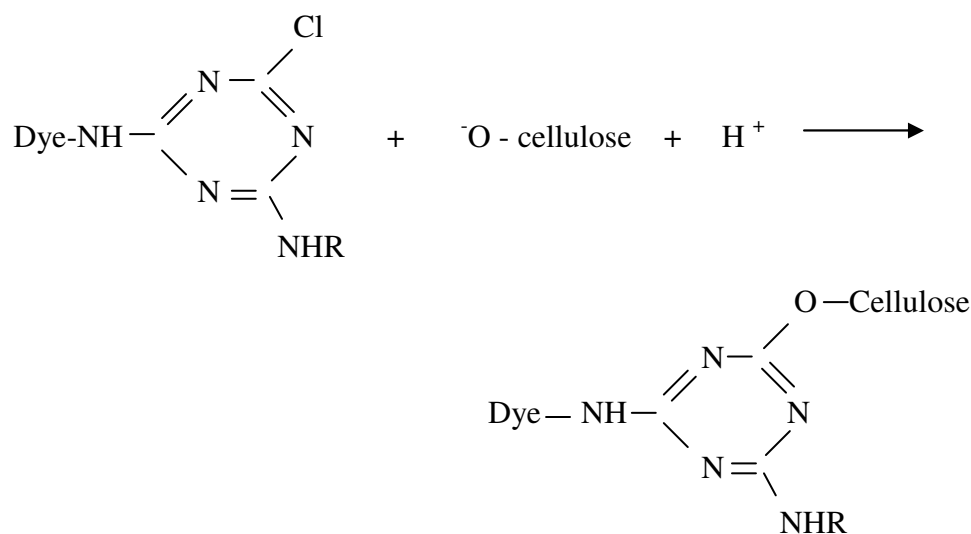
Reactive dyes are used primarily on cotton and rayon. They are highly soluble in water and with the help of large amount of salt; the exhaustion of the dyes is improved. Regarding to the typical dye fixation, variations in the reported values are observed. However, these values are comparable and relatively smaller than the other classes of dyes (Table 1) (Andrady, 2003, and Stead, 1982).

### 1.2.2. Dyeing of cotton with reactive dyes

A reactive dye is a complex molecule which is constituted by a chromophore responsible for the adsorption and re-emission of light rays. It possesses soluble groups onto which a reactive group is attached and which bind to the cellulose by means of covalent bond. The type of reaction between cellulose and the dye can be either one of the substitution or addition (Allegre et al., 2006):

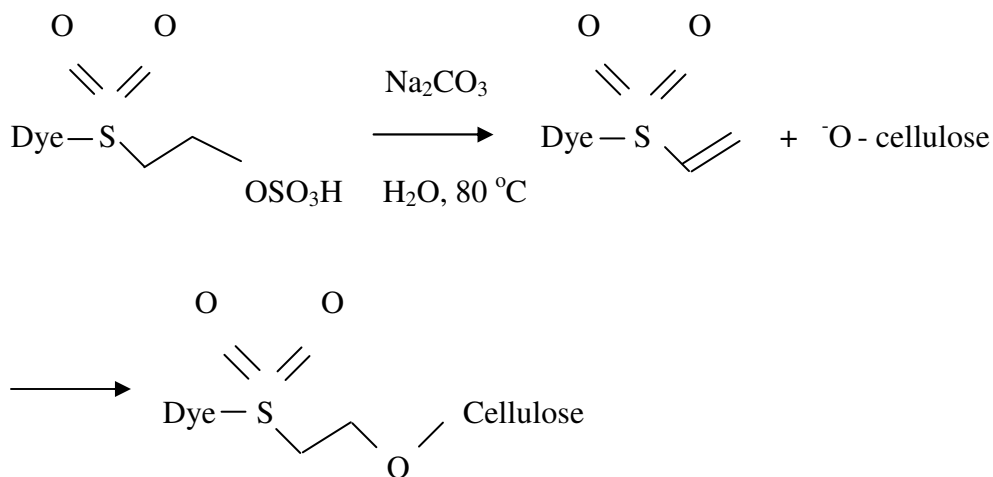
Esterification reaction:

The reactive groups of the dye are present on the heterocyclic containing nitrogen atoms (halotriazinyl amine) (Al-Ghouti, et al., 2003). The electronegative atoms such as chlorine on the reactive group increase the electrophilic nature of the dyestuff. In alkaline solution, cellulose dissociates and thus acquires a pronounced nucleophilic site that is responsible for the reaction with the electrophilic site on the dyestuff. Chlorine atom is substituted by a cellulose ion as indicated below:



Michael reaction:

In alkaline solution, dye with sulfatoethylsulfone groups transform into a vinylsulfone group which is capable to react with the cellulose. Addition of cellulose- O<sup>-</sup> ion to the vinylsulfone group takes place as follows:



### 1.2.3. Photo stability of synthetic dyes

Photostability is one of the important parameters during the development and applications of organic dyes. Dyes and pigment industries are promoting researches towards enhancing the photostability of dyes (Griffiths, Feng, 1999).

The presence of triplet state quenchers play important role in inhibiting the photo fading of organic dyes. This is due to the effective intermolecular triplet-triplet energy transfer (TTET) from the excited molecules of the dyes to the triplet state quencher molecules. When there are multiple chromophores in the same molecule that are linked by covalent bond, the intramolecular transfer of triplet excitation energy between isolated chromophores takes place. In such dyes, one of the chromophores acts as a triplet acceptor of the excess energy. In recent years these types of dyes have been synthesized and it has been reported that some chromophores perform the role as internal photo stabilizers (Tian, Yang, 2002).

Table 1: Typical characteristics of dyes used in textile dyeing operations

<b>Dye Class</b>	<b>Description</b>	<b>Typically Applied to</b>	<b>Fixation (%)</b>	<b>Typical pollutants associated with the dyes</b>
Acid	water-soluble anionic compounds	wool nylon	80-93	Color, organic acids, and unfixed dyes
Basic	water-soluble, applied in weakly acidic dye baths, very bright dyes	acrylic some polyesters	97-98	N/A
Direct	water-soluble, anionic compounds, can be applied directly to celluloses without mordant (or metals like chromium and copper)	cotton rayon other celluloses	70-95	Color, salt, unfixed dye, cationic Fixing agents, surfactant, leveling, retarding agents, finish, diluents
Disperse	non-water soluble	polyester acetate other synthetics	80-92	Color, organic acids, carriers, Leveling agents, phosphates, lubricants, and dispersants
Reactive	water-soluble, anionic compounds, largest dye class	cotton other celluloses wool	60-90	Color, alkali, oxidizing agent, Reducing agent, and unfixed dye
Sulfur	organic compounds containing sulfur or sodium sulfide	cotton other celluloses	60-70	Color, alkali, oxidizing agent, reducing agent, and unfixed dye
Vat	oldest dyes, more chemically complex, water-insoluble	cotton other celluloses	80-95	Color, alkali, oxidizing agents, and reducing agents

Source:(USEPA, 1997)

#### **1.2.4. Metals in dyes**

Metals found as integral parts of the dye chromophores (e.g., phthalocyanine); comprise mainly cobalt, copper, and chromium. However, some dyes have low-level metal impurities that are present incidentally, rather than necessity in terms of functionality and color. When mercury-based compounds are used as catalysts in dye manufacturing, there is a possibility of its presence as trace residue. Very few (e.g., only 2% commercial direct dyes) have metal as an integral part of the dye chromophore (Al-Ghouti et al., 2003, and Andradý, 2003). Unless textile effluent is treated properly, as a result of extensive use of dyes and pigments through out the world, toxic metals associated with the dyes and pigments inevitably reach to aquatic environments, and pose serious treats to aquatic lives and the system (Waranusantigul et al., 2003).

#### **1.3. Available technologies to removal color**

When cotton is dyed with reactive dyes, the resulting wastewaters are characterized by their high BOD/COD, intense color, and high load of salt. Light is one of the components aquatic organisms require for their development, and any deficit caused by colored effluent leads to an imbalance of the ecosystem. Furthermore, if water of rivers that receive the effluent is the source for drinking water, extra treatment cost will be required (Allegre et al., 2006).

Recently, there are increasingly stringent restrictions on the organic content of industrial effluent to minimize, if possible to eliminate dyes from wastewater before it is discharged. Many of the dyes used in textile, paper and plastic industries are toxic and even carcinogenic to pose a serious hazard to aquatic organisms. So far different methods have been proposed to mitigate and address these pressing problems of the aquatic environments. These technologies can be categorized into three: biological, chemical and physical methods. Many of the conventional methods used for treating dye wastewater

have not been widely applied on large scales as a result of the high cost and sludge disposal problems associated with them. Owing to the complex nature of dye effluents, there is no single process that is so efficient to treat the dye wastewater. What is actually practiced is combination of different processes to achieve the desired water quality in the most economical way (Crini, 2006).

### **1.3.1. Biological Methods**

There are different types of biological treatments depending on the presence or absence of oxygen (Table 2). In recent years a number of studies confirm that there are potential benefits from the use of some microorganisms. These microorganisms are responsible for the biodegradation or bioaccumulation of azo dyes in wastewater. Microorganisms such as bacteria, fungi and algae can remove color of a wide range of dyes through anaerobic, aerobic, and sequential anaerobic-aerobic treatment processes (Aksu, 2005).

For instance, it is possible to degrade dyes to have efficiency of removal as much as 90%, by making use of “activated sludge” process. However, most of the dyes resist aerobic biological treatment, and toxic substances in the effluent can hinder or lower the efficiency of the process. In order to alleviate these problems, addition of adsorbents such as bentonite or powdered activated carbon is required to treat the system, and to eliminate the non-biodegradable or toxic substances. Moreover, methods that combine oxidative chemical treatment followed by biological treatment including the possibility of using organic flocculants are other options. However, these methods are very costly (Allegre et al., 2006).

During anaerobic degradation of azo dyes, cytoplasmic azo reductases are responsible to produce colorless aromatic amines. The resulting aromatic amines may be toxic and carcinogenic. However, once the xenobiotic azo component of the dye molecule has been removed, the amines that are resistant to further anaerobic mineralization become good substrate for aerobic biodegradation. This option suggests a choice of sequential anaerobic-aerobic system for dye wastewater treatment (Aksu, 2005, and Crini, 2006)

Table.2. Advantages and disadvantages of some of the biological methods

<b>Organism (process)</b>	<b>Advantages</b>	<b>Disadvantages</b>	<b>References</b>
Bacteria (aerobic)	-decolorize both azo and anthraquinone dyes, -production of biogas	-low decolorization rates, -requires specific oxygen catalyzed enzymes, -requires additional carbon and energy sources	Aksu, 2005, Zee, 2002, Robinson et al., 2001
Bacteria (anaerobic)	-suitable for large scale application, -takes place at neutral pH for sludge treatment system, -allows obligate and facultative bacteria to reduce azo dyes	-generation of toxic substance, -requires post-treatment, -immobilization and recovery of redox mediator presents a challenge	Dos Santos, 2005, Banat et al, 1996, Zee, 2002, Tan, 2001, Forgacs et al.,2004
Fungi	-decolorize anthraquinone and indigo-based dyes at higher rates	-decolorization rate is very low for azo dyes, -requires especial bioreactor and external carbon source, -needs acidic pH (4.5-5), -inhibition by mixture of dyes and chemical in textile effluents	Mutambanengwe, 2006, Zee, 2002

Among the various aerobic processes used to mineralize textile effluents, biochemical oxidation processes suffer significant limitations. This is mainly because more dyestuffs found in the commercial market have been intentionally designed to be resistant to aerobic microbial degradation. Reactive azo dyes are electron deficient in nature and as a result

resist oxidative catabolism. Moreover, the efficiency of biological treatment systems is greatly influenced by technical constraints such as sensitivity towards seasonal variation, toxicity of some chemicals, less flexibility in design and operation and the requirement of large land areas. To get maximum rate of dye removal, optimization of variables of the system such as the level of aeration, temperature, pH, and redox potential are necessary (Aksu, 2005, Crini, 2006, and Zee, 2002).

As one of the studies has confirmed, out of 18 azo dyes, 11 dyes passed through activated sludge process practically untreated. From the 7 dyes affected by the treatment, 4 were adsorbed on waste activated sludge and only three were biodegraded (Forgacs, et al., 2004).

In order to minimize sludge production, which is a major drawback of conventional treatment processes, and improve the biodegradability of dyestuffs, adsorption-biological treatment have been combined and the research continuous in this areas (Crini, 2006).

### **1.3.2. Chemical methods**

Chemical techniques can be used to remove dyes, however, the cost associated with this method is high and disposal of concentrated sludge pose problems (Table 3). In addition, the use of excessive chemicals may result in secondary pollution problems. These and the like limitations made this technique commercially unattractive (Robinson et al., 2002).

### **1.3.3. Physico-chemical Methods**

Among the physico-chemical techniques (Table 4), adsorption, which is a well known equilibrium separation process, is gaining much attention because of its simple design, ease of operation, flexibility and insensitivity to toxic pollutants. Adsorption process will produce high quality treated effluents. It becomes an attractive alternative for the treatment of contaminated water, provided that the adsorbent is inexpensive and does not require much modification before its application (Crini, 2006)

Table 3: Advantages and disadvantages of Chemical methods

<b>Methods</b>	<b>Advantages</b>	<b>Disadvantages</b>	<b>References</b>
Fenton's reagent	Effective decolourisation of both soluble and insoluble dyes	Sludge production	Robinson et al., 2001, Dos Santos, 2005
Ozonation	Applied in gaseous state: no alteration of volume	Short half-life (20 min) of O <sub>3</sub>	Mutambanengwe, 2006, Robinson et al., 2001, Zee, 2002
Photochemical	No sludge production	Formation of by-products	Robinson et al., 2001, Zee, 2002
NaOCl	Initiates and accelerates azo bond cleavage	Release of aromatic amines	Dos Santos, 2005, Robinson et al., 2001
Electrochemical destruction	Breakdown compound are non-hazardous	High cost of electricity	Mutambanengwe, 2006, Dos Santos, 2005, Robinson et al., 2001

The use of agricultural wastes, for instance, corn cobs, rice hulls, wheat straw, etc. for dye removal has got promising advantages, because of widespread availability and low cost. Moreover, regeneration of these materials after adsorption is not required. The other advantages of these material is that adsorption of dyes by agricultural waste allows the dyes to be dealt with on a solid substrate. Through solid state fermentation of the dye adsorbed materials, it is possible simultaneously to enrich nutritional value of a waste. This residue then has a potential to be used as soil conditioner or fertilizer. Hence this method simplifies the attempt to remove the dye and degrade it at the same time (Robinson et al., 2001).

Researches have been conducted on the adsorption characteristics of different organic and inorganic supports, in order to measure and evaluate their capacity to remove synthetic dyes from wastewater. Owing to their good chemical and mechanical stability, high specific surface area, resistance to microbiological degradation, inorganic supports have been usually used in the adsorption studies. The use of other inorganic support such as acid-activated clay, alumina, and waste red mud, a by-product of aluminum production, were reported to remove reactive dyes (Albanis et al., 2000).

Organic supports have recently gained attention for adsorption of dyes over the inorganic ones. This is mainly because; they originate from renewable resources and are wastes or by-products of industrial processes without any or much commercial values. For instance, the use of orange peels (cellulose waste) for the adsorption of Congo red, Procion orange, and Rhodamine B has been investigated (Namasivayam, and Arasi, 1996).

Research results shows that the adsorption of the above dyes by orange peel can be described by Langmuir and Freundlich isotherms and follows first-order kinetics. Acidic pH enhances adsorption, whereas the alkaline pH results in desorption of the dyes. The efficiency for the removal of dyes was also assessed for organic support such as biogas waste slurry, bagasse pith, and waste banana pith. Maximum dye removal efficiency was observed at lower pH. However, independent of the origin of support, there have been some limitations regarding the process of adsorption. The process of adsorption is non-selective and hence components of waste water usually compete with the dye for binding sites on the support. These phenomenons influence the dye binding capacity of the adsorbent in unpredictable manner (Forgacs et al., 2004).

Table 4: Advantages and disadvantages of physico-chemical treatment methods

<b>Physico-chemical methods</b>	<b>Advantages</b>	<b>Disadvantages</b>	<b>References</b>
Activated carbon	removes wide varieties of dyes	very expensive, ineffective against disperse and vat dyes	Dos Santos, 2005, Crini, 2006
Non-conventional adsorbents (agricultural and industrial by-products)	effective adsorbent, inexpensive, widely available, operation is easy, process design is simple	transfer of pollutants from liquid phase to solid matrix (adsorbent) not selective	Crini, 2006, Robinson et al., 2001, Dos Santos, 2005, Mutambanengwe, 2006, Malik et al., 2006, Forgracs et al., 2004
Membrane filtration	removes all dye types, quick method and requires less space	concentrated sludge production, membrane fouling, cost is high & incapable to treat large volume	Zee, 2002, Dos Santos, 2005, Crini, 2006
Ion exchange	regeneration: no adsorbent loss	not effective for all dyes, cost is high,	Dos Santos, 2005, Robinson et al., 2001
Coagulation/ flocculation	economically feasible, process design is simple	generation of sludge	Zee, 2002, Dos Santos, 2005, Crini, 2006

Adsorption techniques employing commercial activated carbon (CAC) are effective for the removal of wide variety of dyes from wastewater. As compared to other expensive techniques, it is an ideal alternative adsorbent. The adsorption capacity of CAC is mainly due to its structural characteristics and porous texture that attribute to large surface areas

and its chemical nature that is easily modified by chemical treatment. However, in spite of all these structural and chemical natures, CAC has got some serious limitations that prevented its wide spread applications. It has high cost, ineffective against disperse and vat dyes, regeneration is expensive and result in lose of the adsorbent. These and other problems triggered researchers to find out more economic adsorbents (Crini, 2006, Chiou, Li, 2003, and Ho, 2006,).

In different parts of the world attempts have been made to find out inexpensive alternative adsorbents, in order to minimize the cost associated with activated carbon. One of the approaches studied so far has been the use of many non-conventional low cost adsorbents especially natural materials, biosrbents, and waste materials from industry and agricultural activities. These materials could be used as a sorbents, for instance, clay materials (bentonite, koalinite), zeolites, siliceous materials (silica beads, alunite, perlite), agricultural wastes (bagasse pith, maize cob, rice husk, coconut shell), industrial waste products (waste carbon slurries, metal hydroxide sludge's), biosorbents (chitosan, peat and biomass) and others (starch, cycoldextrine, cotton) (Crini, 2006 ).

Some waste products from industrial and agricultural operations, and some natural materials become potentially economic alternatives and many of these have been effective to remove dyes from wastewater. These by-products from industrial and agricultural processes can be considered low-cost adsorbents because they are abundant, inexpensive, requires little processing and effective adsorbents. It is evident that these materials are of little or no economic values and usually present disposal problems. Studies conducted by different researchers demonstrated that metal hydroxide sludge is an effective positively charged adsorbent for azo reactive dyes. The mechanism of adsorption involves ion exchange between the surface of adsorbent and the dye (Crini, 2006).

There are a number of advantages when adsorption method is used to control water pollution resulting from dyes. Adsorption system requires less investment in terms of both

initial cost and land, its operation is easy and with a simple design. Furthermore, there is no threat from toxic substances and removes larger extent of organic waste constituents as compared to conventional biological treatment process (Albanis et al., 2000).

Agricultural and industrial by-products are available in large quantities in Ethiopia. Different investigations were carried out to assess the potential application of these by-products in Ethiopia. Dye removal capacity of low cost materials (Gizaw, 2004), industrial by-products (Worku, Feleke, Candravanshi, 2007 and Haimanot, 2007), and locally produced alum (Kifle, 2004), showed that promising results were obtained.

#### **1.4. Objectives of the study**

The general objective of the research will be to assess the dye adsorption capacity of the waste residue, produced during the production of aluminum sulfate from kaolin and sulfuric acid and its potential application in Ethiopia.

Specific objectives of the study will be as follows:

- Examine the analytical procedure for the accurate measurement of different dye concentrations,
- Study the removal efficiency of reactive dyes by locally available materials using synthetic dye solutions,
- Investigate the basic parameters that influence the adsorption process,
- Study the adsorption isotherm and kinetics using single dye solution.

## 2. Materials and Methods

### 2.1. Adsorbate

Cibacron brilliant red 3B-A, obtained from Akaki Textile Factory was used in this experiment. The chemical structure of the dye is shown in Fig. 1 and its general characteristics are indicated in Table 5.

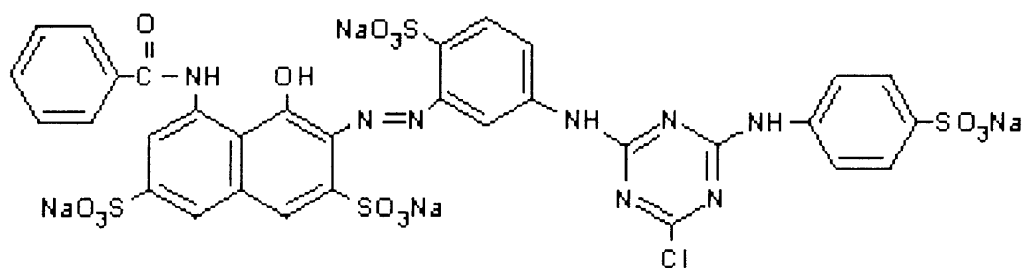


Fig. 1. Chemical structure of Cibacron brilliant red 3B-A

Stock solution of the dye was prepared by weighing 1.00 g of powdered dye. The dye was quantitatively transferred in to 1 L measuring flask which was then filled up with distilled water to have 1000 mg/L dye concentration in the solution.

Table 5: General characteristic of Cibacron brilliant red 3B-A

Dye	Type	Form	Color	Molecular wt. (g/mol)	Maximum wavelength of absorbance ( $\lambda_{max}$ ) (nm)	Color index (CI)
CR	Reactive	Powder	Pinkish	995.23	517	18105

CR: Cibacron brilliant red 3B-A

## 2.2. Adsorbent

This study employed the waste residue that was obtained from Awash Melkassa Aluminum Sulfate and Sulfuric Acid Factory. The waste residue was generated during the manufacturing of aluminum sulfate from kaolin by sulfuric acid process. It was estimated that about 5000 tones of waste residue was accumulated near the factory. The pH of waste residue is about 3. So far no sound method of disposal of this waste is reported. The chemical composition of the residue is given in Table 6. For such type of mixture of compounds, the point of zero charge ( $pH_{PZC}$ ) may vary from 5.5 to about 8.3 (Worku et al., 2007).

The sun-dried waste residue is grounded to fine powder by blender and this was used as unmodified adsorbent. Neutralized adsorbent was prepared by taking a portion of unmodified adsorbent, and it was suspended in distilled water. The resulting lower pH of about 3 was adjusted to pH of 7.3 using aqueous solution of NaOH. The aqueous portion was removed by filtration and it was sun-dried for one day.

Table 6: Chemical composition of adsorbent in percentage

Chemical composition	Percent (wt.%)
Quartz (SiO <sub>2</sub> )	39.991
Kaolin	8.883
Al <sub>2</sub> (SO <sub>4</sub> )	1.778
Al(OH) <sub>3</sub>	0.878
CaSO <sub>4</sub>	0.194
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0.023
Fe <sub>2</sub> O <sub>3</sub>	0.001
MgSO <sub>4</sub>	0.008
Na <sub>2</sub> SO <sub>4</sub>	0.007
K <sub>2</sub> SO <sub>4</sub>	0.005

### 2.3. Analytical methods

Concentrations of the dye were measured at the wavelength of its maximum absorbance ( $\lambda_{\max}$ ) that was determined by Spectronic Genesy 2PC uv-vis spectrophotometer. The final dye concentration was determined spectrometrically corresponding to  $\lambda_{\max}$  of the dye using the Beer – Lambert equation:

$$\text{Absorbance} = \varepsilon C_S l \quad (1)$$

Where  $\varepsilon$  is the molar absorptivity,  $C_S$  the concentration of sample and  $l$  the thickness of absorbing medium (1cm).

pH of the dye solution was measured with pH/ion meter (WTW Inolab pH/ION Level 2, Germany).

### 2.4. Batch adsorption experiments

Batch experiments for the removal of CR were conducted in 500 ml air tight Erlenmeyer flask by taking 200 mL of 50 mg/L dye solution. The system temperature was kept constant at  $21 \pm 2$  °C. Weighed amount of adsorbent was placed in the flask and mixed with magnetic stirrer (Model 04803 – 02: Cole Parmer Instrument, USA) continuously at constant and moderate mixing during the experiment. Samples were withdrawn at predetermined contact times and filtered (Whatman qualitative filter paper No.1, 125 mm Dia) to separate the adsorbent from the dye solution. The concentration of the dye solution was determined spectrometrically and all the experiments were performed in triplicate and the mean value is reported.

The effects of contact time and adsorbent doses (0.5 to 19 g/L) were studied at constant initial dye concentration of 50 mg/L for both types of adsorbents. To investigate the effects of initial dye concentration on the uptake of the dye, experiments were conducted by

varying the initial concentrations of the dye from 30 - 100 mg/L at constant doses of 12 g/L and 15 g/L for unmodified and neutralized adsorbents, respectively.

The effects of final pH on the adsorption of CR were examined by varying the initial pH of the dye from 2 to 10, for unmodified adsorbent. For the neutralized adsorbent, the initial pH of dye solution varied from 3 to 12. The adjustment of initial pH of the dye solutions was made by NaOH and HCl solutions. Mixture of dye and adsorbent was allowed to equilibrate for 90 and 120 minutes in a shaker at  $21 \pm 2$  °C prior to measurement of final pH, for unmodified and neutralized adsorbents, respectively.

In order to construct adsorption isotherms for both types of adsorbents, experiments were carried out by varying adsorbent dose from 0.5 to 19 g/L at initial dye concentration of 50 mg/L and ambient pH of 6. Samples were withdrawn for spectrophotometric analysis at a predetermined duration of time ranging from 5 to 180 minutes. The equilibrium dye concentrations ( $C_e$ ) were then measured and the amount of dye adsorbed per unit weight of the adsorbent at equilibrium ( $q_e$ ) was determined.

The kinetics of adsorption mechanism was studied by employing pseudo first-order and pseudo second-order models together with intra-particle diffusion mechanism. The kinetic parameters were evaluated for initial dye concentration of 40, 60 and 80 mg/L for both unmodified and neutralized adsorbents at their respective optimum doses.

Percentage removal of the dye was calculated on the basis of reduction in absorbance at  $\lambda_{\max}$  value of the dye as follows:

$$\text{Dye removal (\%)} = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

Where  $C_o$  and  $C_e$  are initial and equilibrium dye concentrations, respectively.

The amount of dye adsorbed per unit weight of adsorbent at equilibrium ( $q_e$ ) was calculated as:

$$q_e = (C_o - C_e) \frac{V}{W} \quad (3)$$

Where  $V$  is the volume of experimental solution (L) and  $W$  is the mass of adsorbent (g).

### 3. Results and Discussions

#### 3.1. Wavelength of maximum absorbance and calibration curve

The wavelength of maximum absorbance is indicated in Fig. 2 and Fig. 4, for concentrations of dyes used to construct calibration curves for both types of the adsorbents. Construction of calibration curves shown in Fig. 3 and Fig. 5, for both types of adsorbent were based on the intensity of dye's color.

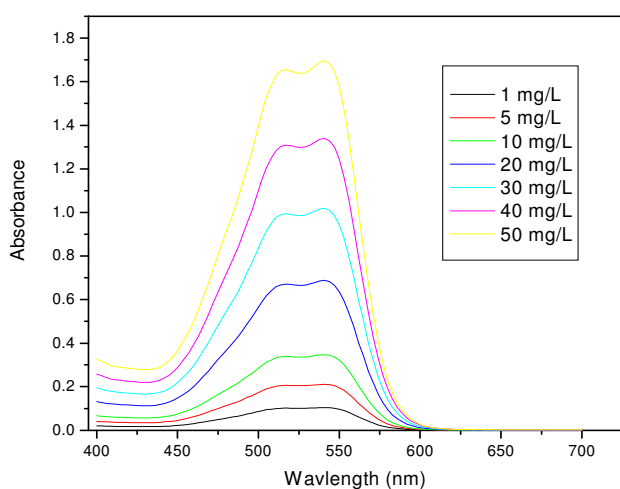


Fig. 2. Selected uv-vis spectrum of CR for the calibration curve (unmodified adsorbent)

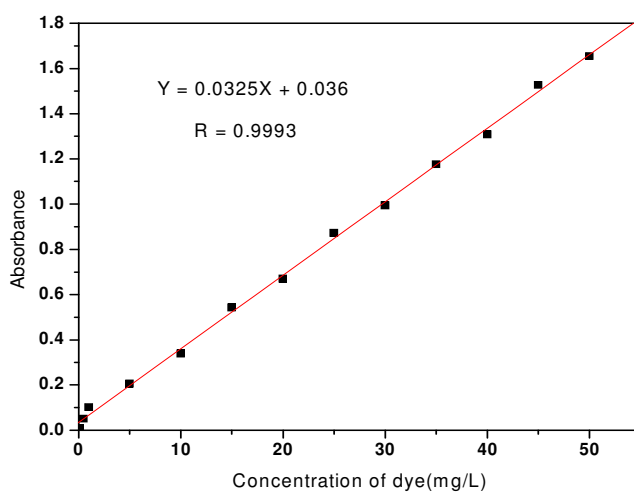


Fig. 3. Calibration curve for CR at  $\lambda_{\max}$  (unmodified adsorbent)

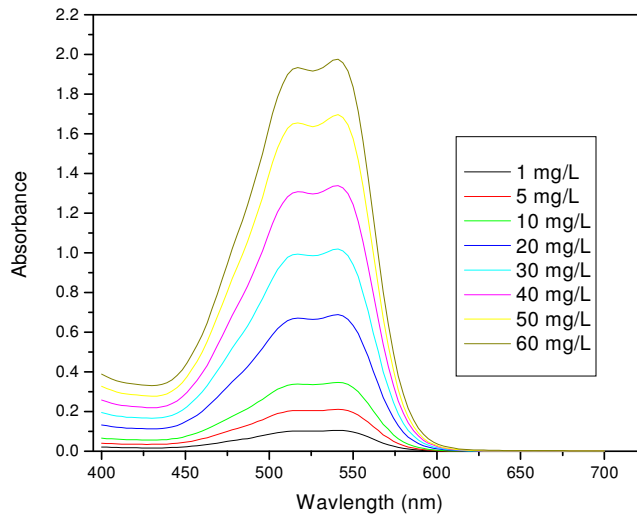


Fig. 4. Selected uv-vis spectrum of CR for the calibration curve (neutralized adsorbent)

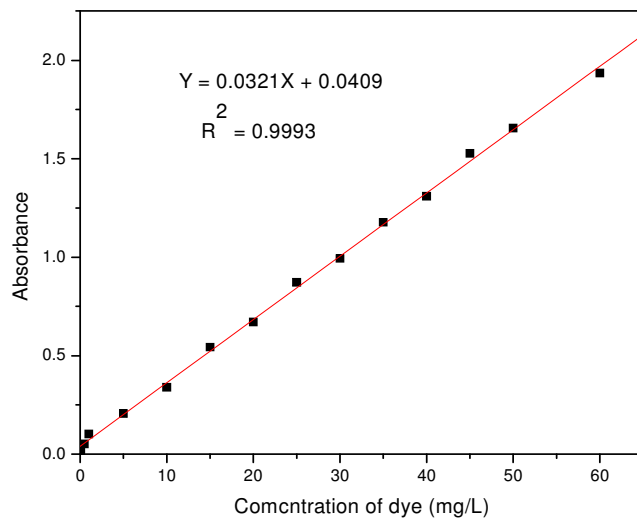


Fig. 5. Calibration curve of reactive red 4 at  $\lambda_{\max}$  (neutralized adsorbent)

### 3.2. Effects of contact time

Contact time is one of the important parameters for the assessment of practical application of adsorption process (Iscen et al., 2007). Figs. 6 and 7 show the uptake of CR as a function of contact time at different doses for unmodified and neutralized adsorbents, respectively.

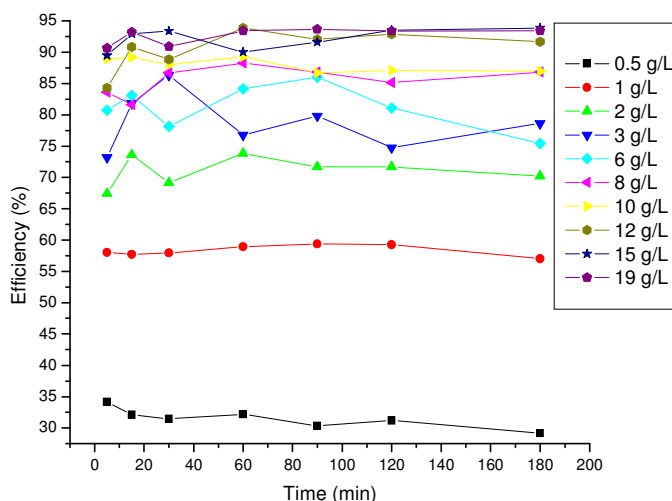


Fig. 6. Effects of contact time on CR adsorption efficiency at different adsorbent /unmodified/ doses (dye concentration: 50mg/L and solution pH 6)

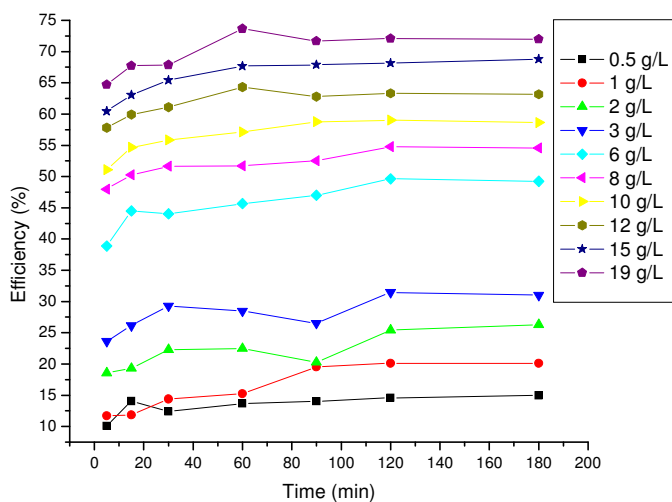


Fig. 7. Effects of contact time on CR adsorption efficiency at different adsorbent/neutralized/ doses (dye concentration: 50mg/L and solution pH 6)

As can be seen in Figs. 6 and 7, most of the adsorption of the dye takes place in the first 15 and 30 minutes of contact time for unmodified and neutralized adsorbents, respectively. Equilibrium is reached within 90 minutes for unmodified and 120 minutes for neutralized adsorbents. Beyond equilibrium time, adsorption is found to be nearly constant. This is mainly because of the fact that at the initial stage of adsorption, vacant surface sites are available, once equilibrium is attained; the remaining vacant sites are difficult to be occupied, probably caused by the repulsive forces between the molecules on the adsorbents the bulk phase (Iscen, Kiran, Ilhan, 2007, Rajoriya et al. 2007 and Wu, 2007).

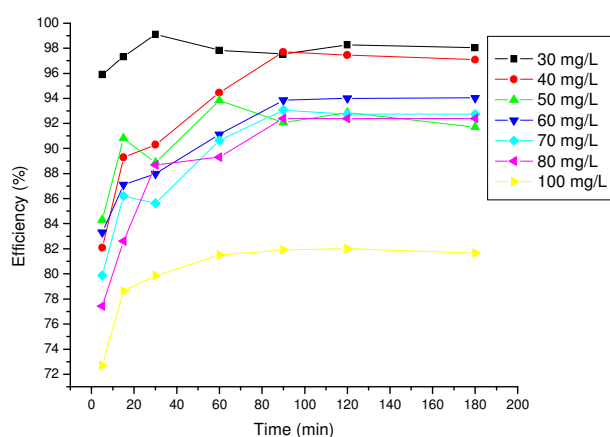


Fig. 8. Effects of contact time on the adsorption efficiency of CR at different initial dye concentrations (dose of adsorbent/unmodified: 12 g/L and solution pH 6)

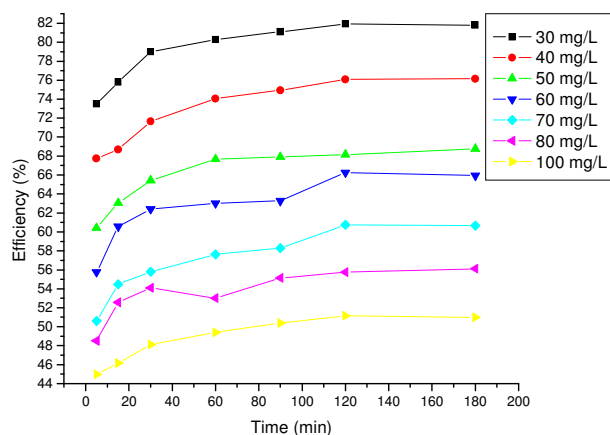


Fig. 9. Effects of contact time on the adsorption efficiency of CR at different initial dye concentrations (neutralized adsorbent dose: 15 g/L and solution pH 6)

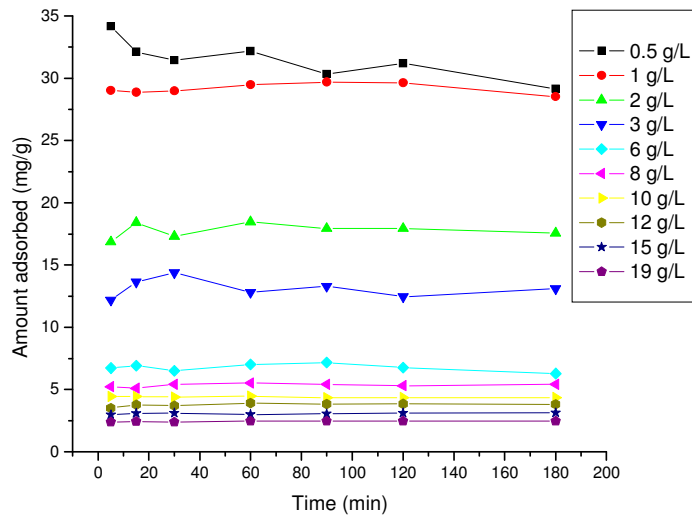


Fig. 10. Effects of contact time on amount of dye adsorbed at different adsorbent /unmodified/ doses (initial dye concentration: 50 mg/L and solution pH 6)

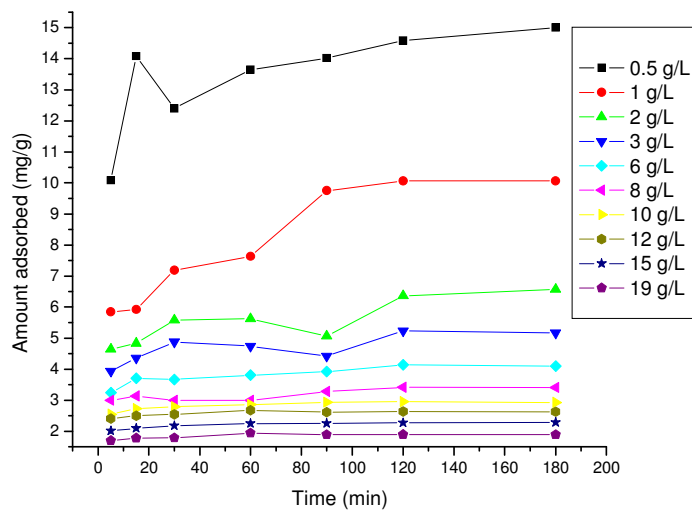


Fig. 11. Effects of contact time on amount of dye adsorbed at different adsorbent /neutralized/ doses (initial dye concentration: 50 mg/L and solution pH 6)

The results of experiment on contact time shows that percentage of dye removal increases with increasing adsorbent doses. As initial dye concentration increased from 30 to 100 mg/L for both unmodified and neutralized adsorbents, the percentage of dye removal also increased

as shown in Figs. 8 and 9. The time required to reach equilibrium, more or less independent of initial dye concentrations. However, for higher doses of adsorbents ( $\geq 15$  g/L) shorter equilibrium time is observed in Figs. 10 and 11. For the experiments following, equilibrium contact time of 90 and 120 minutes were chosen as optimum time for unmodified and neutralized adsorbents, respectively.

### 3.3. Effects of adsorbent dose

Adsorbent dose is one of the important factors because it is used to determine capacity of an adsorbent for initial concentration of adsorbate (Bulut, Gozubenli, Aydem, 2007). By monitoring the amount of adsorbent, it is possible to study the effects of adsorption process to attain maximum adsorption capacity of the adsorbent. To explore the effects of adsorbent dose on the adsorption system of CR, experiments were conducted by varying adsorbent doses from 0.5 g/L to 19 g/L, at constant initial dye concentration of 50 mg/L for both unmodified and neutralized adsorbents. The selection of these doses was based on preliminary adsorption test.

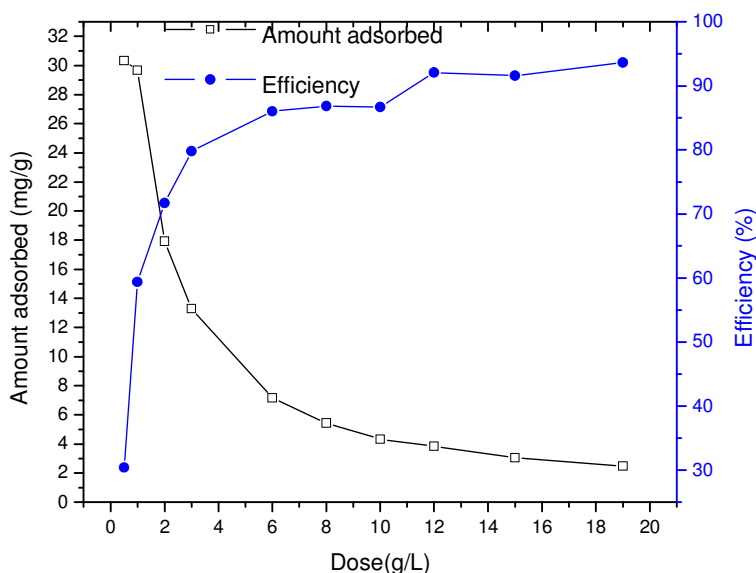


Fig. 12. Effects of dose of unmodified adsorbent on the amount of dye adsorbed and its efficiency (initial dye concentration: 50 mg/L, equilibrium contact time: 90 min and solution pH 6)

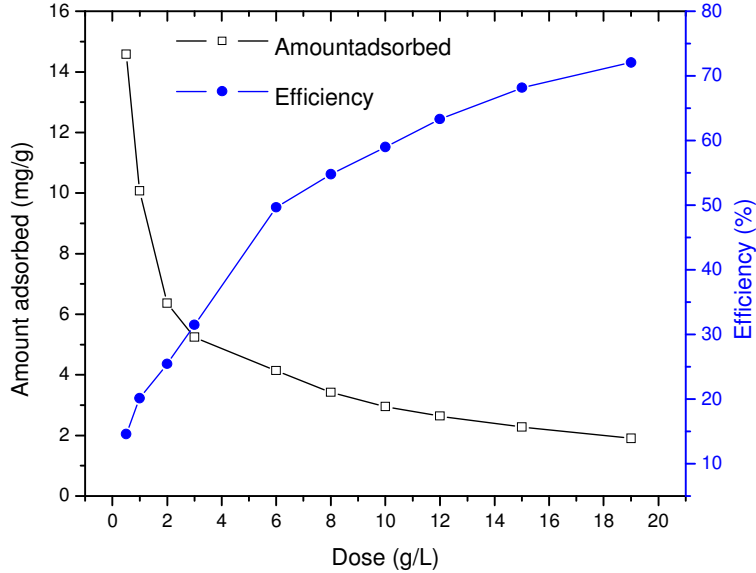


Fig. 13. Effects of dose of neutralized adsorbent on the amount of dye adsorbed and its efficiency (initial dye concentration: 50 mg/L, equilibrium contact time: 120 min and solution pH 6)

The percent adsorption increased from about 30% to 94% as the adsorbent dose increased from 0.5 to 19 g/L for unmodified adsorbent and from 15% to 72% for the neutralized one at their respective equilibrium contact time (Figs. 12 and 13). It is obvious that as adsorbent dose increases, the number of available adsorption sites increases; this in turn increases the up take of the dye. It is understood that percent adsorption increases with increasing adsorbent doses, however, the amount adsorbed per unit mass decreases. When the amount of dose is 0.5 g/L, removal capacity is about 30 mg/g, and 15 mg/g, where as at the dose of 19 g/L, the amount adsorbed per unit mass, is only 2.5 mg/g and 2 mg/g for the unmodified and neutralized adsorbents, respectively. The reason for decrease in the adsorption density with increase in adsorbent dose is unsaturation of adsorption sites through adsorption process (Bulut et al, 2007, Inbaraj et al, 2006 and Malik et al, 2006).

Another possible reason may be the intra-particle interaction, for instance, aggregation, as a result of high adsorbent dose. Because of such aggregation, total surface area of adsorbent decreases and diffusion path length increases (Reddy et al., 2006).

Studies conducted by different researchers showed that when metal hydroxide or oxide sludge is used as adsorbent, the curves of contact time for the removal of reactive dyes rise steeply in the first five minutes of contact time (Netpradist, Thiravetyan, and Towprayoon, 2007). As the reactive dyes are highly soluble in aqueous solution and had greater negative charge density, their tendency of adsorption towards the adsorbent increases accordingly. This may be an indication that the adsorption process was related to electrical attraction between anionic dyes and positively charged surfaces of adsorbent (Rachakornkij, Ruangchuay, and Teachakulwiroj, 2004).

The relationship between amounts of CR adsorbed per gram of adsorbent and the efficiency of adsorption is given in Figs. 12 and 13. It is observed that the efficiency of adsorption for unmodified adsorbent increased rapidly when the amount of adsorbent increased from 0.5 – 3 g/L and slowed down from 6 – 8 g/L, and it remain constant from 8 – 10 g/L. Sorption efficiency of the dye again observed to increase when the dose increases from 10 – 12 g/L. Further increase in the amount of adsorbent did not significantly affect the amount of dye adsorbed per gram of adsorbent. For further experiments a dose of 12 g/L was taken as the optimum dose for the unmodified adsorbent. For neutralized adsorbent, the efficiency of dye up take increased rapidly as the dose of adsorbent increased from 0.5 – 6 g/L,. However, for adsorbent dose of 6 g/L up to 15 g/L, some what a linear increase in sorption efficiency of the dye was observed. Even if the up take of the dye increased by increasing adsorbent doses, beyond a dose of 15 g/L, capacity of adsorbent is very low. Therefore, further increase in the dose result in too much production of sludge and a dose of 15 g/L was taken as an optimum dose for further experiments.

### 3.4. Effects of initial dye concentration

The adsorption process for CR was investigated at concentrations ranging from 30 to 100 mg/L at the pH of 6 and constant temperature. From Figs. 14 and 15, as initial dye concentration increased, the amount adsorbed increased for both unmodified and neutralized adsorbents up to the respective equilibrium contact times. For unmodified adsorbent, the initial rate of adsorption is rapid in the first 15 minutes of contact time and it is greater for higher initial dye concentrations. In the case of neutralized adsorbent, adsorption is fast in the first 30 minutes of contact time and the rate increased as initial dye concentration increased.

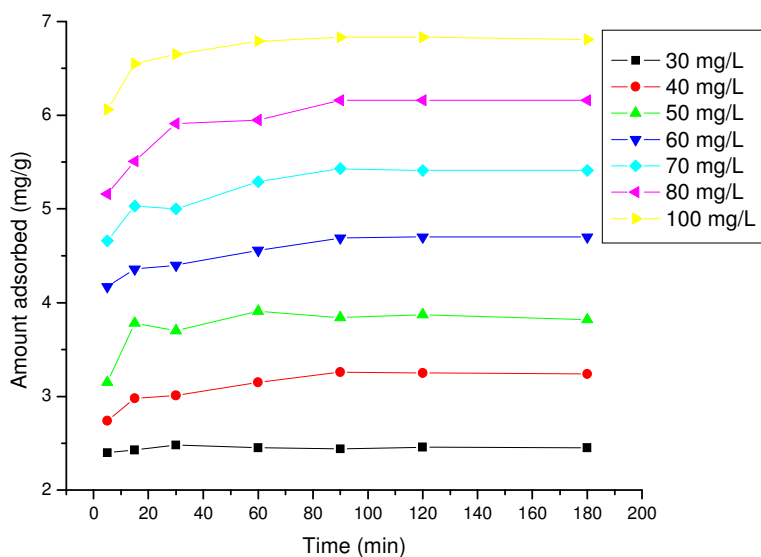


Fig. 14. CR removal capacity as a function of contact time for different initial dye concentrations (adsorbent dose/unmodified: 12 g/L and solution pH 6)

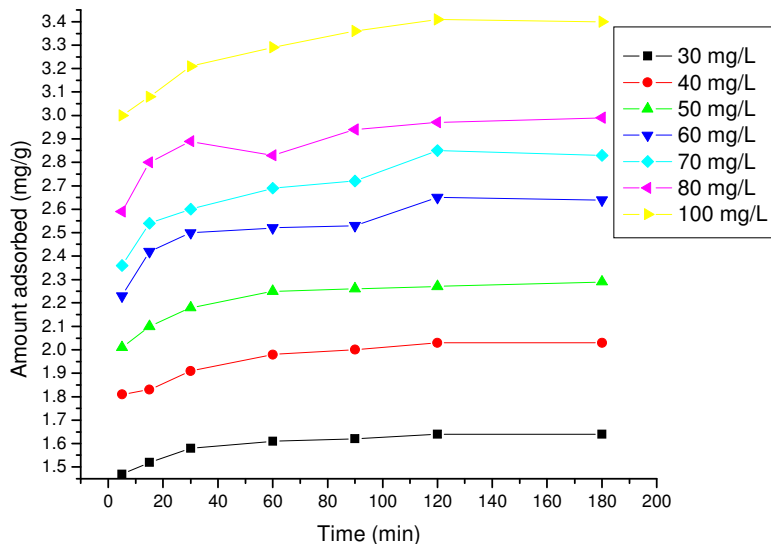


Fig. 15. CR removal capacity as a function of contact time for different initial dye concentrations (adsorbent dose/neutralized: 15 g/L and solution pH 6)

The initial dye concentration provides an important driving force to overcome resistant encountered when molecules are transferred between aqueous and solid phases (Reddy et al., 2006 and Iscen et al., 2007). For the initial concentration in the range of 30 to 100mg/L, the amount of dye adsorbed at equilibrium increased and the relationship between the amounts adsorbed for both unmodified and neutralized adsorbents and initial dye concentrations are indicated in Figs. 16 and 17. At adsorbent dose of 12 g/L, the equilibrium loading capacity for unmodified adsorbent increased from 2.4 to 6.9 mg/g as the initial dye concentration in the test solution increased from 30 to 100 mg/L. Regarding neutralized adsorbent, at a dose of 15 g/L, the equilibrium loading capacity only increased from 1.6 to 3.4 mg/g.

From the result of the experiment, both the capacity and efficiency of adsorption of the neutralized adsorbent is lower than that of unmodified adsorbent at the equilibrium (Robinson et al., 2002). One of the possible reasons for such phenomenon is the difference in surface charge density. It is evident that unmodified adsorbent with lower pH value has much higher surface charge density than the neutralized one (Al-Ghouti et al., 2003). Since reactive dyes are highly soluble in aqueous solutions and thereby develop a net negative charge, and

this intern result in strong electrostatic attraction between the anionic dye and positively charged adsorbent (Netpradist et al., 2007).

To avoid a decreased dye adsorption capacity that results from repulsive forces between dye molecules at adjacent sites on the surface of adsorbent that are responsible for the removal of some dye molecules from the surfaces at high initial dye concentration (Iscen et al., 2007 and Uddin, Sujari, Nawi, 2003), 50 mg/L dye concentration was selected to conduct further experiments. There is a strong linear relationship between the equilibrium loading capacity and initial dye concentrations with correlation coefficients greater than 0.98 for both adsorbents. This result may indicate that there is a possibility to treat textile effluent with relatively higher dye concentration, especially by making use of unmodified adsorbent.

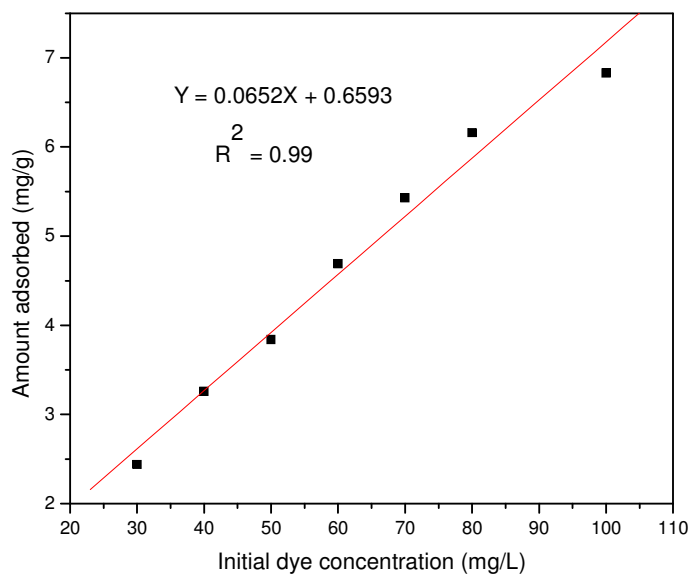


Fig. 16. Effects of initial CR concentration on the amount of adsorbed (adsorbent dose/ unmodified: 12 g/L, equilibrium contact time: 90 min. and solution pH 6)

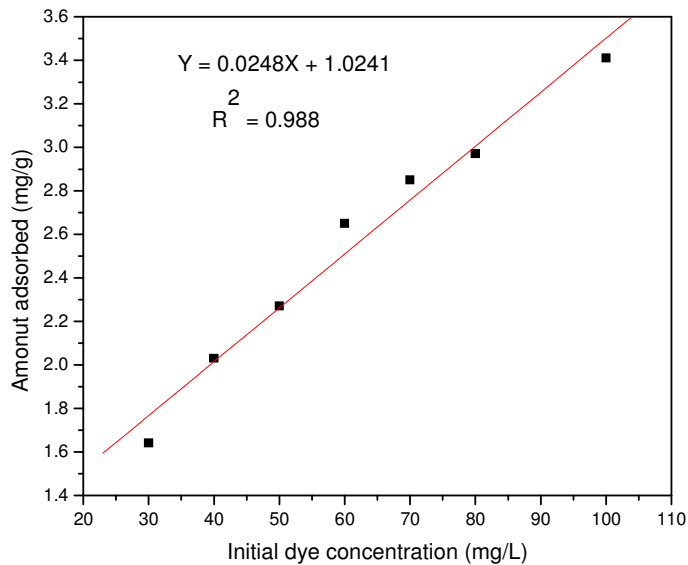


Fig. 17. Effects of initial CR concentration on the amount adsorbed (adsorbent dose/neutralized: 15 g/L, equilibrium contact time: 120 min. and solution pH 6)

### 3.5. The effects of pH

To study the effect of pH on the adsorption capacity of the media for CR, experiments were carried out using different initial pH values, varying from 2 – 10 and 3 – 12 for the unmodified and neutralized adsorbents, respectively. For any adsorption system, pH of the system affects the nature of surface charge of adsorbent. In acidic medium, the oxide surface of adsorbent develops a net positive charge. This in turn renders a strong electrostatic attraction towards anionic dyes than in basic medium (Mahony, Guibal, Tobin, 2002, and Namasivayam et al., 1997).

When the initial pH of the dye solution was increased from 6-10, the final pH for the unmodified adsorbent remain nearly constant at around 3.4 (Figs. 18), and for neutralized adsorbent, as initial pH increased from 3-9, the final pH remained constant at around 7 (Fig. 19). This shows that the adsorbent generated by Awash Melkassa Aluminum Sulfate and Sulfuric Acid Factory acted as a strong buffer. For unmodified adsorbent when initial dye solution pH is 2, for which the final pH is 2.7, the percent removal of the dye is the highest

and is about 99.9% (Fig. 20). At pH 2, maximum adsorption capacity observed was 4.14 mg/g. This result indicates that a significantly high electrostatic attraction exists between the surface of adsorbent and the dye; this is possibly due to the increase in positively charged sites on the adsorbent surface as pH decreased (Netpradist et al., 2007).

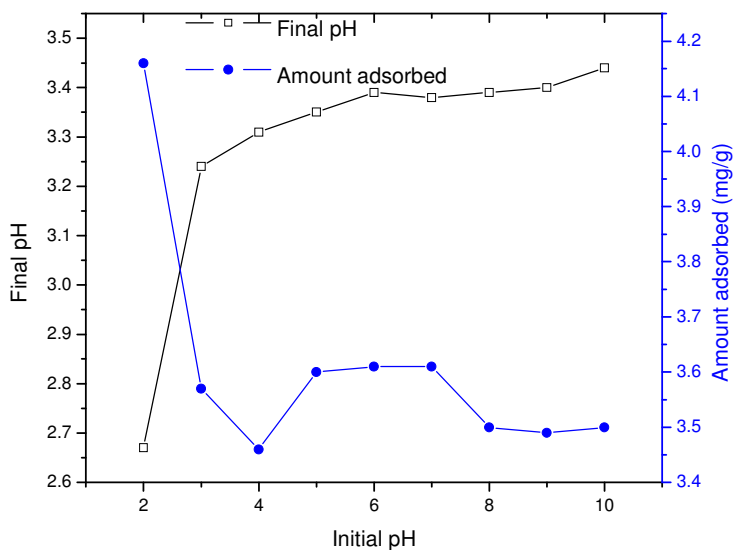


Fig. 18. Effects of initial pH on the final pH and amount of dye adsorbed (concentration of dye: 50 mg/L and adsorbent dose/ unmodified: 12 g/L)

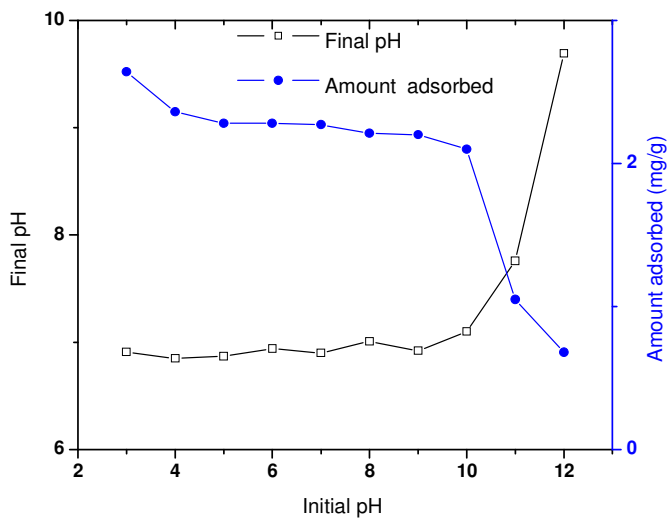


Fig. 19. Effects of initial pH on the system pH and amount of dye adsorbed (concentration of dye: 50 mg/L, adsorbent dose/neutralized: 15 g/L)

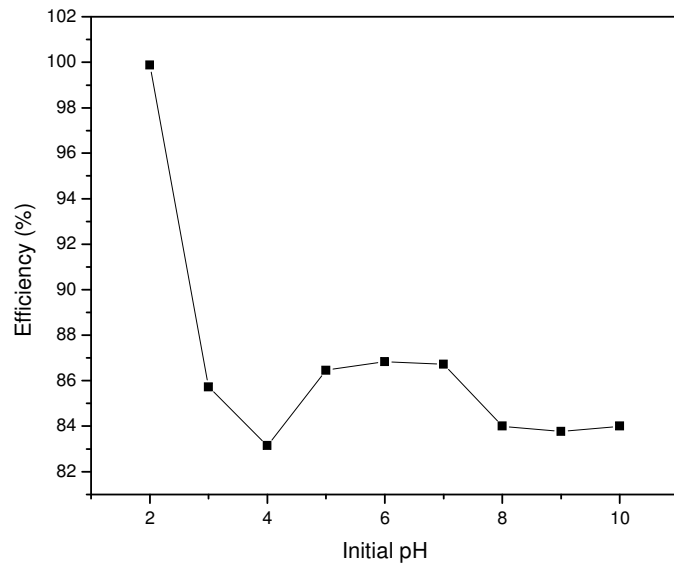


Fig. 20. Plots of initial pH of the dye solution versus adsorption efficiency (concentration of dye: 50 mg/L and adsorbent dose/unmodified: 12 g/L)

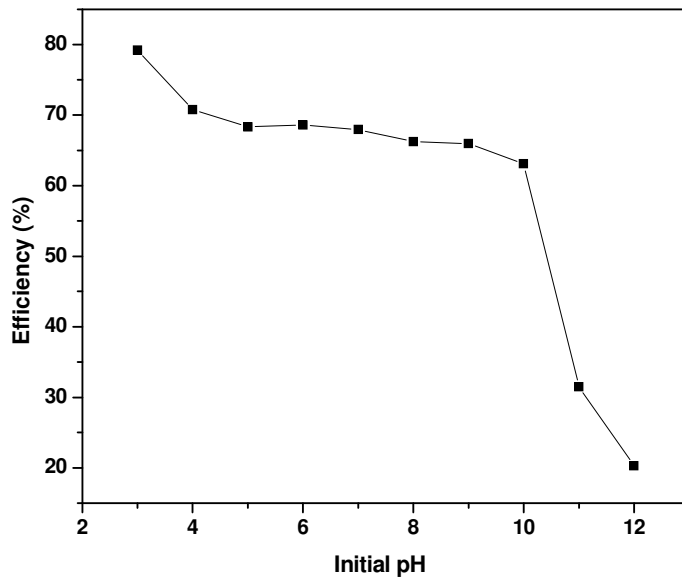


Fig. 21. Plots of initial pH of the dye solution versus adsorption efficiency (concentration of dye: 50 mg/L and adsorbent dose/neutralized: 15 g/L)

Regarding neutralized adsorbent, maximum percent removal was observed at initial pH value of 3 (final pH 6.9), and is about 80%. Removal efficiency for neutralized adsorbent decreases and reaches minimum of 20% at a pH of 12 (Fig. 21).

At lower pH values, the surface sites of adsorbent are protonated as shown in equation (4), and the surface became positively charged while the dye is still negatively charged as shown in equation (5). When pH increased, positive charge density of the surface decreased. As the dye solution is acidified with hydrochloric acid, the outer surface of positively charged interface of the adsorbent will be associated with  $\text{Cl}^-$  ions. The chloride ions are exchanged with anionic dye.

As shown in Table 6, about 40 % of the composition of the adsorbent is quartz ( $\text{SiO}_2$ ). The surface of silica contains silanol groups (Fig. 22) that spread over the matrix of silica. The silanol group has a strong tendency to react with many polar organic compounds and various functional groups. In the presence of water, surfaces of mineral oxides, such as those of Al, Fe and Si are usually covered with hydroxyl groups. As a result of surface hydration and dissociation of these groups, pH dependent surface charge is formed. The magnitude of surface charge depends on the degree of ionization and pH of the system (Al-Ghouti et al., 2003, and Stumm et al., 1996).

Next to quartz, kaolin supports the largest composition of the adsorbent. Kaolin has many types of surface functional groups.  $\equiv \text{SiOH}$ ,  $\equiv \text{AlOH}$  and Lewis acid site are the principal surface complex forming positions of kaolinite (Harris, Wells, Johnson, 2001 and Weerasooriya, Wickramarathne, Dharmagunawardhane, 1998).

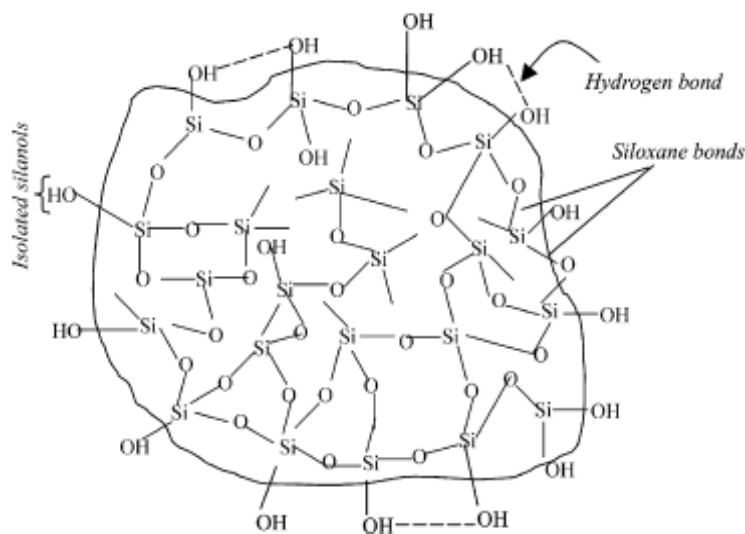


Fig. 22. Structure of silica surface depicting the various types of bonds and silanol groups present

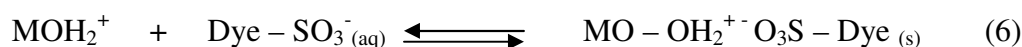
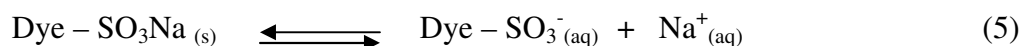
At lower pH, the  $-NH_2$  groups of the dye are protonated and the positive charge develops on the dye molecule. However, CR is an ionic dye with four  $NaSO_3^-$  groups that contribute for its solubility in aqueous solution (Mutambanengwe, 2006). Therefore, at lower pH, the negative charge due to the sulfonic groups predominates and is responsible for the electrostatic interaction with the adsorbent. At higher pH, the dye is negatively charged. The removal of the dye at higher pH could be attributed to the formation of surface hydrogen bonds between the surface hydrogen bonds of the hydroxyl group on adsorbent surface and oxygen atoms of the sulfonic groups on the dye. Nitrogen atoms of the dye could also form hydrogen bonds with the hydrogen atoms of the hydroxyl group on the adsorbent surface (Al-Ghouti et al., 2003).

At lower pH, surface sites of the adsorbent are protonated and the surface becomes positively charged (Harris et al., 2001):



Where M can be surface functional groups of kaolinite ( $\equiv \text{SiOH}$  and  $\equiv \text{AlOH}$ ).

The interaction of dye and positively charged surface of the adsorbent at lower pH is as shown in equations (4), (5) and (6) (Al-Ghouti et al., 2003 and Weerasooriya et al., 1998):



Similar results of pH effects were reported for the adsorption of hydrolyzed reactive dyes on *Rhizopus arrhizus* biomass (Mahony et al., 2002), sewage sludge derived from activated carbons (Reddy et al., 2006), and diatomaceous earth (Al-Ghouti et al., 2003).

### 3.6. Adsorption isotherms

An adsorption isotherm is a graphical representation expressing the relation between the mass of dye adsorbed at constant temperature per unit mass of adsorbent and liquid phase dye concentration at equilibrium. It shows how dye can be distributed between the liquid and solid phases at various equilibrium concentrations. Adsorption isotherms have many important practical implications, for instance; it provides information on how adsorption system proceeds, and indicates how efficiently a given adsorbent interacts with adsorbate. It also helps to estimate economic feasibility of an adsorbent for specific commercial applications. There are a number of factors that determine the shape of isotherm. The major factors are the number of compounds in the solution, their relative adsorbabilities, initial concentration of adsorbate in the solution, and the degree of competition among solutes for adsorption sites (Ng et al., 2002).

Adsorption isotherms can be generated based on theoretical principles. Four isotherm equations have been tested in the present research, namely, Langmuir, Freundlich, Dubinin–Radushkevich (D-R), and Temkin, in order to describe the equilibrium characteristics of adsorption.

Monolayer adsorption can be often described by Langmuir equation. The model assumes a uniform energy of adsorption, a single layer of adsorbed solute at a constant temperature (Al-Ghouti et al., 2003, and Nemasivayam et al., 1997).

Langmuir equation has been used as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (7)$$

The linear form of equation 7 is given as:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m} \left( \frac{1}{C_e} \right) \quad (8)$$

Where  $q_e$  (mg/g) is the amount of dye adsorbed at equilibrium,  $q_m$  (mg/g), the amount of dye adsorbed when saturation is attained,  $C_e$  is the equilibrium dye concentration (mg/L), and  $K_L$  is Langmuir constant related to the binding strength of dye on to the adsorbent.

The Freundlich equation is one of the well known models applicable for a single solute system. It is an empirical equation used to describe the distribution of solute between solid and aqueous phases at a point of saturation. The basic assumption of this model is that there is an exponential variation in site energies of adsorbent and also surface adsorption is not rate limiting step. The strength of linear relationship can be expressed by correlation coefficient ( $R^2$ ). Its value is used to evaluate how the Freundlich model represents the experimental data. There is an assumption that with a 95% level of significance, Freundlich model is adequate to represent the experimental data (Ng et al., 2002).

The basic Freundlich equation has the form:

$$q_e = K_F C_e^{1/n} \quad (9)$$

The linearized form of equation 9 is expressed as:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (10)$$

Where  $k_f$  and  $n$  are the Freundlich isotherm constants that represent adsorption capacity and strength, respectively.  $k_f$  and  $1/n$  can be obtained from the intercept and slope of the linear plot of  $\log q_e$  versus  $\log C_e$ . The magnitude of  $1/n$  indicates the extent of favorability adsorbent/adsorbate system and the degree of heterogeneity of the adsorbent surface. When the value of  $1/n$  is less than unity, the adsorption is favorable and new adsorption site occurs (Bayramoglu, Arica, 2007, Ng et al., 2002 and Wu, 2007).

Temkin's isotherm basic assumption is that the heat of adsorption decreases linearly with the coverage owing to the adsorbent – adsorbate interactions (Abdelwahab, 2007 and Rajoriya et al., 2004)

Temkin isotherm has been given as:

$$q_e = \frac{RT}{b} \ln(K_T C_e) \quad (11)$$

The linearized form of equation 11 has the following form:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (12)$$

Where  $\frac{RT}{b} = B_1$ ,  $K_T$  (mol/L) is the equilibrium binding constant corresponding to maximum binding energy, and  $B_1$  is the constant related to the differential surface capacity for the dye sorption per unit binding energy. Plotting  $q_e$  versus  $\ln C_e$  enables to determine isotherm constants  $B_1$  and  $K_T$  from slopes and intercepts, respectively.

The Dubinin – Radushkevich (D–R) isotherm, as compared to the Langmuir model, it is more general and does not assume a homogeneous or constant adsorption potential. D–R model is applicable to distinguish between chemical and physical types of adsorptions (Kiran et al., 2006).

The D–R equation is given as:

$$q_e = q_s \exp(-\beta \varepsilon^2) \quad (13)$$

The linear form of equation 13 is written as:

$$\ln q_e = \ln q_s - \beta \varepsilon^2 \quad (14)$$

Where  $\beta$  is a constant related to the mean free energy of adsorption per mol of the dye ( $\text{mol}^2 \text{kJ}^{-2}$ ) when it is transferred to the surface of the adsorbent from infinity in solution,  $q_s$  is the theoretical saturation capacity,  $\varepsilon$  is the Polanyi potential and given as:

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \text{ and } R \text{ (J. mol}^{-1} \cdot \text{K}^{-1}) \text{ is a gas constant.}$$

By making certain assumptions, the mean energy of adsorption,  $E$ , can be calculated from the  $\beta$  value employing the relation:

$$E = (-2\beta)^{-1/2} \quad (15)$$

Therefore, the D–R model can be used to estimate both of the maximum adsorption capacity and average free energy value exclusive to the dye – adsorbent system (Hsieh et al., 2000).

Figs. 23 and 24 show the plots of Langmuir isotherms for both unmodified and neutralized adsorbents. A summary of results in Table 7 shows that Langmuir isotherm was not used to describe the experimental results for both unmodified and neutralized adsorbents, even though the correlation coefficients are the highest in the case of neutralized adsorbent. This is mainly because the experimental adsorption isotherm data ( $C_e$  versus  $q_e$ ), as shown in Figs. 16 and 17, do not show the trend of leveling out as the dye concentration increased from 30 – 100 mg/L for both unmodified and neutralized adsorbents (Hsieh et al., 2000). The amount of dye adsorbed at equilibrium,  $q_e$ , increases as the equilibrium dye concentration,  $C_e$ , increases. Therefore, for a given adsorption isotherm data to fit Langmuir isotherm, adsorption isotherm data satisfies the following conditions: rising initial curve that indicates active site for binding adsorbate and then a plateau that signifies the monolayer formation (Ceyhan, and Bayabas, 2001).

Figs. 25 and 26 show the plot of linear form of Freundlich isotherms for the unmodified and neutralized adsorbents, respectively. The values of  $K_F$  and  $n$  (Table 5) are comparable to what is reported in the literature for the adsorption of reactive black and yellow (Al-Ghouti et al., 2003).  $K_F$  value, the parameter indicating adsorption capacity for neutralized adsorbent is much lower than that of unmodified adsorbent. This suggests that the affinity of CR for the unmodified adsorbent is higher than that of neutralized one. However, the values of  $1/n$  for both type of adsorbent are greater than unity and this indicates that the adsorption is unfavorable (Wu, 2007).

Table 7. Adsorption isotherm parameters of unmodified and neutralized adsorbents  
(Initial dye concentration: 50 mg/L, pH 6 and temperature: 21 °C)

Isotherms	Constants	Correlation coefficient ( $R^2$ )
Langmuir (unmodified)	$q_m$ (mg/g) = — , $B$ (l/mg) = —	0.969
" (neutralized)	" = — , " = —	0.991
Freundlich (unmodified)	$K_F$ (mg/g) = 0.65 , $1/n$ = 1.18	0.968
" (neutralized)	" = 0.03, " = 1.57	0.957
D – R (unmodified)	$q_s$ (mg/g) = 9397.8, $E$ (kJ/mol) = 7.91	0.971
" (neutralized)	" = 17,705.5, " = 6.35	0.955
Temkin (unmodified)	$K_T$ (L/mg) = 0.074, $B_1$ = $1.35 \times 10^{-5}$	0.957
" (neutralized)	" = 0.074, " = $8.59 \times 10^{-6}$	0.845

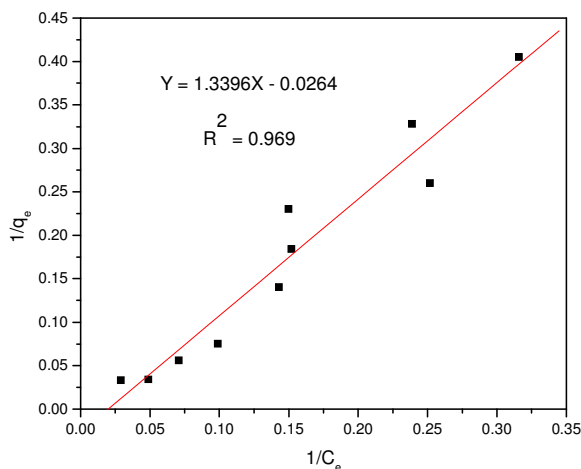


Fig. 23. Langmuir adsorption isotherm for unmodified adsorbent (initial dye concentration: 50 mg/L, equilibrium contact time: 90 min., temperature: 21°C and solution pH 6)

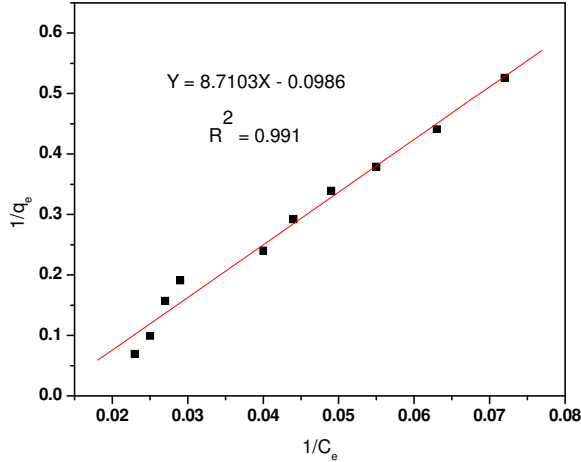


Fig. 24. Langmuir adsorption isotherm for neutralized adsorbent (initial dyeconcentration: 50 mg/L, equilibrium contact time: 120 min., temperature: 21°C and solution pH 6)

The plot of  $\ln q_s$  against  $\varepsilon^2$  for the D–R isotherm is shown in Fig. 27 for unmodified adsorbent. As compared to the Freundlich and Temkin isotherms, the correlation coefficient for D–R isotherm is the highest and is about 0.97. The value of saturation capacity,  $q_s$ , was found to be 9397.8 mg/g. If the magnitude of free energy of adsorption is between 8 and 16 kJ/mol, the adsorption process corresponds to chemical ion-exchange type, and the value of  $E < 8$  kJ/mol represents a physical adsorption (Kiran et al., 2006). The calculated mean energy value of adsorption for the dye is about 7.9 kJ/mol. Under the experimental conditions, the D-R model fits well to the isotherm data and this may implies that the adsorption mechanism of CR on the adsorbent can be possibly described by both physical and chemical ion-exchange type (Lydersen et al., 2003). For neutralized adsorbent, the D–R plot is shown in Fig. 28. The value of mean energy of adsorption is about 6, and it is in the range of physical adsorption. The correlation coefficient for D–R model is about 0.96 and the saturation capacity of adsorption is about 17,705 mg/g. Therefore, the mechanism of adsorption of the dye for both unmodified and neutralized adsorbents can be better described by the D–R model.

Figs. 29 and 30 show Temkin isotherm for both unmodified and neutralized adsorbents. For the unmodified adsorbent, the value of correlation coefficient is slightly lower than that of Freundlich and D–R isotherm values. Based on the assumption of Temkin isotherm, there is an interaction between the dye and adsorbent, and thus the heat of adsorption of CR in the layer decreases linearly with coverage (Rajoriya et al., 2007). Together with D–R models, Temkin model is also used to describe the adsorption mechanism of the dye for unmodified adsorbent. However, for the neutralized adsorbent, the value of correlation coefficient is much lower than that of unmodified adsorbent, and can not be used to describe the adsorption isotherm data.

Similar trends in adsorption isotherms were observed for hydrolyzed reactive black and yellow dyes, where the diatomaceous earth was used as adsorbent (Al-Ghouti et al., 2003). Comparable results were also obtained for the adsorption isotherm of reactive dye such as Remazole orange and CR (Mahony et al., 2002).

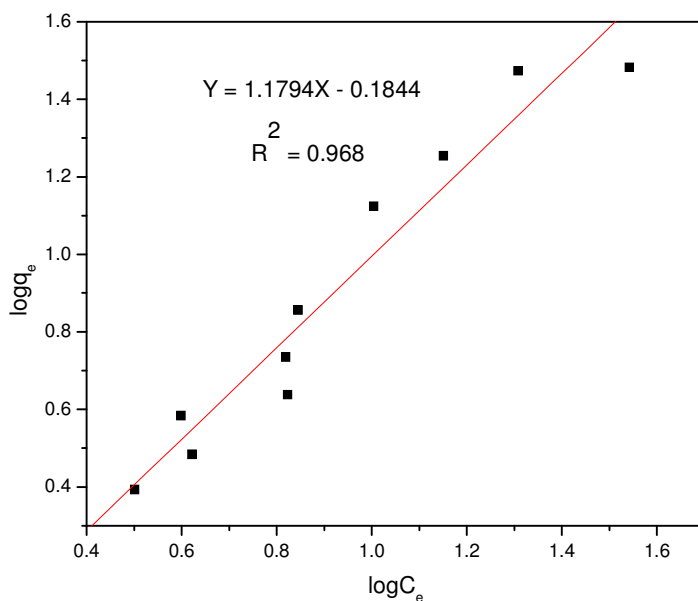


Fig. 25. Freundlich isotherm for unmodified adsorbent (initial dye concentration: 50 mg/L, equilibrium contact time: 90 minutes and temperature: 21 °C and solution pH 6)

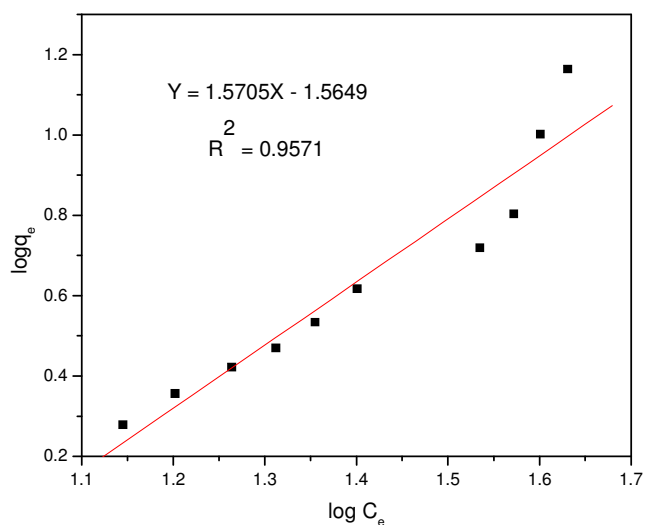


Fig. 26. Freundlich isotherm for neutralized adsorbent (initial dye concentration: 50 mg/L, equilibrium contact time: 120 minutes and temperature: 21 °C and solution pH 6)

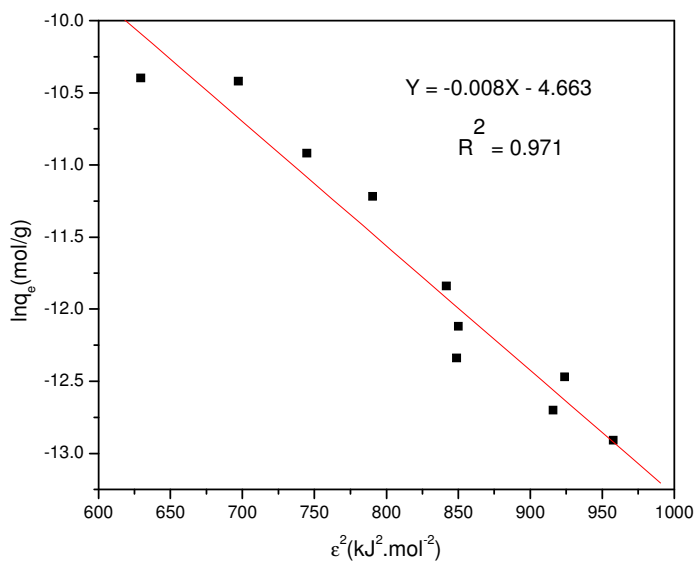


Fig. 27. D-R isotherm for unmodified adsorbent (initial dye concentration: 50 mg/L, equilibrium contact time: 90 minutes and temperature: 21 °C and solution pH 6)

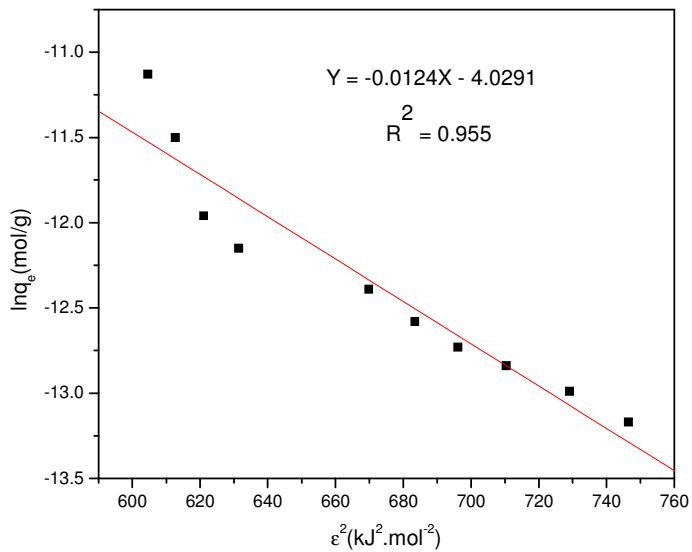


Fig. 28. D-R isotherm for neutralized adsorbent (initial dye concentration: 50 mg/L, equilibrium contact time: 120 minutes and temperature: 21 °C and solution pH 6)

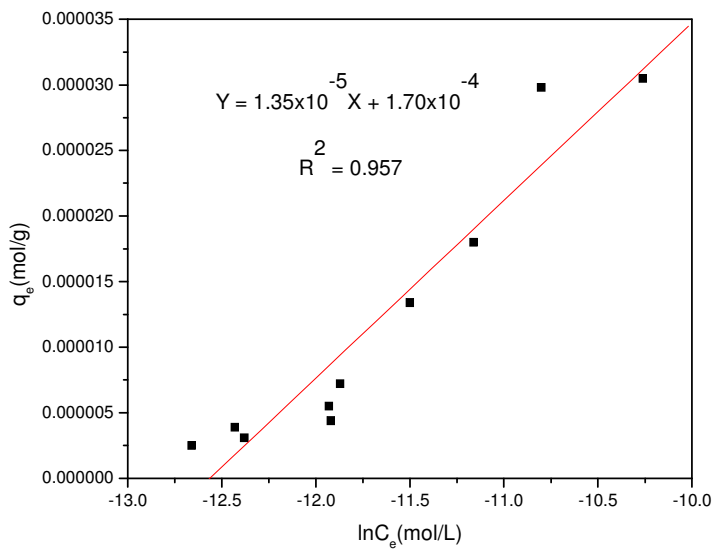


Fig. 29. Temkin isotherm for unmodified adsorbent (initial dye concentration: 50 mg/L, equilibrium contact time: 90 minutes and temperature: 21 °C and solution pH 6)

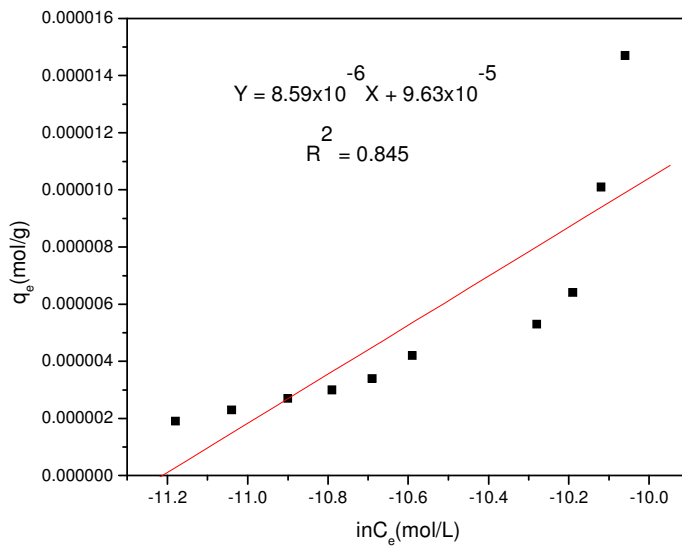


Fig. 30. Temkin isotherm for neutralized adsorbent (initial dye concentration: 50 mg/L, equilibrium contact time: 120 minutes and temperature: 21 °C and solution pH 6)

### 3.7. Adsorption kinetics

Study of adsorption kinetics is desirable because it provides information regarding the mechanisms of adsorption that is important for the efficiency of the process. Adsorption is a time dependent process. During removing contaminants from wastewater, it is important to know the rate of adsorption to optimize the design parameters (Asku, Tezer, 2006). This is because kinetics of system controls the adsorbate residence time and reactors dimensions. Therefore, predicting the rate at which adsorption takes place for a given system is probably the most important factor in adsorption system design (Ho, 2006, Eren, Acar, 2007, and Inbaraj et al., 2006). Characteristics adsorption rate constants obtained from pseudo first order and pseudo second order models were used to investigate the mechanism of adsorption (Bulut et al., 2007 and Dogan, Alkan, 2003). Determination of best-fit kinetic model is the most common way to predict the optimum adsorption kinetic expression (Kumar, Sivanesan, 2006).

Pseudo-first and second order models and intra particle diffusion model were used to test the experimental data so as to predict the kinetic of adsorption process. The non-linear form of pseudo-first order model equation is given by (Inbaraj et al., 2006 and Wu, 2007).

$$q_t = q_e [1 - \exp(-k_1 t)] \quad (16)$$

The linear of equation 16 can be expressed as:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (17)$$

Where  $q_e$  and  $q_t$  are amount of the dye adsorbed (mg/g) on the adsorbent at equilibrium and various time  $t$ , respectively.  $k_1$  ( $\text{min}^{-1}$ ) the adsorption rate constant of pseudo first-order model. The values of  $q_e$  and  $k_1$  can be determined from the intercept and slope of the linear plot of  $\ln(q_e - q_t)$  versus  $t$ .

The differential equation for a pseudo second-order reaction can be written as (Inbaraj et al., 2006):

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (18)$$

Where  $k_2$  (g/mg.min) is pseudo second-order rate constant.

When equation 18 is integrated for boundary conditions  $t = 0$  to  $t = 1$  and  $q_t = q_e$ , it becomes:

$$q_t = \frac{1}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}} \quad (19)$$

After rearranging the integrated rate law equation, the well known linear form is written as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \quad (20)$$

$$h = k_2 q_e^2 \quad (21)$$

Where  $k_2$  (g/mg/min) is pseudo second-order rate constant and  $h$  is the initial adsorption rate (mg/g.min).

The kinetics analysis of concentration effects was evaluated by taking three different dye concentrations (40, 60 and 80 mg/L) at a pH of 6 and a system temperature of  $21 \pm 2$  °C. For unmodified adsorbent, the kinetic plots are characterized by a fast dye uptake and sharp rise in the solid phase concentration of dye was observed (Fig. 31). Maximum adsorption (>85%) was accomplished within 15 minutes for initial dye concentrations of 40 and 60 mg/L and it is 30 minutes for 80 mg/L. In the case of neutralized adsorbent, for initial concentrations of 40 mg/L (>70%) and 60 mg/L (>60%) adsorption took place in the first 30 minutes and for 80 mg/L (>55) adsorption of dye was observed within 90 minutes of contact times (Fig. 32). In general an increase in initial dye concentration leads to an increase in the adsorption rate of the dye on the adsorbent (Chiou et al., 2003, and Inbjara, et al., 2006).

The experimental kinetic data of adsorption studies were applied to first-order and second-order kinetic models. In order to study specific rate constants of CR adsorption, the first-order rate equation was tested, but straight lines were not obtained for both unmodified and neutralized adsorbents (Figs. 33 and 34). Although the correlation coefficients for the model were reasonably high in some cases, however, all the intercepts of the straight line plots did not yield predicted  $q_e$  values equal or reasonably close to the experimental  $q_e$  values (Table 8). Therefore, first-order rate equation was not used to describe the reaction kinetics of CR adsorption on the adsorbent.

Table 8: Pseudo first-order kinetic parameters for the removal of CR

(Unmodified adsorbent)					(Neutralized adsorbent)		
$C_0$ (mg/L)	$q_{e,exp}$ (mg/g)	$q_{e,cal.}$ (mg/g)	$k_1$ (min <sup>-1</sup> )	$R^2$	$q_{e,cal}$ (mg/g)	$k_1$ (min <sup>-1</sup> )	$R^2$
40	3.26	0.51	0.026	0.97	0.26	0.025	0.99
60	4.69	0.54	0.024	0.98	0.31	0.013	0.84
80	6.16	0.94	0.028	0.90	0.29	0.023	0.85

Where  $q_{e,exp.}$  is experimental value of  $q_e$  and given by:

$$q_{e,exp.} = (C_0 - C_e) \frac{V}{W} \quad \text{and}$$

$q_{e,cal.}$  is the calculated value of  $q_e$  that was obtained from the intercept of linear plot of  $\ln(q_e - q_t)$  versus  $t$ .

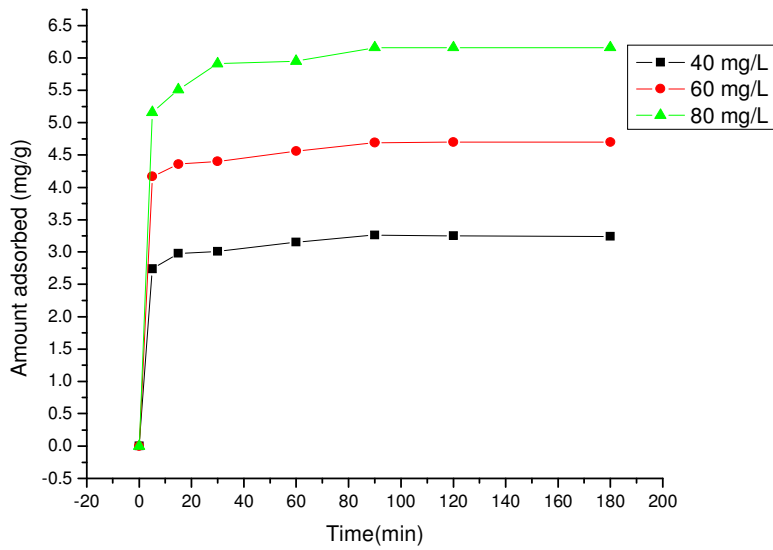


Fig. 31. Adsorption kinetics (second-order model) of CR on sludge at different initial dye concentrations for unmodified absorbent (dose: 12 g/L and solution pH 6)

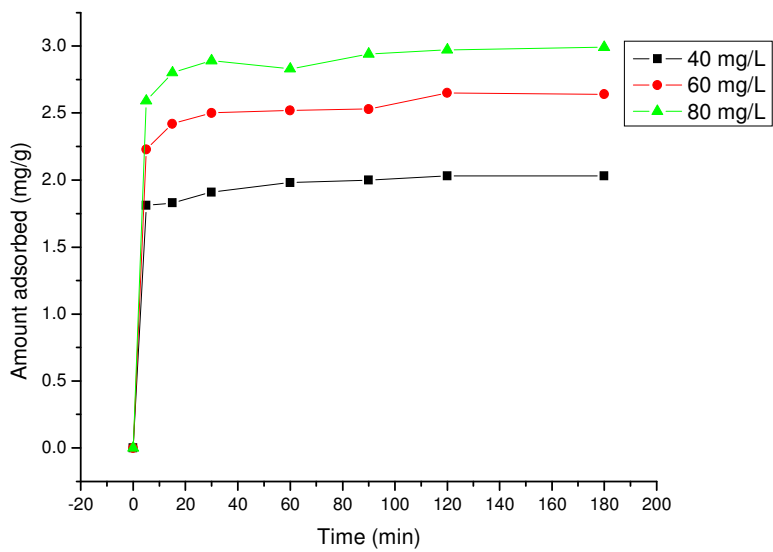


Fig. 32. Adsorption kinetics (second-order model) of CR on sludge at different initial dye concentrations for neutralized absorbent (dose: 15 g/L and solution pH 6)

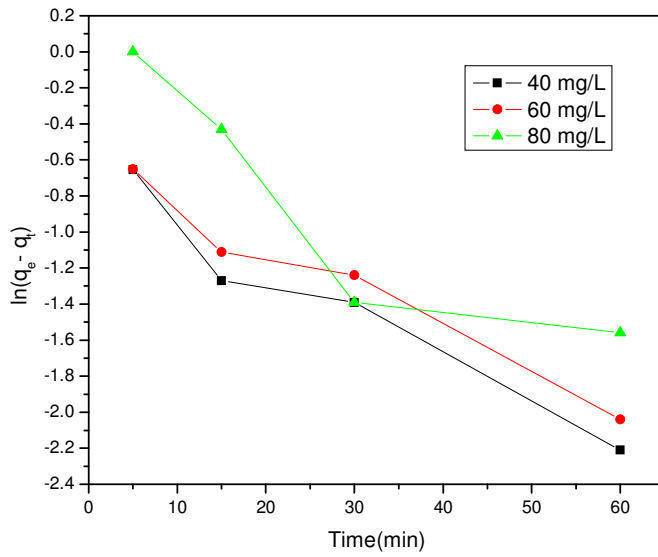


Fig. 33. Pseudo-first order kinetic plot for the removal of CR (adsorbent dose/unmodified: 12 g/L and solution pH 6)

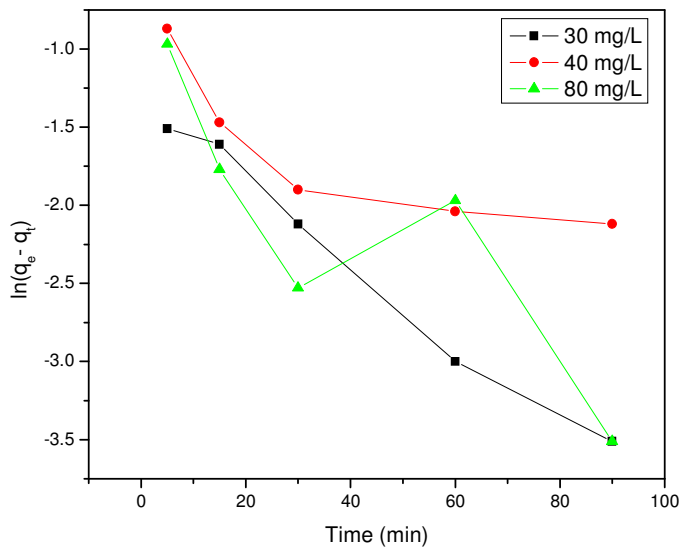


Fig. 34. Pseudo-first order kinetic plot for the removal of CR (adsorbent dose/neutralized: 15 g/L and solution pH 6)

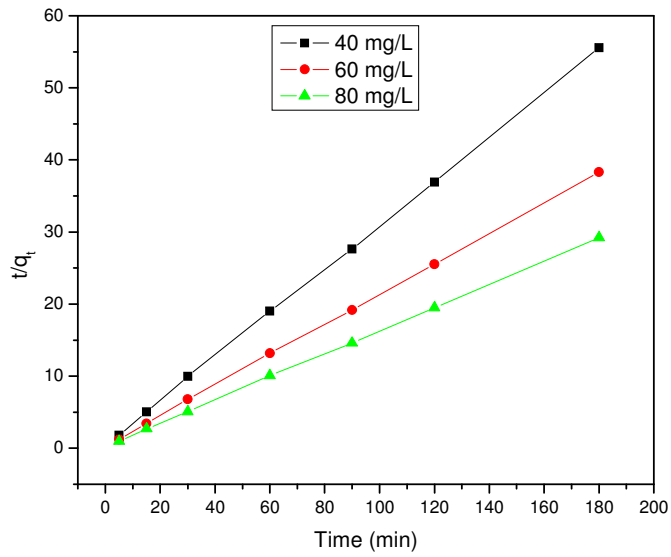


Fig. 35. Pseudo second-order kinetic plot for the removal of CR (adsorbent dose/ unmodified: 12g/L and solution pH 6)

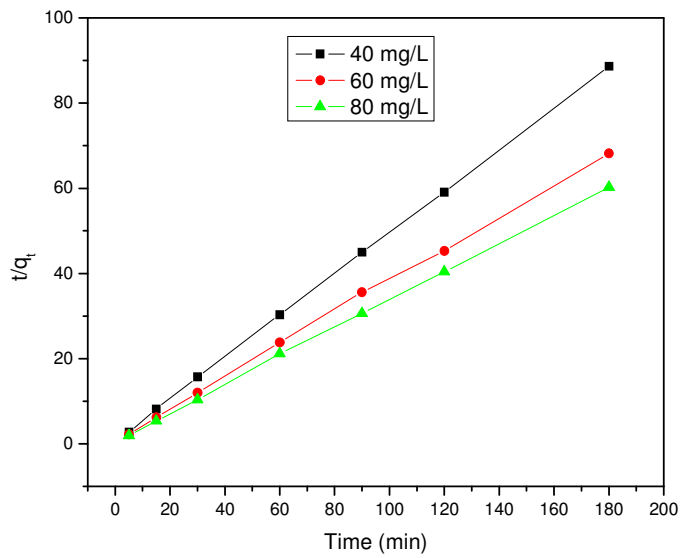


Fig. 36. Pseudo second-order kinetic plot for the removal of CR (adsorbent dose/ neutralized: 15g/L and solution pH 6)

A more accurate fit of kinetic data was obtained for pseudo second-order model (Figs. 35 and 36). The regressed kinetics adsorption parameters of the model together with the error functions for the experimental results were summarized in Table 9.

Table 9: Pseudo second-order kinetic parameters and error functions for the adsorption of CR

<u>Unmodified adsorbent</u>						
$C_o$ (mg/L)	$q_{e,exp}$ (mg/g)	$q_{e,cal.}$ (mg/g)	$k_2$ (g/mg.min)	$h$ (mg/g.min)	S.D. (%)	$R^2$
40	3.26	3.28	0.189	2.03	9.9	0.9999
60	4.69	4.74	0.142	3.19	7.5	0.9999
80	6.16	6.22	0.099	3.83	10.3	0.9999

<u>Neutralized adsorbent</u>						
$C_o$ (mg/L)	$q_{e,exp.}$ (mg/g)	$q_{e,cal.}$ (mg/g)	$k_2$ (g/mg.min)	$h$ (mg/g.min)	S.D.(%)	$R^2$
40	2.03	2.05	0.30	1.26	8.1	0.9999
60	2.65	2.66	0.18	1.27	9.7	0.9997
80	2.97	3.01	0.21	1.9	7.9	0.9998

Where  $q_{e,exp.}$  is the experimental value of  $q_e$  given by:

$$q_{e,cal.} = (C_o - C_e) \frac{V}{W} \text{ and}$$

$q_{e,cal.}$  is the calculated value of  $q_e$  that was obtained from the intercept of linear plot of  $t/q_t$  versus  $t$ .

The value of rate constant for unmodified adsorbent decreases with increasing initial dye concentration (Table 9), while the initial adsorption rate increases with increasing initial dye concentration, and it is lower than the corresponding rate constant value of neutralized adsorbent. This suggests that the rate of adsorption for unmodified adsorbent was faster than that of the neutralized adsorbent (Worku et al., 2007). For lower initial adsorption rate, longer time is required to reach equilibrium (Chiou, 2003). For the neutralized adsorbent, the time required to reach equilibrium is longer than that of unmodified adsorbent. Moreover, for the unmodified adsorbent, adsorption capacity increase as initial dye concentration increases. Increase in initial dye concentration thus result in a significant increase in the amount of dye adsorbed at equilibrium ( $q_{e,exp}$  and  $q_{e,cal}$ ) for unmodified adsorbent as compared to the neutralized one. Similar trend was observed for the adsorption of reactive dyes such as reactive black 5 ( Iscen et al., 2007) and reactive red 189 (Chiou et al., 2003).

From the observations made, pseudo second-order adsorption mechanism is predominant model and the overall rate of dye adsorption process might be controlled by chemisorption mechanism (Bayramoglu et al., 2007, Chiou et al., 2003 and Inbaraj et al., 2007). However, thermodynamic analysis was more appropriate to reach at a decision whether the adsorption of CR was a physisorption or a chemisorption process (Wu, 2007).

### **3.8. Intra-particle diffusion**

If the transport of the dye molecules from the bulk solution to the liquid film or boundary surrounding the adsorbent is ignored, the adsorption mechanism of the dye consists of the following sequence of steps: transport of the dye molecules from the boundary film to the external surface of the adsorbent (film diffusion), transport of the dye molecules from the surface of adsorbent to intra-particle site and uptake of the dye molecules by the active sites of adsorbent (Asku, 2005, Doang et al., 2003, and Waranusantigul et al., 2003). The overall rate of dye adsorption will be controlled by the slowest step, which could be either film diffusion or intra-particle diffusion. The rate of adsorption of the dye to active sites of

adsorbent is assumed to be rapid (Wang, Wu, 2006, and Dogan et al., 2003). During the design of wastewater treatment process, the determination of potential rate controlling adsorption mechanism is important (Aksu, 2005).

According to Weber and Morris, if the intra particle diffusion is the rate controlling factor, uptake of adsorbate varies with square root of time. Hence it is possible to measure the rate of adsorption of the dye through determination of adsorption capacity of adsorbent as a function of the square root of time. Intra-particle diffusion model can be represented as (Bulut et al., 2007 and Wu, 2007):

$$q_e = k_3 t^{1/2} + C \quad (22)$$

Where  $k_3$  ( $\text{mg/g}\cdot\text{min}^{-1/2}$ ) is the intra-particle diffusion rate constant and  $C$  ( $\text{mg/g}$ ) is the intercept. The value of  $k_3$  is evaluated from the slope of straight line portion of plot of  $q_e$  versus  $t$ . The value of  $C$  provides evidence about the thickness of boundary layer, and for larger value of  $C$ , the boundary layer effect is greater (Rajoria et al., 2007).

If the mechanism of adsorption follows intra-particle diffusion process, the plot of  $q_t$  versus  $t^{1/2}$  should be straight line and pass through origin. Figs. 37 and 38 show the intra-particle diffusion plots for both unmodified and neutralized adsorbents. In the plot of  $q_t$  versus  $t^{1/2}$ , it may be observed that there are two separate regions that represent the steps involved during the process of adsorption (Porkodis et al., 2007, and Mane, Mall, Srivastava, 2006). The initial curve portion was due to bulk diffusion and the linear portion corresponds to the intra-particle diffusion.

The values of intra-particle diffusion constants and intercepts for unmodified adsorbent were greater than that of neutralized adsorbent, even though the values of correlation coefficients were comparable for the respective concentrations. For both types of adsorbents, the plots were not best-fit straight lines passing through origin (Table 8). This phenomenon indicates that there is boundary layer resistance. One of the possible reasons

for the deviation of straight line from the origin is that there is a difference in the rate of mass transfer in the initial and final stage of dye adsorption. The results of the experiment suggest that the intra-particle diffusion was not the only step controlling adsorption of the dye (Bulut et al., 2007, Rajoria et al., 2007, and Wu, 2007).

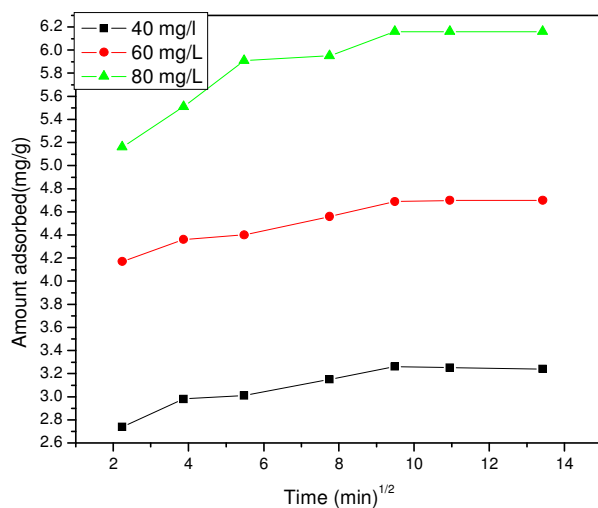


Fig. 37. Weber and Morris intra-particle diffusion plot for the removal of CR at various initial concentrations of dye (adsorbent dose/unmodified: 12 g/L and solution pH 6)

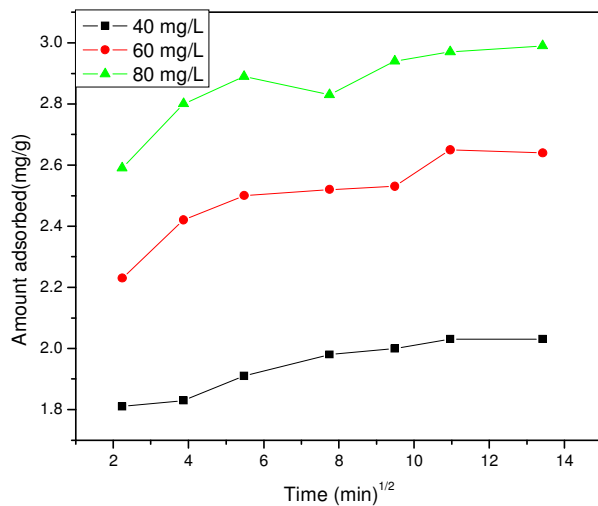


Fig. 38. Weber and Morris intra-particle diffusion plot for the removal of CR at various initial concentrations of dye (adsorbent dose/neutralized: 15 g/L and solution pH 6)

Table 10: Parameters of intra-particle diffusion model (initial dye concentration: 50 mg/L, pH 7 and temperature: 21°C)

Unmodified adsorbent				Neutralized adsorbent		
$C_0$	$k_3$	$C$	$R^2$	$k_3$	$C$	$R^2$
(mg/L)	( $\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1/2}$ )	(mg/g)		( $\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1/2}$ )	(mg/g)	
40	0.044	2.76	0.91	0.022	1.77	0.95
60	0.049	4.14	0.95	0.033	2.25	0.91
80	0.086	5.20	0.90	0.03	2.63	0.87

## **4. Conclusion and Recommendations**

### **4.1. Conclusion**

A batch system was applied to study the adsorption of CR from water by adsorbent obtained from Awash Melkassa Aluminum Sulfate and Sulfuric Acid Factory. The color removal efficiency of the dye was investigated by employing both unmodified and neutralized adsorbents. The results of the experiment showed that most of the dye adsorption took place in the first 15 and 30 minutes of contact times, and equilibrium is reached within 90 and 120 minutes for unmodified and neutralized adsorbents, at optimum doses of 12 and 15 g/L, respectively. The system pH played a significant role on the adsorption of the dye. As pH decreased, percent removal of the dye increased. The results of experiment showed that without any modification, about 92% removal efficiency was obtained within 90 minutes of equilibrium contact time from simulated dye solution of 50 mg/L at a dose of 12 g/L. The D-R isotherm model with a capacity of 9397.8 mg/g fitted well to the experimental results. On the basis of kinetic studies, the calculated rate constants involved showed that pseudo second-order model fit better to the experimental results. Furthermore, intra-particle diffusion was not the only step controlling adsorption of the dye.

## **4.2. Recommendations**

Recently, there are increasingly stringent restrictions on the organic contents of industrial effluents. However, many textile industries fail to meet the effluent discharge standards set by regulatory bodies. One of the reasons for the failure is the cost associated with activated carbons and other available technologies used to remove contaminants from the effluent. As it was discussed in the literature part, different methods have been proposed to solve problems related to textile effluents. So far there is no single method that is efficient to treat wastewater. Currently different processes are combined in most economical ways to get the desired water quality.

The waste residue obtained from Awash Melkassa Aluminum Sulfate and Sulfuric Acid Factory can be considered as low cost adsorbent. Furthermore, this adsorbent is abundant and has no economic values and even it presents the disposal problems. Thus there is a promising benefit for large scale application of the adsorbent to remove the most problematic, water soluble reactive azo dyes from textile effluent. However, much work is necessary in the area of predicting the performance of adsorption process for dye removal from real textile effluents under range of operating conditions. Moreover, better understanding of adsorption mechanism is also essential to estimate economic feasibility of the sludge for large scale application.

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