

**Enhancing Adsorption Capacity of Bentonite for Dye
Removal: Physiochemical Modification and Characterization**

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ABBREVIATIONS

AA	Acid Activation
ATA	Acid and Thermal Activation
BET	Braunneur – Emmet – Teller
CR	Congo Red
FTIR	Fourier Transform Infra Red Spectroscopy
RB	Raw Bentonite
SEM	Scanning Electron Microscopy
TA	Thermal Activation

ABSTRACT

Bentonite, enormously abundant natural clay, has been considered as a potential absorbent for removing pollutants from water and wastewater. Nonetheless, the effective application of bentonite for water treatment is limited due to small surface area and presence of net negative surface charge, leading to its low adsorption capacity. The net negative charge on the surface of bentonite is the prime factor that restricts the use of bentonite for the adsorption of cationic dyes. As a result, the focus of this research was directed towards the modification of the physical structure and the chemical properties of bentonite to maximize its adsorption capacity. To achieve this aim, the research study was carried out by two stages; (1) modification of Australian raw bentonite and (2) characterization and optimization of adsorption performance and kinetics of the modified Australian bentonite for removing recalcitrant organic dye Congo red (CR).

The modification of raw bentonite was carried out by three physiochemical methods; (1) thermal activation (TA), (2) acid activation (AA) and (3) combined acid and thermal activation (ATA). The characterization of the physiochemically modified bentonite clays was carried out by Braunneur – Emmet – Teller (BET) method for surface area, scanning electron microscopy (SEM) for morphology and Fourier transformation infrared (FTIR) spectroscopy for the determination of the effect of acid attack. The increase in surface area of the modified bentonite was recorded as 20%, 65% and 69.45% by TA, AA and ATA, respectively. The microscopic images obtained through SEM showed that the

structure of the modified clay has become more porous, offering additional adsorption sites enhancing the surface properties of bentonite.

The modified bentonites by TA, AA and ATA were examined for their performance as an adsorbent for the CR removal. The effect of key operational parameters, such as contact time, initial dye concentration, adsorbent dosage, pH and temperature was experimentally studied. The CR adsorption increased with an increase in contact time. A CR removal of 96.65%, 92.75% and 91.62% was obtained within first 2h using the bentonite modified by ATA, AA and TA, respectively. Near 100% of dye removal was achieved in 22h. The adsorption capability of bentonite increased steadily with an increase in initial dye concentration. The pH changes appeared to have insignificant impact on the CR adsorption. The adsorption capacity decreased slightly with an increase in temperature, suggesting favorable adsorption at low temperatures for all modified bentonites. The evaluation of thermodynamic parameters revealed that adsorption process is spontaneous and exothermic.

The equilibrium data was analyzed using Langmuir and Freundlich adsorption isotherms. Freundlich isotherm provided a better fit to the data. Results from kinetic study revealed that the CR adsorption on all modified bentonites occurs in multilayers, and does not form a monolayer. It was approved by a steady increase in CR adsorption with the increase in initial dye concentration. 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 follows pseudo second-order kinetics. The

mechanism of adsorption was interpreted from the intraparticle diffusion model and it was found that apart from intraparticle diffusion there are other factors that control the adsorption.

The results from this study suggest that a combination of thermal and acidification, as referred ATA in this study be an effective method to improve adsorption capacity of the bentonite. The bentonite modified by ATA provides the maximum surface area and adsorption capacity and can be successfully employed for the removal of dyes from wastewater. Bentonite is abundant natural adsorbent. Therefore, application of the simple and low cost modification techniques employed in this study can make the bentonite as cost-effective adsorbent for removal of many organic and inorganic pollutants.

DECLARATION

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CHAPTER 1

INTRODUCTION

1.1 Background

Water is one of the vital necessities for the survival of human beings. Earth is a planet with 71% of its surface covered by water. Of the total available water on earth 97% is seawater and unavailable for human consumption, only 3% is available as fresh water. Out of this 3%, only a meager 0.06% can be easily accessed as the rest comprises of the frozen polar ice cap, groundwater and swamp (Rijsberman, 2006). The water demand doubles globally every 21 years due to the rapid increase in the population and the industrial activities. Compounded with this is the decrease in rainfall in the previous decade (Humphreys, 2009). More than 80 countries accounting for 40% of the world's population are facing major water crises. It has been estimated by UN that by 2025, 2.7 billion people will be affected by water deficiency (Ahuja, 2009). Many countries are facing the shortage of clean drinking water and it is estimated that 1.2 billion people are already drinking unclean water (Rijsberman, 2006). Furthermore, 5-10 million people die annually due to various diseases caused by the consumption of contaminated water. Thus, exploitation of safe water sources to overcome the scarcity of water has been a global challenge for many countries like Australia. The increasing demand of clean water has attracted much of the

attention of government organizations and water industries to develop cost-effective technologies for water/wastewater treatment and reclamation.

Wastewater reclamation, recycling and reuse are vital to meet the water requirements for irrigation, industry and domestic uses due to increasing population and development in many parts of the world. The term reclamation refers to the treatment of wastewater which produces water with high quality being reused for agricultural and industrial applications. Wastewater recycling implies reuse of the captured effluent from one user by returning it to the system (Asano et al., 1998). The reuse of reclaimed wastewater is essential for sustainable development in the 21st century (Stikker et al., 1998). The water scarcity is not only a problem of developing countries but also has affected many developed countries as well. Australia is one of the driest continents of the world that faces drought roughly once in every hundred years (Viessman and Hammer, 1998). South Australia is the driest region in Australia receiving the lowest rainfalls. It is predicted that by 2030 the average rainfall may reduce up to 10% (Humphreys, 2009). The major share of water consumption goes to agriculture industry, accounting for 75% of total consumption (Gabrecht and Piechota, 2006). This high demand for irrigation in South Australia has initiated the urgency to regulate the existing water and develop new methods for reclamation and reuse.

Wastewater can be reclaimed from various sources such as industrial effluent, municipal wastewater, agricultural return flows and stormwater. Depending upon

the physical, chemical and biological constituents, water can be reclaimed by different methods. The selection of wastewater treatment technique is very critical and has to be made considering the contaminants present in wastewater. Industrial wastewaters largely possess organic and inorganic materials such as dyes, phenolic compounds, aromatic compounds and heavy metals (Asheh et al., 2003). Almost all the dyes, even the naturally occurring dyes, used today are now synthesized chemically. Annually, a total of more than 7×10^5 tonnes of dyes are produced out of which azo dyes account for 60-70% (Zohra et al., 2008). Over the years the use of dyes has increased and is immensely used in industries like textile, cosmetics, pulp and paper, paint, pharmaceutical, food, carpet and printing. The discharge from these industries is highly colored as enormous amount of dyes remains unfixed during coloring and washing (Santos and Boaventura, 2008). These traces of dye are discharged into the effluent (Zohra et al., 2008). Thus the treatment of this effluent is crucial. The discharge of effluent without proper treatment can get mixed with surface and ground waters and eventually can enter the drinking water (Acemioğlu, 2004). Furthermore, dye effluent if discharged untreated affects the photosynthesis of aquatic plants by preventing the light to penetrate through water. The oxygen levels are affected and in extreme cases may lead to suffocation of aquatic flora and fauna (Purkait et al., 2007) as azo dyes can be degraded to more dangerous substances under anaerobic conditions (Song et al., 2009).

The reclamation and reuse of the water are essential for the sustainable supply of water in the future to meet the growing demand of freshwater for the increasing industry development and population growth. The prerequisite for the synthesis of dyes is to impart strong color that is stable and does not degrade with time and on exposure to light. Therefore most of the dyes have complex chemical structure and bear an aromatic ring which is hard to break (Damardji et al., 2009; Unuabonah et al., 2008). The dyes are toxic and non-biodegradable, and can lead to increasing pollutants concentrations and environmental risks, if they are discharged into the waterways. Eventually the pollutant concentration will reach high enough levels that will prevent re-establishment of a microbial population as a result water quality will degrade permanently (Bulut et al., 2008). In humans, toxic dyes can cause dysfunction of kidneys, reproductive system, liver, allergy, dermatitis, skin irritation and cancer (Özcan and Özcan, 2004).

The reclamation of wastewater requires cost effective techniques that can generate high quality water for reuse. The reclamation of wastewater may reduce the demand for freshwater. In recent decade increasing practices for many water industries have focused on using treated and recycled water. For instance, Keller (2006) has described the water reclamation at a brewery at Yatala, Australia. The brewery required 8-10L of fresh water for production of 1L of beer. After the installation of the improved water treatment plant 60-65% of effluent was recovered and reused. This practice can reduce the fresh water requirement down to 2.5L. Although, the cost of treatment plant involved high capital but the

estimation of operating costs revealed that recycled water (\$0.85/kL) is cheaper than the potable water (\$1/kL) supplied by the local Council. This is an example of the inclination of industries towards reclamation and reuse of wastewater.

Most of the currently available technologies are inadequate for the removal of colour-induced toxic pollutants such as dyes from textile wastewater (Benkli et al., 2005). Most of the conventional methods of wastewater treatment such as coagulation and flocculation, sedimentation and floatation, membrane filtration, disinfection are either expensive or not very effective. These technologies mostly transform pollutants from one phase to another and do not completely eliminate them (Gu et al., 2008). Even though membrane filtration produces high quality water, it has a major limitation of clogging of micro- or ultra-filtration membranes adding to the operating cost. (Abdessemed et al., 2000). In a disinfection process by chlorination, chlorine sometimes reacts with organic pollutants and produces disinfection by-products, such as trihalomethanes and haloacetic acid, which are mutagenic and carcinogenic and pose threats to human and aquatic life (Ratnayaka et al., 2009). Dyes have adverse aesthetic effects and the presence of even 0.005ppm of dye in water is highly visible (Unuabonah et al., 2008; Özcan et al., 2007). Governments of most countries are imposing stringent legislations for the removal of dyes from industrial effluents and are demanding zero synthetic chemical discharge (Robinson et al., 2001). These strict rules are compelling industries and scientists to search for novel effective and economical methods of dye removal.

Adsorption has been recognized as a potential technology for the removal of dyes from wastewater. In comparison to other physical, chemical and biological methods available for the treatment of textile industry effluent, adsorption is the most preferred technique due to simple and flexible design and easy operation. The adsorption process may generate little or no toxic pollutants and involve low initial capital and operating costs (Crini, 2006). Moreover, it does not have environment issues as it does not produce any sludge (Unuabonah et al., 2008) and yields treated water with high quality (Nandi et al., 2009). Although adsorption is a proven technology for the removal of dye, it has a major limitation to its application due to sparse availability of low-cost adsorbents (Shi et al., 2007). Activated carbon is one of the most widely used adsorbents because of its high surface area and excellent adsorption capacity. But the high cost and regeneration difficulties of activated carbon have augmented the need to explore low cost, reusable, and biodegradable adsorbents for the removal of dyes (Bhatnagar and Jain, 2005). Various low-cost adsorbents that have been successfully implemented for the adsorption of dyes from wastewater are natural and modified clays (Crini, 2006), spent brewery grain (Unuabonah et al., 2008; McKay et al., 1985), modified agricultural by-products (Šćiban et al., 2008), industrial wastes (Kabra et al., 2004), coir pith (Santhy and Selvapathy, 2006; Namasivayam and Sangeetha; 2006), chitosan (Monvisade and Siriphannon, 2009) fly ash, peat, coal, baggase and neem leaves (Crini, 2006 and Beragaya et al., 2006).

Natural clays are acquiring prominence as low-cost adsorbents over the last a few decades due to their local and abundant availability and the capability to undergo modification to enhance the surface area, adsorption capacity and range of applicability (Monvisade and Siriphannon, 2009). Among natural clays, bentonite has been proven to be a promising adsorbent for dye removal. The presence of net negative charge on the surface confines the use of bentonite for the effective removal of basic dyes only (Jiuhui, 2008; An and Dultz, 2007). In addition, the adsorption capacity of natural bentonite is hampered by its small surface area. 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 bentonites have high potential to provide an alternative to most widely used activated carbon. Therefore in order to ameliorate the adsorption properties and the range to applicability, a number of physical and chemical methods have been investigated to modify the bentonites, including heat treatment (Al-Asheh et al., 2003), acid activation (Kara et al., 2003; Lian et al., 2009), treating the cationic surfactants (Yıldız et al., 2005; Wang and Wang, 2008) and polymer modification (Chen et al., 2008; Liu, 2007). Australia possesses bountiful deposits of natural bentonite such as 22 million tonnes in Miles, Queensland (Gates et al., 2002) and 40 to 70 million tonnes of bentonite exists in Arumpo, New South Wales (Churchman et al., 2002), Australia. Since the discovery of bentonite deposits in Miles, Queensland, Australia in 1971 only a meager 1.2 million tonnes have been used so far. The sole use of bentonite from this reserve is as a sorbent for pet litter (Gates et al., 2002). The productive use of these reserves necessitates

the exploration of the physico-chemical properties of the bentonite deposits. To increase the range of applicability of these reserves there is a requisite of enhancing the physico-chemical properties for specific uses.

The modification of bentonite which is itself a low-cost adsorbent drives the need for the development of a modification technique that is simple and cost-effective. The modification of bentonite by acid activation is a common technique for the past two decades. Currently, the modification of bentonite by acid activation is still experiencing a series of technical challenges. The acid activation of bentonites at a low temperature and a low acid concentration is still rarely studied. Additionally, the lucrative use of bentonite requires the modification of bentonite without seriously damaging its structure. The application of acid activated bentonites for the removal of anionic dyes such as Congo red is still not well known. It is expected that the solution to all these technical issues can be a key to economical, sustainable and technically robust technology which can provide alternative to the existing methods of modification of clays and treatment of dye effluents.

1.2 Aims and objectives

The aim of this 1.5 year thesis study is to modify the physiochemical properties of the Australian clay mineral - bentonite, to enhance its adsorption capacity to remove chemical contaminants from industrial wastewater. The research focus is

to identify and use economically and technically feasible modification techniques to enhance adsorption capacity of bentonite, making it as a low-cost and high efficiency adsorbent for removal of dye pollutant from industrial wastewater.

Specific objectives of this thesis study are to

1. Describe, evaluate and select cost-effective technique for the modification of bentonite to maximize its adsorption capacity,
2. Characterize physical properties of modified bentonite,
3. Study adsorption kinetics and performance of the modified bentonite with respect to the systemic conditions.

The main focus of the study is on the modification and characterisation of the physio-chemical properties of Australian clay minerals such as porosity, structure, surface area by acid and thermal activation and a combination of acid and thermal activation where acid activated clay will be subjected to thermal activation to improve its capability for wastewater treatment. The characterisation of the modified clay minerals will be evaluated by exploring surface area, morphology and structural changes via a series of tests like Brauner-Emmert-Teller (BET) method, scanning electron microscopy (SEM) and Fourier's transform infrared (FTIR) spectroscopy. The synthesized acid activated clays are to be used for the adsorption of an anionic dye, Congo red. The optimum operating conditions for adsorption are to be investigated by varying the material properties and other operating parameters.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The pollutant from dyeing industries is highly toxic. The removal of dyes from wastewater before its discharge is a necessary practice for water industry (Acemioğlu, 2004). The significant increase in the use of dyes by various industries is causing severe damage to the environment due to non-biodegradability and high toxicity of these compounds. Adsorption is one of the most effective dye removal techniques. Adsorbents play a vital role in the efficiency of adsorption process. The major cost of the adsorption process is incurred in the adsorbents. Various commonly used adsorbents that provide significant removal of dyes have been discussed. The use of activated carbon is wide spread, though its high cost is creating the need for development of low-cost adsorbents.

This chapter will provide detailed information and discussion about the release of dyes from dyeing industries and their harmful effects on environment and human health. Furthermore an insight into the currently available techniques for dye removal will be reviewed. Special attention will be given to current adsorption technologies for dye removal, which is the research focus of this study. Commonly used adsorbent and its activation technologies will be detailed.

2.2 Dyes and Water Pollution

Dye is an organic compound that imparts colour to substances such as textile fibre, leather, hair, plastic materials or wax either in solution or dispersion (Zollinger et al., 1991). Dyes have long been known to man and in the prehistoric times they were derived from natural plants, mainly for colouring fabric. At present almost all the dyes are manufactured artificially even the natural dyes. The artificial dyes are thoughtfully delineated to have distinctive characteristics such as; ability to impart specific colour to the substance, resistance to fade when exposed to light, chemicals and washing (Özcan et al., 2007) and resistance towards acids and bases. The groups that modify the ability of chromophores to absorb light are called auxochromes (NO_2 , NO , $\text{N}=\text{N}$). The part of molecules which provides the colour by absorbing wavelength is called chromophores (OH , NH_2 , NHR , NR_2 , Cl and COOH). Dyes can be broadly classified in two ways either based upon chemical composition or application. Table 2.1 provides the classification of dyes based on chemical composition.

Dyes have a wide range of application and are used as a coloring agent for many different substances. Dyes are widely used to impart colour to fabrics and plastics (Zollinger et al., 1991). They are also used in food industry, printing and leather industry (Srinivasan et al., 2007). Recently, dyes have gained popularity in another field that is in hair coloring (Khenifi et al., 2007). Table 2.2 presents the classification of dyes based on their application.

Table 2.1 Classification of dyes based on chemical composition (Zollinger et al., 1991; Banat et al., 1996, Forgacs et al., 2004, Martínez-Hutile and Brillas 2009)

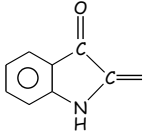
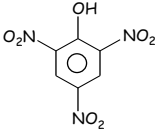
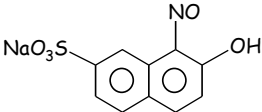
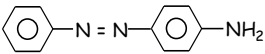
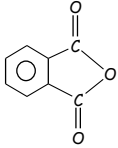
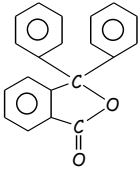
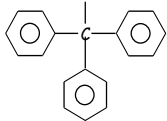
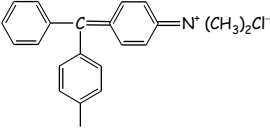
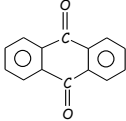
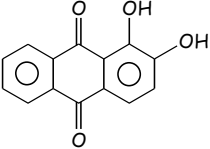
Type of dye	Structural unit	Example	
Indigoid dyes		Indigo Caramine	Oldest known dye, earlier isolated from plants of indigofera group but now prepared synthetically.
Nitro dyes	-NO ₂ group	 Picric acid	Oldest known synthetic dyes but not commercially important
Nitroso dyes	-NO group	 Naphthahol green B	Generally possess hydroxyl group (OH) at ortho position to the nitroso (-NO) group
Azo dyes	-N=N-	 Aniline yellow (p-amino azobenzene)	Largest class of synthetic dye. Other examples include Congo red, Methyl orange, Methyl red.
Phthalein dye	 Phthalein group	 Phenolphthalein	Obtained by treating phenol with phthalic anhydride
Triarylmethane dyes	 Triphenylmethane	 Malachite Green	Prepared by introducing one or more -NH ₂ , NR ₂ or OH groups into the triphenylmethane rings
Anthraquinoid dyes	 Anthraquinoid group	 Alizarin	

Table 2.2 Classification of dyes based on application (Zollinger et al., 1991; Banat et al., 1996, Forgacs et al., 2004, Martínez-Hutile and Brillas 2009)

Type of dye	Example	Application
Acid dyes	Methyl orange, Methyl red, Orange I, Orange II, and Congo red	Wool, Silk, Polyurethane fibers, nylon
Basic dyes	Aniline yellow, Butter yellow, Methylene blue and Malachite green	Reinforced nylon, polyesters
Direct dyes	Martius yellow and Congo red	Cotton, Rayon, Wool, Silk and Nylon
Disperse dyes	Celliton fast pink B, Celliton fast blue B	synthetic polyamide fibers, polyesters, nylon and polyacrylonitriles
Fiber Reactive dye	Procion dye (2, 4, 6-trichloro 1, 3, 5-triazine)	Cotton, Wool and Silk
Ingrain azo dyes	Para red	Cotton (Cellulose), Silk, Nylon, Polyester, Polyester and Leather, colouring agent in food
Vat dyes	Indigo, Tyrian purple, Benzanthrone	Wool, colouring agent in food
Mordant	Alizarin	Cotton and wools

Azo dyes are immensely used as commercial dyes. These dyes have been widely applied in virtually all industries, such as textile, cosmetics, pulp and paper, paint, pharmaceutical, carpet and printing, textile, leather and food etc. Dyes are toxic (Khenifi et al., 2007) due to the presence of benzene and aromatic ring in their structure (Banat et al., 1996). In humans, the contact with colour wastewater may cause serious health problems and hazards-induced diseases, such as allergy, skin diseases, mutation and cancer (Bhatnagar and Jain, 2005, Chatterjee et al., 2009). They can also lead to dysfunctioning of kidneys, liver, brain and central nervous system (Özcan and Özcan, 2004). The presence of color in water system reduces the penetration of light which affects the photosynthesis of aquatic biota (Bhatnagar and Jain, 2005).

The increase in the discharge of coloring effluent has become considerable environmental and healthy issues. The dye effluent is discharged at several stages. It is estimated that during synthesis of dye 1-2% remains unfixed and is discharged in the effluent. In addition, 1-10% is lost during the process of dyeing of substances in industries (Forgacs et al., 2004). The effluent from dye industries generally constitutes colored solutions, dissolved organics, inorganic solids and suspended solids (Robinson et al., 2001). However color is highly visible to human eye among all contaminants. Color is the first pollutant to attract attention (Banat et al., 1996) and presence of even 0.005 ppm can be easily detected by human eye (Unuabonah et al., 2008; Özcan et al., 2005).

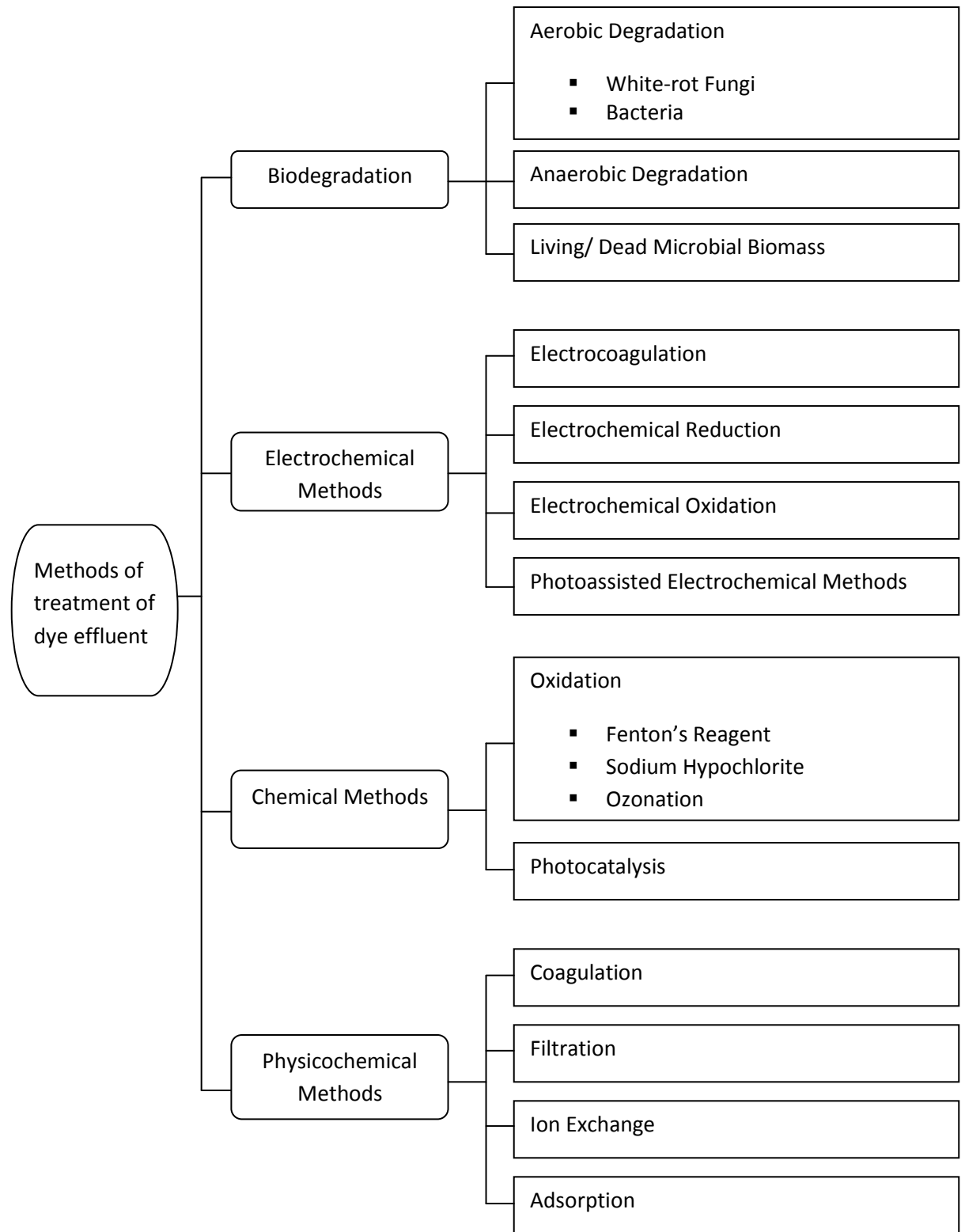


Figure 2.1 Current dye removal techniques (adapted from Martínez-Hutile and Brillas 2009)

For the past two decades several methods for dye removal have been proposed and developed by many scientists and research engineers (Robinson et al., 2001; Crini, 2006; Martínez-Hutile and Brillas, 2009). Some of these techniques have found practical applications and are used by the industries. However, the use of these technologies for industrial processes is still limited due to high-cost, and low-efficiency and capability to remove dyes (Banat et al., 1996). The methods for dye removal that have been successfully used in the dyeing industry for wastewater treatments are categorized as: biological treatment, electrochemical methods, chemical and physico-chemical methods. Figure 2.1 deciphers the technologies most widely used for dyeing effluent.

2.3 Current Dye Removal Techniques

2.3.1 Biodegradation

Biological treatment of wastewater for the removal of pollutants is widely used. The application of microorganisms for the degradation of dyes started almost two decades ago. The removal of synthetic dyes by microorganisms is a simple method but involves a complex mechanism (Forgacs et al., 2004). The growth of microorganisms is complex and requires in-depth knowledge of the suitable environment in which microorganisms can grow. Biodegradation possesses lots of advantages, including 1) the low-cost process: low infrastructure and operating costs, 2) complete mineralization with non-toxic end products, and 3) no other

chemicals which are themselves associated with potential health hazards (Stoltz, 2001).

2.3.1.1 Aerobic Degradation

White-rot Fungi

White-rot fungi; *Phanerochaete Chrysosporium* has been extensively used for the removal of dyes (Capalash and Sharma, 1992; Glenn and Gold, 1983; Cripps et al., 1990). There are various fungi studied by researchers that are capable of biodegradation of dye and some of these are provided in Table 2.3. The decolorisation of Orange II, Tropaeolin 0, Congo red and Azure B under aerobic condition by white-rot fungi has been analyzed. Although 93-100% dye removal can be achieved the degradation rate is very low (Cripps et al., 1990). Nearly 40% removal of sulphonated azo dyes has been achieved in 21 days (Pasczynski et al., 1992). The high capability of *P. Chrysosporium* for biodegradation of dyes from wastewater is due to the presence of lignin peroxidase. The enzyme, lignin peroxidase, is not specific in nature offering a wide range of applicability for degradation of dyes by *P. Chrysosporium* (Rai et al., 2005). However, Wang and Jain (1999) reported that the practical application of *P. Chrysosporium* for the treatment of real wastewater is not possible. This is due to the fact that the growth of lignin peroxidase, an enzyme responsible for degradation of dyes, is inhibited by the presence of carbon or nitrogen (Perie and Gold, 1991).

Table 2.3: Adsorption capacities of various fungi for dyes (adapted from Banat et al., 1996)

Culture	Dye	Conc. (mgL ⁻¹)	Removal time	%age removal	Reference
<i>Aspergillus</i>	Amaranth	10.0	5days	97.8	Ryu and
<i>sojae</i>	Sudan III	10.0	5days	97.4	Weon, 1992
B-10	CongoRed	10.0	5days	93.0	
<i>Myrothecum</i>	Orange II	200.0	5h	70.0	Brahimi-
<i>Verrucaria</i>	10B(Blue)	200.0	5h	86.0	Horn et al.
	RS (Red)	200.0	5h	95.0	(1992)
<i>Myrothecum</i>	Orange II	100.0	24h	25-91%	Mou et al.
sp.	10B(Blue)	100.0	24h	58-98%	(1991)
	RS (Red)	100.0	24h	81-98%	
<i>Neurospora</i>	Vermelho	16-32	24h	89-91%	Corso et al.,
<i>crassa</i>	Reanil P8B				(1981)
<i>Pycnoporus</i>	Pigment plant	Unknown	3days	90%	Schliephake
<i>cinnabarinus</i>	effluent				et al. (1993)
<i>Trichoderma</i>	Hardwood	Unknown	3days	85%	Prasad and
sp.	extraction effluent				Joyce (1991)
<i>Candida</i> sp.	Procyon Black	100.0	2h	93.8%	De Angelis
	Procyon Blue	100.0	2h	96.8%	and
	Procyon Red	100.0	2h	98.9%	Rodrigues
	Procyon Orange	100.0	2h	96.8%	(1987)

Moreover lignin peroxidase requires additional reagents such as hydrogen peroxide and veratryl alcohol for degradation of dyes. In the industrial wastewater it is difficult to maintain a balance between lignin peroxidase, hydrogen peroxide and veratryl alcohol (Banat et al., 1996). Wang and Jain (1999) proposed the use of *Trametes versicolor* for the removal of dyes from textile effluent. The enzyme, such as laccase, is an oxidase that is mainly responsible for the decolorisation of dyes.

Laccase can be generated even in the presence of carbon or nitrogen and does not require any secondary metabolites to catalyze the oxidation. *T. versicolor* is very effective in the removal of anthraquinoid dyes but for the decolorization of indigo and azo dyes, redox mediators are required (Robinson et al., 2001). Campos et al. (2001) analyzed the decolorization of an indigo dye by laccase and found that no decolorization was obtained. However with the addition of redox mediator complete decolorization was achieved. The removal of dye by fungus depends on dye complexity, availability of nitrogen in the media and ligninolytic activity in the culture (Banat et al., 1996).

Bacteria

The study of decolorization of dye under aerobic conditions by bacteria started more than two decades ago (Rai et al., 2005, Banat et al., 1996). Recently some biodegradation processes using bacterial strains have been proved to be very successful in mineralization of dyes under aerobic conditions and are presented in

Table 2.4. Several other strains have been successfully employed for the removal of dyes such as *Aeromonas hydrophilia* (Jiang and Bishop, 1994), *Pseudomonas* (Kulla et al., 1983), *Pseudomonas luteola* (Hu, 1994) and *Bacillus subtilis* (Azmi and Banerjee, 2001). It has also been affirmed that most of the strains require additional carbon and energy sources (Zissi et al., 1997). It is suspected that these additional carbon and energy sources lead to the formation of micro anaerobic zones within an aerobic system. Furthermore it is expected that these micro anaerobic zones might have facilitated the anaerobic reduction of azo dyes (Costerton et al., 1994). The bacterial degradation of sulfonated azo dyes is also affected by the presence of sulfo groups (Kulla et al., 1983).

Table 2.4: Bacteria strains commonly used for degradation of dyes

Culture	Dye	Reference
S5 (from <i>Hydrogenophaga palleronii</i> S1)	Sulfonated azo dye	Blumel et al., 1998
MI2 (from aerobic biofilm reactor)	Acid orange 7, Acid orange 8	Coughlin et al., 1997
1CX (<i>Sphingomonas</i> sp.)	Acid orange 8, Acid orange 10 Acid red 4, Acid red 88	Coughlin et al., 1999
<i>Kurthia</i> sp.	Magenta, Crystal violet Brilliant green, Malachite green	Sani and Banerjee, 1999

Other Cultures

Learoyd et al. (1992) investigated the removal of some dyes by food spoilage bacteria. Their results revealed that the reduction rate highly depends on degradation ability of bacteria. Apart from that it is also influenced by the sensitivity of dyes to reduction mechanism. Algae such as *Chlorella pyrenoidsa*, *C. vulgaris* and *Oscillatoria tenuis* have been used for degradation of azo dyes (Forgacs et al., 2004, Banat et al., 1996). The decolorization of azo dyes by algae is brought about by the azo reductase. The degradation mechanism involves the breaking of azo linkage by azo reductase (Liu and Liu, 1992). The azo compounds thus transform to aromatic amines to simpler organic compounds or CO₂ (Banat et al., 1996). Mixed cultures offer the advantage of attacking the dye molecule by a specific strain at a particular position. The decomposition product may be useful for another strain to attack the dye molecules. Nonetheless, the control over the strains becomes difficult as during the decomposition process the composition of mixed cultures changes (Forgacs et al., 2004).

2.3.1.2 Anaerobic Degradation

The decolorization of azo dyes by anaerobic degradation has also delivered successful results and has been studied since 1970 (Rai et al., 2005). The anaerobic degradation of azo dyes has been studied by various researchers (Carliell et al., 1996; Banat et al. 1996; Van der Zee et al., 2000; Baughman and

Weber, 1994). However, the exact mechanism of decolourization is still not well known (Robinson et al., 2001). It has been presumed that the biodegradation of azo dyes occurs by oxidation-reduction mechanism (Carliell et al., 1996).

The co-substrates such as glucose, yeast extract, acetate and propionate are commonly used as electron donors (Forgacs et al., 2004; Banat et al., 1996). Apart from co-substrates, the reaction conditions such as pH and temperature also control the dye removal mechanism. In addition to co-substrates, mediators that facilitate the electron transport also accelerate the azo reduction rate (Van der Zee et al., 2000; Robinson et al., 2001).

The presences of salts also 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). It was found that the half-life for anaerobic decolorization in anoxic settled bottom sediments of some dyes varied from a few days (Solvent Red 1) to several months (Solvent Yellow 33) (Baughman and Weber, 1994). A combined aerobic and anaerobic process is preferred as it can provide complete degradation of dyes. The intermediate products generated during anaerobic process have to be degraded by an aerobic process (Forgacs et al., 2004, Rai et al., 2005).

2.3.1.3 Living/Dead Microbial Biomass

Dead bacteria, yeast and fungi also have the capability to degrade dye. The removal capacity of microorganism depends on the affinity of the dye for binding with microorganisms (Robinson et al., 2001). Modak and Natarajan (1995) suggested that use of microbial biomass delivers effective results in the removal of dyes when dyes are very toxic. In such cases the growth of microorganisms is affected by the toxicity of dye and sometimes the growth of microorganisms is not possible. The degradation of dye by microbial biomass is faster in comparison to bacteria and algae. The faster degradation rate is attributed to an increase in surface area caused by cell rupture during autoclaving (Polman and Brekenridge, 1996, Robinson et al., 2001).

Biological treatment process alone is not capable of 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 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).

2.3.2 Electrochemical Methods

2.3.2.1 *Electrocoagulation*

Electrocoagulation is the modification of conventional coagulation process for wastewater treatment. The coagulating agents such as Fe^{3+} and Al^{3+} facilitate the formation of coagulants and are produced by the anodes that are immersed in the wastewater (Brillas et al., 2003). This results in the separation of dye from wastewater. The coagulants are then removed from the wastewater either by sedimentation or by electroflotation with evolved hydrogen gas (Ibanez et al., 1998). The removal of dyes by electrocoagulation is affected by the electrolytic system, solution pH, stirring and current density (Daneshvar et al., 2007, Golder et al., 2005).

The removal of various dyes such as Acid orange 7 and Acid orange 10 (Mollah et al., 2004), Basic blue 3 and Basic blue 46 (Daneshvar et al., 2007) have been performed by electrocoagulation using an iron anode and 93 -100% removal of all dyes was achieved. On the other hand 94-97 % removal of dye was achieved using aluminum anode for the removal of Disperse blue 139, Disperse red 74, Disperse yellow 126 (Szpyrkowicz, 2005), Reactive orange 64 and Reactive red 198 (Can et al., 2003).

The removal of the dyes in electrocoagulation is affected by the type of anode used for production of the coagulating agents (Martínez-Hutile and Brillas, 2009).

The removal of dyes by electrocoagulation is fast, and, therefore, requires small amount of chemicals and lower operating costs (Chen, 2004 and Lin and Peng, 1994). On the other hand the anode performance and the sludge deposit can hamper the effective removal of dyes (Brillas et al., 2009).

2.3.2.2 *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. The removal mechanism of dye by electrochemical reduction has been discussed in detail by Brillas et al. (2009). The removal of dyes such as Acid yellow 23 (Jain et al., 2003), Reactofix golden yellow 3 (Jain et al., 2007) and Reactive blue 4 (Carneiro et al., 2004) has been studied. Jain et al. (2003) investigated the adsorption of Active Yellow 23 on Pt and steel cathode. The results revealed that the time required for decolorizing by steel cathode (2h) was half in comparison to Pt cathode (4h).

2.3.2.3 *Electrochemical Oxidation*

The electrochemical oxidation of dyes is widely used among the electrochemical methods of dye removal. The degradation of dyes in the electrolytic cell may take place by direct anodic oxidation. The direct anodic oxidation does not provide complete degradation of dyes due to the formation of some by-products during the process (Panizza and Cerisola, 2007). However complete removal of dyes can be

achieved by chemical reaction with electrogenerated oxidizing agents (Brillas et al., 2003). Table 2.5 represents the percentage color removal obtained on different anodes.

Table 2.5: Percentage removal of dyes on different anodes (Martínez-Hutile and Brillas, 2009)

Dye	Conc.	Electrolysis time (h)	% colour removal	References
<i>PbO₂ anode</i>				
Blue Reactive 19	25 mgdm ⁻³	2.00	100.0	Andrade et al., 2007
Basic Brown 4	100 mgdm ⁻³	0.50	100.0	Awad and Galwa, 2005
<i>Ti/Sb₂O₅-SnO₂ anode</i>				
Acid Orange 7	750 mgdm ⁻³	6.25	98.0	Chen et al., 2003
Reactive Red 120	1500 mgdm ⁻³	6.25	95.0	Chen et al., 2003
<i>Ti/Ru_{0.3}Ti_{0.7}O₂ anode</i>				
Reactive Red 198	30 mgdm ⁻³	3.00	80.0	Catanho et al., 2006
Direct Red 81	0.1 mM	3.00	100.0	Socha et al., 2006
Direct Black 36	0.1 mM	3.00	40.0	Socha et al., 2006
Acid Violet 1	0.1 mM	3.00	100.0	Socha et al., 2007
<i>Pt anode</i>				
Acid Red 27	100 mgdm ⁻³	3.00	100.0	Hattori et al., 2003
Reactive Orange 4	100 mgdm ⁻³	1.00	91.0	López-Grimau and Gutiérrez (2006)
<i>ACF anode</i>				
Acid Red 27	80 mgdm ⁻³	8.00	99.0	Fan et al., 2006
<i>Graphite anode</i>				
Vat Blue 1	200 mgdm ⁻³	0.50	14.0	Cameselle et al., 2005
<i>Polypyrrole anode</i>				
Direct Red 80	350 mgdm ⁻³	70.00	100.0	Lopez 2004

The commonly used electrochemical systems are three-electrode cells with one (Xiong et al., 2001 and Fan et al., 2006) or two compartments (Chen and Chen, 2006). Flow cells with parallel electrodes (Panizza and Cerisola, 2007) and flow plants with three phase three dimensional electrode reactor (Xiong et al., 2001) are also widely used for removal of dyes from wastewater. A wide range of electrodes such as granular activated carbon, activated carbon filter, glassy carbon, graphite and Pt (Xiong et al., 2001, Fan et al., 2006, Carneiro et al., 2005 and Panizza and Cerisola, 2007) are commonly used for the electrochemical oxidation for decolorisation of dyes. The choice of anode for the removal of dyes from wastewater is vital as the degree of mineralization highly depends on the type of anode employed (Martínez-Hutile and Brillas, 2009).

2.3.2.4 Photoassisted Electrochemical Methods

The mechanism of dye removal by photoassisted electrochemical method is similar to that of advanced oxidation processes (AOPs) based on the use of UV irradiation (Brillas et al., 2003). The extent of degradation of dyes depends on the intensity and wavelength of the incident light. The photoassisted Fenton ($\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ system) method involves the exposure of dye effluent to UV light. This results in the production of free hydroxyl ions and photodegradation of iron complexes by organics (Peralta-Hernández et al., 2008). The photoassisted method delivers better removal efficiency compared to electrochemical oxidation or electrocoagulation (Martínez-Hutile and Brillas, 2009). 100% removal of Acid

orange 7 (Peralta-Hernández et al., 2008) and Acid blue 64 (Flox et al., 2006) was achieved by photoassisted electro-Fenton method after 1h and 7h respectively. The photoassisted electro-Fenton requires less time for the degradation of dyes compared to standard electro-Fenton method (Martínez-Hutile and Brillas, 2009), although in some cases the complete mineralization is not achieved (Golder et al., 2005).

The photocatalytic degradation is normally carried out by TiO_2 catalyst. The UV light provides the energy for the excitation of electrons from the valence band to the conduction band. TiO_2 is most widely used catalyst due to low cost, low toxicity and wide energy gap of 3.2 eV (Peralta-Hernández et al., 2006). Zainal et al. (2005) investigated the removal of Methyl orange by using TiO_2 catalyst. The results revealed that the removal efficiency is affected by the light source and the intensity of light. It has also been found that 94% dye removal was achieved by 300W tungsten lamp in contrast to 93% removal of Methyl orange by 100W UVA lamp. Other dyes that have been successfully removed by photoelectrocatalysis are Reactive blue 4, Reactive orange 16, Acid orange 52, Direct red 81 and Acid violet 1 (Carneiro et al., 2005, Zainal et al., 2005, Catanho et al., 2006, Socha et al., 2007). The major drawback of photoelectrocatalysis lies in the huge amount of energy that is involved in the photoassisted systems which incur high cost for the process (Martínez-Hutile and Brillas, 2009).

Although the removal of dyes by electrochemical methods is fast but it requires additional treatment such as sedimentation or filtration. The electrochemical removal of dyes requires control over operating parameters (Daneshvar et al., 2007, Golder et al., 2005). In some cases complete removal of dyes could not be achieved due to formation of hazardous by-products during the process. The electrochemical methods involve high operating cost and require high energy for the removal of dyes.

2.3.3 Chemical Methods

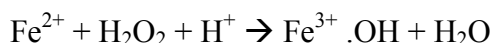
2.3.3.1 Oxidation

Chemical oxidation is the traditionally used technique for the removal of impurities such as taste, color and odor. Oxidants such as chlorine, ozone, chlorine dioxide and hydrogen peroxide are used for wastewater treatment. The chromophores that impart the colour are attacked by the oxidizing agents for the removal of colour (Letterman, 1999). The removal of dye from dye effluents results in the cleavage of aromatic rings (Raghavacharya, 1997).

Fenton's reagent

H₂O₂ is commonly known as Fenton's reagent and is widely used for the degradation of pollutants (Neysens and Baeyens, 2003). Iron salts such as iron sulfate are most commonly used for activation of Fenton's reagent which

facilitates higher removal of dye at higher concentrations (Forgacs et al., 2004). The removal efficiency of Fenton's process depends on the generation of hydroxyl radicals, the major oxidant.



Bandara et al. (1997) studied the removal of the azo dye Orange II by Fenton's reagent. The result revealed that efficient mineralization of the dye was achieved by the application of iron powder in combination with hydrogen peroxide. 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 (Robinson et al., 2001). It has been found that cationic dyes do not coagulate at all, although acid, reactive, direct, vat and mordant dyes coagulate. The floc formed is generally of poor quality and low settling ability (Raghavacharya, 1997). 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 (Huang

et al., 2008). The decolorized of Reactive black 5 in textile wastewaters by UV/ H₂O₂ oxidation process (Ince and Gonenc, 1997). Song et al. (2009) found that the breaking azo linkage of Acid red 88 produced some carbonyl compounds. The results indicated that the combination of Fenton's reagent with ultrasonic irradiation facilitated the degradation of the dye but complete mineralization of the dye could not be achieved. The analysis of different types of dyes to evaluate the application of UV/ H₂O₂ revealed that successful decolorization of acid dyes, direct dyes, basic dyes and reactive dyes was achieved though it was found to be ineffective for vat and disperse dyes (Yang et al., 1998).

The formulation of a generalized oxidation method for dye removal is not possible as optimal conditions vary with the type of dye (Tang and Chen, 1996). The effective removal of dyes by oxidation depends largely on the efficiency of oxidant (Forgacs et al., 2004). The limited use of hydrogen peroxide (H₂O₂) as an oxidizing agent is attributed to low oxidation power (Khadhraoui et al., 2009).

Sodium hypochlorite

Traditionally chlorine gas was a vital oxidizing agent in wastewater treatment. The use of chlorine in water treatment is now restricted due to the formation of disinfection by-products, such as trihalomethanes and haloacetic acid, which are mutagenic and carcinogenic and pose a threat to human and aquatic life (Ratnayaka et al., 2009). The use of hypochlorite in the oxidation process is

restricted due to presence of chlorine (Khadhraoui et al., 2009). Presence of chlorine above 400 ppm can be harmful for aquatic life (Lu et al., 2009). The chlorine in the sodium hypochlorite attacks the amino group of the dye resulting in the cleavage of azo bonds (Robinson et al., 2001). Sodium hypochlorite reacts with dye molecules, resulting in the formation of aromatic amines which are toxic and carcinogenic (Banat et al., 1996).

Ozonation

Ozonation is an oxidation process and is effectively used in the decolorization of synthetic dyes (Forgacs et al., 2004). In ozonation, the ozone gas breaks the conjugated double (-N=N-) bond in azo dyes, responsible for imparting the colour to the dyes (Srinivasan et al., 2009). Ozonation is mainly carried out in two ways, either by direct application or indirect application. In the direct method molecular ozone is applied whereas the free radicals generated during decomposition of ozone in water are applied in the indirect method. Ozonation of dye generally results in the formation of some decomposition products. The decolorization of Orange II resulted in the formation of oxalate, formate and benzene sulfonate ions as the decomposition by-products (Tang and An., 1995). 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 but there was only small reduction in chemical oxygen demand. Moreover the efficient mineralization of the dye was not obtained.

The removal of dyes by ozonation has various advantages as decolorisation is fast, no sludge or any toxic by-products are produced (Ince and Gonenc, 1997, Gahr et al., 1994). However, the major disadvantage is that the half-life is short (20min.). Salts, pH and temperature influence the stability of ozone. The instability can further reduce the half-life. The effective decolorisation requires continuous ozonation and therefore the process involves high operating costs (Xu and Lebrun, 1999). Furthermore, the effect of ozonation on the toxicity of the wastewater effluent depends on the type of dye being decomposed (Hitchcock et al., 1998).

2.3.3.2 Photocatalysis

Photocatalysis is widely used for the removal of organic contaminants. Semiconductors have a region known as band gap which can be described as a region between the top of the valence band and the bottom of the conduction band. In this region no energy is available for the combination of electron. Therefore, a hole is generated by the photo-activation. Thus, to overcome this energy gap, photon energy, $h\nu$, equal to or more than the band gap is required to excite an electron (e^-) from the valence band to the conduction band. The electron that has moved to the conduction band leaves a hole (h^+) in the valence band which is positively charged. Usually, ultraviolet photons are required to carry out this reaction (Kabra et al., 2004):



The life span of an electron hole pair is of the order of nanoseconds but this is sufficient for initiating a redox reaction (Bussi et al., 2002). The reaction can proceed in many ways depending on the mechanism of photoreaction. The hole in the valence band can combine with water to oxidise and produce hydroxyl radicals which initiates the chain reaction resulting in oxidation of organic pollutants, or it can combine with the electrons of the donor species (Kabra et al., 2004). In a similar way electron in the conduction band can combine with electron acceptor such as an oxygen molecule form to a superoxide radical, or it can combine with metal ions whose redox potential is more positive than the band gap of the photocatalyst (Linsebigler et al., 1995).

The rate of photodecomposition increases in the presence of photocatalysts. TiO_2 , ZnO , ZrO_2 , CdS , MoS_2 , Fe_2O_3 and WO_3 are most widely used photocatalysts for the degradation of organic and inorganic compounds. These catalysts are often modified to improve their performance (Kabra et al., 2004). Several studies were reported on the degradation of dyes by UV irradiation in the presence of TiO_2 (Shu et al., 1994, Shu and Huang, 1995 and Vinodgopal et al., 1998). Liakou et al., (1997) examined the degradation of Acid blue 40, Basic yellow 15, Direct blue 87, Direct blue 160 and Reactive red 120. The results revealed that the degradation of dyes depends on their chemical structure and pH. Photocatalytic degradation of synthetic dyes requires optimal selection of the photocatalytic conditions as these dyes are generally resistant to photodegradation (Forgacs et al., 2004).

In most chemical methods an oxidizing agent is needed for the removal of dyes. These oxidizing agents produce some disinfection by-products which are harmful to human beings. The selection of oxidizing agent depends on its oxidation power. The removal of dyes depends on the ability of dye to form flocs on application of oxidizing agents. Ozonation is a successful chemical method but its half life is very short and the impact of ozonation on treated water depends on the toxicity of dye (Zhang et al., 2002). The removal of dyes by photocatalysis highly depends on the operating conditions as most dyes are resistant to photodegradation (Kabra et al., 2004).

2.3.4 Physicochemical Methods

2.3.4.1 *Coagulation*

Coagulation is a popular conventional physico-chemical method employed for the treatment of wastewater. Coagulants such as alum and iron salts are added to wastewater to increase the tendency of the smaller particles to aggregate (Martínez-Hutle and Brillas, 2009). The coagulation alone cannot be applied for the removal of pollutants from wastewater. It requires subsequent processes such as sedimentation, filtration and disinfection (Letterman, 1999).

2.3.4.2 *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). Unlike other physico-chemical methods filtration is resistant to temperature, chemical and microbial attack. The treated dye effluent can be recycled within the textile industry; however reuse of water treated by filtration is not very feasible (Mishra and Tripathy, 1993). On the flip side, the disposal of sludge formed during treatment is a major problem (Letterman et al., 1999). In addition, filtration involves high capital cost and tendency of membranes to clog which affects the performance of the filtration process (Robinson et al., 2001).

2.3.4.3 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 in dye effluent is limited (Slokar and Le Marechal, 1997). The advantages of ion exchange include the availability of a wide range of resins for specific application and there is no loss of sorbent. Ion exchange can be used for the removal of soluble dyes, however, it is ineffective for insoluble dyes (Mishra and Tripathy, 1993). Drawbacks of ion exchange are high capital cost and expensive organic solvents (Robinson et al., 2001).

2.3.4.4 Adsorption

The phenomenon of attracting and retaining the molecules on the surface of a solid is called adsorption. The substance that adsorbs on the surface is called adsorbate, and the substance on which it adsorbs is called adsorbent. The removal of adsorbed substance from the surface is called desorption (Treybal, 1981). Adsorption occurs due to the difference in the properties of the surface of the adsorbent than the bulk. The unbalanced inward forces of attraction or free valences at the surface have the property to attract and retain the molecules onto their surface with which they come in contact (Jiuhui, 2008).

When the molecules of an adsorbate are held on the surface of adsorbent by Van der Waal forces without resulting into the formation of any chemical bond between them is called physical adsorption or physisorption. This type of adsorption is characterized by low heats of adsorption about -20 to 40kJmol^{-1} . Physisorption is generally reversible in nature (Treybal, 1981). When the molecules of an adsorbate are held on the surface of an adsorbent result in the formation of a chemical bond between them is called chemical adsorption. It is also known as Langmuir adsorption or chemisorption. This type of adsorption evolves high heats. Chemisorption is usually irreversible in nature (Treybal, 1981; Jiuhui, 2008). Adsorption is widely used for the removal of colour from dye effluent, edible oils, and sugar industry. It can also remove the trihalomethanes which are toxic and carcinogenic.

Adsorption process can operate independently for the removal of colour. It has the capability of degrading organic compounds that are chemically and biologically stable (McKay, 1996). Parameters associated with an adsorption process, such as initial dye concentration, adsorbent dosage, contact time and temperature affect the adsorption of dyes from dye effluent. Furthermore, an equilibrium relationship between the amounts of dye adsorbed on the surface of an adsorbent is generally established through adsorption isotherms (Bulut et al., 2008). The most commonly used adsorption isotherms for evaluation of adsorption data are Langmuir and Freundlich adsorption isotherms. The kinetics of adsorption is investigated using pseudo first order and pseudo second order kinetic models.

Advantages of adsorption

Adsorption is one of the preferred processes for dye removal over conventional methods due to its high efficiency, fast and easy operation and simple and flexible design. Moreover the adsorbent can be easily recovered and reused (Özcan et al., 2005).

Adsorption is widely used for the removal of textile pollutants from wastewater due to its low capital costs and the wide availability of low cost adsorbents. The adsorption process may generate little or no toxic pollutants and has low initial capital and operating costs (Crini, 2006). Adsorption is safe from the environmental point of view as no sludge is produced (Unuabonah et al., 2008).

The effluent produced after adsorption is generally of high-quality (Nandi et al., 2009). In adsorption the pollutants present in the wastewater attach to the surface of the adsorbent. The interactions between the adsorbate and the adsorbent can be expressed by adsorptive characteristics and physical properties (Lian et al., 2009).

Physicochemical methods are very simple and feasible compared to all other dye treatment methods. Major drawback associated with most physico-chemical methods is the handling and disposal of sludge produced during the removal of dyes (Khadhraoui et al., 2009). Adsorption is the preferred physico-chemical method due to its wide range of applicability. A wide variety of low-cost adsorbents are available (Crini, 2006). The adsorption capacity of these low-cost adsorbents can be easily enhanced with simple and economically feasible methods.

2.4 Drawbacks of Current Dye Removal Techniques

The time required for biodegradation of dye is generally very large (few days). Most of the dyes are non-biodegradable so it is difficult to degrade them biologically. The effect of biodegradation by-products on the environment is not yet completely known (Forgacs et al., 2004).

Oxidation using hydrogen peroxide is restricted due to low oxidation power. Other oxidizing agents such as chlorine and sodium hypochlorite are not widely

used these days due to the generation of disinfection by-products which are mutagenic and carcinogenic.

Ozonation may result in the formation of toxic by-products even from biodegradable substances. The water treated by ozonation may pose considerable threat if discharged without analyzing the toxicity and phytotoxicity of the compounds produced during the process. Moreover it involves high capital cost (Zhang et al., 2002).

The application of photocatalysis for wastewater treatment involves expensive catalysts which increase the overall treatment cost and makes it less economical compared to conventional methods. The efficiency of some catalysts is not very high and the potential hazards posed by the photocatalysts are not reported anywhere. No research has been done on the end use of photocatalysts or reuse or disposal methods (Kabra et al., 2004).

The removal of pollutants by ion exchange, precipitation and reverse osmosis is very difficult as these processes are technically very complex and expensive (Faur-Brasquet et al., 2002). The major drawback of reverse osmosis is membrane failure. The organic pollutants and dye molecules in the effluent either clog the membrane or result in fouling affecting the capacity of pollutant removal (Srinivasan et al., 2009).

Table 2.6: 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	Slow process, availability of suitable environment for the growth of microorganisms
Electrochemical	No hazardous degradation by-products	Requires high energy and high operating cost
Chemical		
<i>Fenton's reagent</i>	Rapid and efficient process	Sludge formation
<i>Sodium hypochlorite</i>	Initiates and accelerated azo bond cleavage	Release of aromatic amines
<i>Ozonation</i>	Can be applied in gaseous state; causes no change in volume	Short half-life (20min)
<i>Photocatalysis</i>	No sludge formation	Generation of hazardous by-products
Physicochemical		
<i>Coagulation</i>	Simple, economically feasible	High sludge production, handling and disposal problem
<i>Filtration</i>	Capable of treating all dyes and high quality of treated effluent	High pressures, expensive, incapable of treating large volumes and clogging of membranes
<i>Ion exchange</i>	Effective and no loss of sorbent during regeneration	Economically not feasible and ineffective for disperse dyes.
<i>Adsorption</i>	Effective, suitable for all types of dyes, treated effluent is of high-quality. Availability of low-cost adsorbents	High cost of adsorbent (activated carbon) and low surface area of some low-cost adsorbents

Coagulation and flocculation result in the production of large amounts of sludge thereby giving rise to a new problem of effective sludge disposal (Khadhraoui et

al., 2009). The use of adsorption for the removal of dyes is restricted due to the high cost of activated carbon. Table 2.6 summarizes the advantage and disadvantages of currently available dye removal methods.

2.5 Adsorbents

The applicability of adsorption process depends on the adsorbents and their physical and chemical properties. An adsorbent is expected to have high selectivity, high adsorption capacity and long life. Furthermore, an adsorbent should be available in abundance at economical costs (McKay, 1996). A wide variety of adsorbent are commercially available and successfully used for the removal of organic and inorganic pollutants. Activated carbon is the most widely employed adsorbent. A large number of low cost adsorbents such as acid activated red mud, chitosan, biomass, fly-ash, diatomite and industrial waste are used for removal of dyes (Crini, 2006 and McKay, 1996).

2.5.1 Activated Carbon

Activated carbons include a wide range of amorphous carbon-based materials prepared to exhibit a high degree of porosity and extended interparticulate surface area essential for an adsorbent (McKay, 1996). The activated carbons are classified as granular activated carbon (GAC) and powdered activated carbon (PAC). All activated carbons have porous structures and the number and size of pores and pore size distribution varies from carbon to carbon depending upon the

nature of raw materials and the method and history of its preparation (Crini, 2006).

Table 2.7: Removal of dye by adsorption on commercial activated carbons (adapted from Crini et al., 2006)

Dye	Amount adsorbed (q_m) (mgg^{-1})	References
Acid yellow	1179.00	Chern and Wu (2001)
Remazol yellow	1111.00	Al-Degs et al (2000)
Basic yellow 21	860.00	Allen et al (2003)
Basic red 22	720.00	Allen et al (2003)
Reactive orange 107	714.00	Aksu and Tezer (2005)
Reactive red 2	712.30	Chiou et al (2004)
Basic dye	309.20	Meshko et al (2001)
Congo red	300.00	Purkiat et al (2007)
Basic blue 9	296.30	Kannan and Sundaram (2001)
Reactive red 5	278.00	Aksu and Tezer (2005)
Direct red 81	240.70	Chiou et al (2004)
Acid yellow 117	155.80	Choy et al (2000)
Congo red	142.58	Lian et al (2009)
Acid blue 40	133.30	Özacar and Sengil (2002)
Acid blue 80	112.30	Choy et al (2000)
Acid red 88	109.00	Venkatamohan et al (1999)
Basic red 46	106.00	Martin et al (2003)
Acid red 114	103.50	Choy et al (2000)
Acid yellow 17	57.47	Özacar and Sengil (2002)
Direct red 28	16.81	Fu and Viraraghavan (2002)
Direct brown 1	7.69	Venkatamohan et al (2002)

Coal is the commonly used material for the production of activated carbon due to its cheap and abundant availability. However, it could also be derived from coconut shell, lignite, agricultural and wood by-products etc. (McKay, 1996). Apart from surface area, the adsorption properties of activated carbon are also influenced by the presence of carbon-oxygen surface groups (Purkait et al., 2007). A large number of studies have been carried out on the removal of dyes from dye effluent by adsorption on activated carbon. Table 2.7 reports the account of the recent studies performed on the removal of dyes by activated carbon.

Difficulty and high cost associated with the regeneration of activated carbons are a major factors contributing to its decreasing popularity. Purkait et al. (2007) found that regeneration of activated carbon by anionic surfactants is better compared to cationic surfactants. They studied the adsorption of Congo red on activated carbon. The regeneration of activated carbon results in loss of 10-15% of adsorbent adding to the operational cost (Lian et al., 2009). This limitation of activated carbon has made it necessary to develop low-cost adsorbents.

2.5.2 Low-Cost Adsorbents

The application of adsorption for wastewater treatment is restricted in some cases due to the high cost of activated carbon and for its regeneration. This has led to the research and development of low-cost adsorbents. Bailey et al. (1999) has proposed that a low-cost adsorbent is an adsorbent that is available in abundance,

requires little pre-treatment or that could be produced from any waste material. Various low-cost adsorbents, that have been successfully implemented for the adsorption of dyes from wastewater, include clays (Crini, 2006), spent brewery grain (Unuabonah et al., 2008; McKay et al., 1985) modified agricultural by-products (Šćiban et al., 2008), industrial wastes (Kabra et al., 2004), coir pith (Santhy and Selvapathy, 2006; Namasivayam and Sangeetha, 2006), chitosan (Monvisade and Siriphannon, 2009), fly ash, peat, coal, baggase, neem leaves and natural and modified clay minerals (Crini, 2006)

2.5.2.1 Biosorbents

Chitosan is a natural, biodegradable and non-toxic polysaccharide, and has been found in crustaceans, fungi, insects, annelids and molluscs (Crini, 2006, Chiou et al., 2004). Chitosan is a linear biopolymer of glucosamine which has degrees of polymerisation around 2000 – 4000 (McKay, 2006). The chemical deacetylation of crustacean chitin results in the formation of industrial chitosan (Guibal, 2004 and Dolphen et al., 2007). The adsorbents made from chitosan are available in different forms such as flakes, beads, hydrogels and fibres. Chatterjee et al. (2009) found that impregnation of a small amount of non-ionic, anionic or cationic surfactant can considerably enhance the adsorption capacity of chitosan beads. It has delivered promising results for the adsorption of reactive and acidic dyes (Chiou et al., 2004). Its use is limited due to high market cost. The high content of

amino and hydroxyl groups attribute to the high adsorption capacity of chitosan towards anionic dyes (Crini, 2006).

Monvisade and Siriphannon (2009) have modified montmorillonite by intercalating chitosan to enhance its ability to adsorb dyes. The decrease in surface area of chitosan intercalated montmorillonite is due to the close packing of chitosan molecules in the interlayer spaces preventing the penetration of nitrogen molecules. Higher adsorption of the cationic dyes on chitosan intercalated montmorillonite was recorded than those on Na⁺ montmorillonite. Wu et al. (2000) investigated the adsorption of Reactive red 222 on chitosan flakes and beads. The results revealed that adsorption on flakes (293mgg⁻¹) were less in comparison to beads (1103mgg⁻¹). A higher adsorption capacity of beads was attributed to a higher surface area. Wong et al. (2004) analysed the adsorption of acidic dyes on chitosan. The amount of Acid orange 12, Acid orange 10, Acid red 73, Acid red 18 and Acid green 25 adsorbed on chitosan was reported as 973.3, 922.9, 728.2, 693.2 and 645.1mgg⁻¹, respectively. Chitosan has a limitation in that it is insoluble in most of the solvents; however it is soluble in an acidic medium (McKay, 1996 and Crini, 2006).

2.5.2.2 Agricultural and Industrial by-products

Modified agricultural by-products such as rice bran (Šćiban et al., 2008), orange peel (Arami et al., 2005), baggase and neem leaves were used as cheap and

renewable adsorbents (An and Dultz, 2007). These lignocellulosic materials are composed of cellulose, chemicelluloses, lignin and extractive matters. They possess certain cellulose hydroxyl groups and other polar functional groups in lignin. Šćiban et al. (2008) examined the adsorption capabilities of various agricultural by-products such as raw wheat, soybean straws, corn stalks and corn cobs for copper, cadmium, nickel and lead ions. All the biomasses showed different adsorption abilities to remove different metal ions. The biomasses were modified to prevent the leaching of extractive matter during adsorption which increases the content of organic matter in effluent. Modification of biomass was performed by treating it with formaldehyde in acidic medium, sodium hydroxide (both with and without pre-treatment with formaldehyde), acid solution and simple washing. The results revealed that the adsorption capacities of biomass did not improve on modification.

Saw dust has also shown good adsorption capability for acidic and basic dyes (Khattri and Singh 2000, Ho and McKay 1998, Özacar and Sengil, 2005). Although, the ionic character of sawdust favours the adsorption of basic dyes over acidic dyes (Ho and McKay, 1998). Khattri and Singh (2000) adsorbed Basic violet 23 and Basic green 4 on neem sawdust. Bark is another agricultural waste that shows usefulness in the adsorption of dyes from dye effluent (Crini, 2006). McKay et al. (1999) reported the adsorption of Basic red 2 and Basic blue 9 on bark for which the maximum adsorption capacities were found to be 1119 and 914 mgg^{-1} , respectively.

Industrial wastes such as red mud and fly ash also possess the capability of dye removal (Crini, 2006). Red mud is an unwanted by-product of alkaline-leaching of bauxite (Tor and Cengelöglu, 2006). Namasivayam and Arasi (1997) studied the adsorption of Congo red on red mud. The maximum adsorption was reported to be 4.05mgg^{-1} . The properties of red mud can be altered by acid treatment. Tor and Cengelöglu (2006) treated red mud with HCl to enhance its adsorption capacity. The surface area of acid activated red mud was found to be $20\text{m}^2\text{g}^{-1}$. The maximum adsorption of Congo red on acid activated red mud was found to be 7mgg^{-1} .

Fly ash is the product of burning coal and lignite particles. Alumina, calcium oxide, iron oxide and residual carbon are the main constituents of fly ash (Wang et al., 2005). The fly ash obtained from coal and lignite varies in composition and properties. Fly ash obtained from coal contains large amount of SiO_2 , small amount of Al_2O_3 with a very small amount of CaO. However, the main constituent of fly ash obtained from lignite is SiO_2 and CaO with a very small amount of SO_3 . Based on the total amount of SiO_2 , Al_2O_3 and Fe_2O_3 fly ashes are categorized as type C and type F (Acemioğlu 2004). Fly ash is type C if the total amount of the constituents is 50%. However if the total amount is 70% it is type F. The properties of fly ash depend largely on its origin (Wang et al., 2005). Acemioğlu (2004) employed calcium-rich fly ash for the adsorption of Congo red and observed that adsorption increased with increase in concentration and temperature but decreased with increasing pH. Congo red was successfully

adsorbed on calcium-rich fly ash but the adsorption capacity was less compared to clays.

Bhatnagar and Jain (2005) used industrial waste from steel and fertilizer industries for the adsorption of cationic dyes Rhodamine B and Bismark brown R. The adsorbents prepared from blast furnace sludge, dust and slag have poor porosity and low surface area showing low efficiency for dyes. However adsorbents prepared from fertilizer industry waste are carbonaceous in nature and possess high porosity and surface area adsorbing appreciable amounts of dyes.

2.5.2.3 *Natural Clays*

Clays are lamellar aluminosilicates possessing a wide range of physicochemical properties such as swelling, adsorption, ion exchange and surface acidity (Yang et al., 2006). Natural clay minerals are gaining importance among low-cost adsorbents because of their easy and abundant availability and high adsorption capabilities for cations and polar molecules (Monvisade and Siriphannon, 2009). The presence of, net negative charges on clay favours the adsorption of basic dyes (Jiuhui, 2008). There are a large number of clays which are widely used for the removal of dyes from wastewater, including kaolin (Nandi et al. 2009; Unuabonah et al., 2008), montmorillonite (Damardji et al., 2009; Yan et al., 2007) bentonite (Özcan et al., 2007; Vimonses et al., 2009), clinoptilolite (Li and Bowman, 1997), smectite (Díaz and De Souza Santos, 2001), sepiolite (Kara et al., 2003) and zeolite (Vimonses et al., 2009).

Kaolin

Kaolin is also known as China clay and has a structure that is dioctahedral 1:1 layer clay with alternating tetrahedral silica and octahedral alumina sheets, respectively (Figure 2.2). The chemical formula of Kaolin is $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$ (Beragaya et al., 2006). The charge within the structural unit is balanced. Kaolin is also referred to nonexpanding phyllosilicate as there is no expansion between the layers (Vimonses et al., 2009). There are small amounts of anatase, rutile, feldspar, iron oxide, mica, montmorillonite and quartz in almost all kaolins (Newman, 1987). The surface area of kaolinites is generally smaller than montmorillonites. The isomorphous substitutions in kaolinite are less compared to montmorillonite resulting in lower cation absorbing capacity (Bhattacharyya and Sengupta, 2006). Unuabonah et al. (2008) evaluated the adsorption of aniline blue on kaolinite and sodium tetraborate (NTB) modified kaolinite. The surface area of NTB-kaolinite was 15.84 compared to 10.56 m^2g^{-1} of raw kaolinite. The results indicate that on modification the adsorption capacity of kaolinite increases which was explained by an increase in surface area after modification.

Zeolite

The main constituent is clinoptilolite which has chemical formula $\text{Na}_6[(\text{AlO}_2)_6(\text{SiO}_2)_{30}]\cdot 24\text{H}_2\text{O}$. The crystal structure of zeolite is three dimensional with two dimensions carrying exchangeable Na, K, Ca and Mg ions as shown in Figure 2.2. Organic and inorganic cations can replace these exchangeable cations (Benkli

et al., 2005). Zeolites are also called tectosilicates due to a well connected SiO_4 and AlO_4 tetrahedral framework joined by coordinating oxygen atoms. Silicon and aluminium ratio is vital in aluminosilicate zeolites. If the Si/Al ratio is high, zeolite is strongly hydrophilic in nature but this ratio can be altered by treating with acid that can render the material surface hydrophobic in nature (Vimonses et al., 2009). Benkli et al. (2005) reported that natural zeolite possesses a negative charge and it is not capable of adsorbing reactive dyes which contain negatively charged sulphonate groups as natural zeolite. The modification of zeolite with cationic surfactant hexadecyl trimethyl ammonium bromide improves the adsorption capacity of zeolite. Vimonses et al (2009) investigated the adsorption of Congo red on zeolite, kaolin and bentonite. Results revealed that zeolite among the three clay minerals showed least adsorption of Congo red.

Bentonite

Bentonite, a 2:1 type clay, is a natural silicate mainly composed of montmorillonite. The basic structure of bentonite is made up of two silica tetrahedral sheets with an intermediate aluminium octahedral sheet (Vimonses et al., 2009) as can be seen in Figure 2.2. The charge between the octahedral and tetrahedral sheets is not balanced due to isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral sheet and generally Mg^{2+} for Al^{3+} in the octahedral sheet (Özcan et al., 2005). The substitution by these ions of lower valency induces a permanent negative charge in the lattice structure. The negative charge is balanced by

treating it with cations such as sodium, calcium or magnesium. These cations are exchangeable cations in the lattice structure due to loose binding (Vimonses et al., 2009). Depending on the exchangeable cations, commercial bentonites are known as Ca-bentonite or Na-bentonite (Babaki et al., 2008).

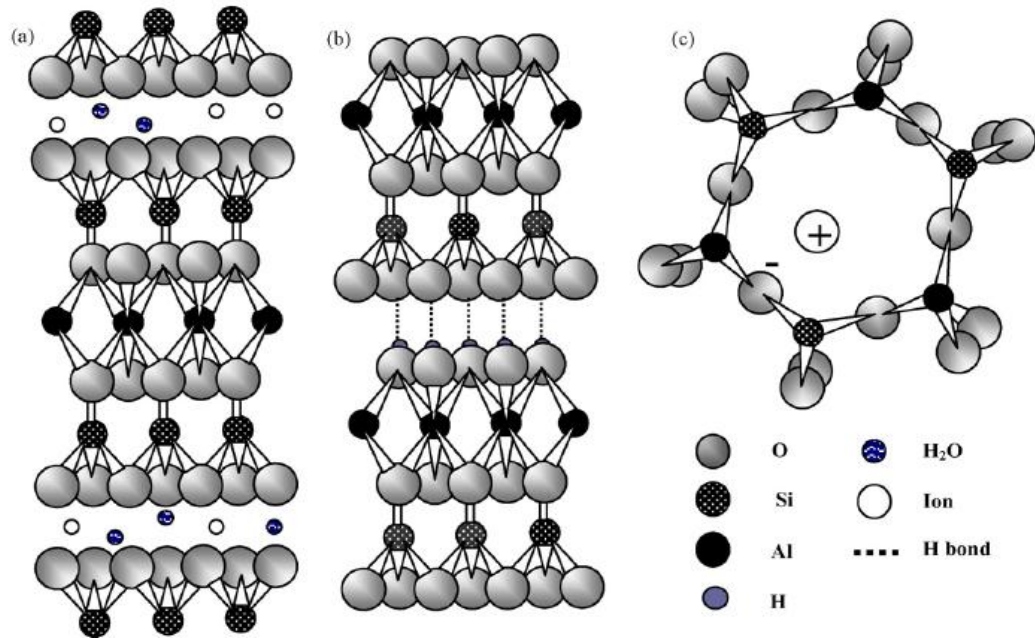


Figure 2.2 Structure of (a) Bentonite, (b) Kaolin (c) Zeolite (adapted from Vimonses et al., 2009)

Bentonite is widely used in various industrial products and processes such as pharmaceuticals, cosmetics and drilling fluids to modify the rheology and control the stability of systems (Faur-Brasquet et al., 2002). It is used as a plasticizer in ceramics, as an emulsifying agent in asphaltic substances, as thickener and extender for paints, as adhesive in concrete mixtures, horticultural sprays and

insecticides, adsorbent in removal of dyes and heavy metals and in bleaching earth in refining oils and fats (Pushpaletha et al., 2005).

The widespread use of bentonite can be attributed to its physical and chemical properties such as small particle size, high porosity, large surface area and high cation exchange capacity (Doulia et al., 2009). The bentonite has excellent adsorption capacity and its adsorption ability is determined by the chemical nature and pore structure (Koyuncu, 2008). The porous structure of bentonite is broadly classified into three categories as micropores, mesopores and macropores. Micropores are smaller than 2nm, between 2nm and 50nm are mesopores and larger than 50nm are macropores. The physico-chemical properties such as adsorption capacity largely depend on the presence of micro and mesopores; and, the effect of macropores is found to be insignificant (Babaki et al., 2008).

The wide range of application of bentonite is also attributed to the possession of natural mesopores in its structure. Bentonites are plastic, impermeable and highly viscous when suspended in water (Churchman et al., 2002). In addition, it is available in abundance in almost all parts of world (Khenifi et al, 2007) with its reserves accounting for approximate production of 8 million tonnes in 1992 (Murray, 1995). Recently a large reserve of bentonite has been found in Arumpo, southern New South Wales, Australia. It is estimated that deposit accounts for 40-70 million tonnes (Churchman et al., 2002). Another reserve has long been known in Miles, south central Queensland in Australia (Gates et al., 2002). Another

reason for the wide use of bentonite is the ease of modification by using simple methods (Sanjay and Sugunan, 2008).

The usefulness of bentonite in the removal dyes has been proven by various researchers (Vimonses et al., 2009; Babaki et al., 2008; Zohra et al., 2008; Özcan and Özcan, 2004; Bulut et al., 2008; Lian et al., 2009; Christidis et al., 1997; Jovanović and Jonačković, 1991). However, studies have shown that bentonite is more efficient in adsorption of basic dyes than acidic dyes (Wang and Wang, 2007). The excess negative charge is responsible for lower efficiency of bentonite towards acidic dyes (Khenifi et al., 2007). The modification of bentonite thus becomes necessary to enhance its adsorption capacity and make it suitable for the adsorption of acidic dyes (Özcan et al., 2007).

Diatomite

Diatomite, also known as diatomaceous earth, is primarily composed of microfossils of aquatic unicellular algae. It is a pale coloured, soft and light weight sedimentary rock. Shawabkeh and Tutunji (2003) adsorbed basic dye Methylene blue on diatomite obtained from Jordan and concluded that diatomite can remove Methylene blue at low concentration, however modification of the diatomite is desirable to enhance its adsorption capacity. Table 2.8 summarises the advantages and disadvantages of adsorbents.

Table 2.8 Advantages and Disadvantages of adsorbents

Adsorbent	Advantages	Disadvantages
Activated Carbon	High surface area	High cost
Biosorbents	High adsorption capacity	High market cost
Agricultural and industrial by-products	Available in abundance	Sorption properties depend on origin
Bentonite	High surface area, high cation exchange capacity and low cost	Need modification for adsorption of anionic dyes
Zeolite	High ion exchange capacity and surface area	Complex sorption mechanism

2.6 Modification of Clays

Modification can alter the clay structure to enlarge its surface area, therefore increasing the adsorption capacities (Dai and Huang, 1991). Modification of bentonite is vital to increase the range of applicability of bentonite for the adsorption of acidic dyes (An and Dultz, 2007). The chemical composition of clay minerals varies depending upon the origin influencing the layer charge, cation exchange capacity, adsorption capacity and morphology. These factors play a significant role in the modification of the natural clays (Steudel et al., 2009). After modification with cationic surfactants the organic groups are attached to the surface of the natural clays and largely change the surface properties (Dai and

Huang, 1991). The physical, chemical and biological properties of modified adsorbents are different from the original adsorbent (Jiuhui, 2008).

2.7 Methods of Modification of Clay Minerals

The term activation refers to chemical and physical treatments employed to enhance the adsorption capacities of clays (Christidis et al., 1997). There are various methods for modification of clay minerals, such as, acid activation (Stuedel et al., 2009), treatment with cationic surfactant (He et al., 2006), clay-rubber composite (Dai and Huang, 1991), thermal treatment (Al-Asheh et al., 2003), polymer addition, pillaring by different types of poly (hydroxo metal) cations, intraparticle and interparticle polymerization, dehydroxylation and calcination, delamination and reaggregation of smectites, and lyophilisation, ultrasound and plasma (Paiva et al., 2008) adsorption and ion exchange with inorganic and organic cations, binding of inorganic and organic anions (mainly at the edges) and grafting of organic compounds (Liu, 2007).

2.7.1 Pillared Clays

Pillared clays are prepared by intercalating natural clays with bulky polyoxycations such as Al or Zr. Calcination at high temperatures results in transforming the intercalated polyoxycations into rigid oxide pillars producing pillared clays. Pillared clays have a highly porous structure. The use of pillared clays is limited due to lack of thermal stability of the clay (Carvalho et al., 2003).

Furthermore the process for industrial scale production of pillared clays is not fully known (Auer and Hofman, 1992).

2.7.2 Polymer Modified Clay

The adsorption properties of clays can be enhanced by the incorporation of polymers in the interlayer spaces (Ding et al., 2006). The polymer modified clays are generally formed by physical adsorption, chemical grafting or ion exchange with surfactants. Polyacrylamide is most widely used for preparing polymer modified clays (Chen et al., 2008). The physical adsorption enhances the physical and chemical properties of the clay, but does not affect the structure of the clay. The drawback of this method is that the bond between the clay and the adsorbed molecules is not very strong (Liu, 2007). The properties of polymer modified clays largely depend on the modification technique. The modification of clays by an ion exchange method using polymeric quaternary ammonium ions is less expensive than chemical grafting (Ding et al., 2006).

Chen et al. (2008) synthesised polymer modified clay using oligomeric poly (styrene-co-acrylamide). The reactions of trimethylamine with oligomeric polystyrene-acrylamide-vinylbenzylchloride by free radical polymerization of a mixture of styrene, acrylamide and vinylbenzylchloride synthesised oligomeric poly (styrene-acrylamid-vinylbenzylchloride) quaternary ammonium salts. This modified clay has high thermal stability.

Yue et al. (2007) studied the adsorption of disperse and reactive dyes namely Disperse yellow SE-6GRL, Disperse red S-R, Reactive reddish violet K2-BP and Reactive jade blue K-GL on natural and epichlorohydrin-dimethylamine polyamine (EPI-DMA). The intercalation of EPI-DMA into the clay layers expands the layer space. The modified clay becomes more hydrophobic than the natural clay. The addition of cationic polymer render the clay surface positive making it suitable for adsorption of disperse and reactive dyes. EPI-DMA bentonite efficiently removes the anionic dye however a relatively large amount of polymer is required for transition of clay surface from negative to positive. The adsorption of cationic dyes on humic acid immobilized polyacrylamide bentonite was investigated by Anirudhan et al. (2009). They found that composites with amine functionality in the bentonite enhanced its adsorption capacity.

The modification of clay using metal extracting complexing agents such as ammonium pyrrolidinedithiocarbamate, diethylenetriaminepentaacetic acid and ethylenediaminetetraacetic acid (Nagy et al., 1998; Lim et al., 2005) have been used for the removal of metal ions. These materials are widely used to form polymeric adsorbents, however the chemical bonding to polymers is difficult and expensive. Bosco et al. (2006) modified zeolite by addition of ammonium pyrrolidinedithiocarbamate, disodium salt of ethylenediaminetetraacetic acid and diethylenetriaminepentaacetic acid.

2.7.3 Organoclays

The cationic surfactants such as quaternary ammonium salts of the form $(\text{CH}_3)_3\text{NR}^+$ (where R is an alkyl hydrocarbon) (Yildiz et al, 2005) are commonly used for the formulation of organoclays (Paiva et al., 2008). The wide use of bentonite for the fabrication of organoclays is due to its high cation-exchange capacity, surface area, adsorption capacity and swelling capacity (Atia, 2008). The preparation of organoclays from cationic surfactants is a two-step process, which comprises cation-exchange and hydrophobic bonding. When the concentration of the cationic surfactants is low, only ion exchange takes place forming a monolayer. The formation of bilayer takes place when the concentration of the cationic surfactants increases as the Van der Waal interactions become prominent between the hydrocarbon tails (Li and Bowman, 1997).

Zohra et al. (2008) modified bentonite by intercalating long chain cationic surfactant, cetyltrimethyl ammonium bromide (CTAB-bentonite) into the interlayer surfaces and employed the modified clay for the adsorption of a direct dye, Benzopurpurin 4B (Direct red 2). They suggested that increased adsorption of the dye on CTAB-bentonite is attributed to the presence of alkyl chains in the interlamellar spaces. There were two modes of adsorption; one is the sulphonic group of dye with the positively charged clay surface and the second is hydrophobic binding, which is much stronger than the first one.

These organic cations change the surface of the clay from hydrophilic to hydrophobic by replacing the exchange sites of clay with the alkyl hydrocarbons (Song et al., 2009; Yıldız et al., 2005; Karahan et al., 2006), resulting in increasing adsorption capacity for organic pollutants (Wang and Wang, 2008). The cationic surfactants such as ODTMA adsorb large amount of hydrophobic pesticides onto them by increasing the density of organic phase in the clays (Unuabonah et al., 2008). Özcan et al. (2005) modified bentonite by benzyltrimethyl ammonium bromide (BTMA-bentonite) for the adsorption of Acid blue 193 (AB193). The adsorption of dye on BTMA-bentonite was enhanced in acidic pH due to the strong electrostatic interaction between the dye molecules and the clay surface.

Özcan et al. (2007) employed cationic surfactant dodecyltrimethyl ammonium bromide (DTMA-bentonite) to modify bentonite by an ion exchange mechanism resulting in the increase in adsorption capacity of bentonite compared to natural bentonite. The natural and DTMA-bentonite were tested for adsorption of a synthetic textile dye, Reactive blue (RB19) and results revealed that modified bentonite possess higher adsorption capacity adsorbing higher amounts of dye compared to natural bentonite. Though lipophilic surface of organobentonites makes them an excellent adsorbent for organic pollutants, they have a drawback as large amount of quaternary ammonium salts are required for the modification (Yue et al., 2007). A large scale production of organoclays is not practical due to

the complexity of the process (Faur-Brasquet et al., 2002) and the cost of modification of clays by surfactants is significantly high (Wang and Wang, 2008).

2.7.4 Thermal Activation

The thermal activation of clay is a physical treatment which involves calcination of clays at high temperatures (Al-Asheh et al., 2003). The change in structure and composition upon heating is different for different clays and largely depends on the particle size and the heating regime (Beragaya et al., 2006). Furthermore, the clay minerals are generally calcined prior to their use in order to remove any impurities or moisture attached to the clay particles (Steudel et al., 2009). The thermal activated clays are extensively used in textile, oil and sugar industry to remove colour and other impurities (Sennour et al., 2009).

Initially, in the dehydration stage, the adsorbed and hydrated water and impurities attached to the clay particles are removed. This results in the weight loss of the clay particles and increase in surface area, providing access to more sites for adsorption (Beragaya et al., 2006). Further heating corresponds to the dehydroxylation. If heating is continued beyond dehydroxylation the clay structure and the surface functional groups are altered. Breakdown of the bonds within the clay structure takes place resulting in the collapse of structure and reduction in surface area (Beragaya et al., 2006, Vimonses et al., 2009).

González-Pradas et al. (1994) studied the adsorption of cadmium and zinc ions on bentonite. The modification of bentonite was conducted by simple heating at 100 and 200°C and acid activation was carried in the range from 0.5 to 2.5M H₂SO₄. The thermal activated clay at 200°C is much more effective compared to other activated clay. Chaari et al. (2008) studied the adsorption of lead on thermal activated clays. The results revealed that adsorption of lead on the smectitic clay increased with the increase in calcination temperature due to the removal of physisorbed water and then decreased with further increase in temperature because of decrease in surface area.

2.7.5 Acid Activation

The clay formulated by treating it with inorganic acids at high temperatures is termed acid activated clays (Koyuncu, 2008). The acid activation of the clays is normally done by treating it with HCl or H₂SO₄ (Díaz and De Souza Santos, 2001) and the cost of production of these acid activated clays is low (Kara et al., 2003). The acid activation of the clays alters the physical properties, such as, enhancing the surface area and average pore volume (Doulia et al., 2009). It can also change the chemical properties such as cation exchange capacity and the surface acidity of the clays, thus, generating the desirable characteristics required for an effective adsorbent (Lian et al., 2009). Acid activation is a favourable method for increasing surface area as the decomposition of the crystalline structure can be controlled (Chaari et al., 2008).

2.7.5.1 Mechanism of Acid Activation

The acid activation of the clays is a two-step procedure in which the splitting of particles within the octahedral sheet takes place. 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 (Steudel et al., 2009). The octahedral Al^{3+} cations could be more easily leached by acid attack than the 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, 1991) and decrease in the surface area of the clay (Díaz and De Souza Santos, 2001), it is essential to use the appropriate amount of acid. Hajjaji and El-Arfaoui (2009) investigated the adsorption of Methylene blue on raw and acid activated bentonite. The adsorption capability can decreased after acid activation using certain acid at a high concentration. The acid activation of bentonite was carried out by treating it with 6.7N HCl at boiling temperature for 3h. The high acid strength and temperature may have caused the decomposition of the montmorillonite structure and formation of excess amorphous silica.

Apart from leaching of cations from octahedral and tetrahedral sheets, acid activation also removes impurities like calcite and exposes the edges of platelets leading to an increase in surface area. The acid activated clays have a lower layer charge, lower cation exchange efficiency and higher surface area than the natural

clays, and could be desirable for adsorption (Steudel et al., 2009). Jovanović and Jonačković (1991) activated bentonite with HCl over a concentration range of 0.5-4M. It was found that surface area of bentonite increased with severity of acid. The maximum surface area and optimal porosity is achieved by activation with 2M HCl and decreases with further increase in acid concentration. The increase in surface area at a low concentration is attributed to cation exchange and removal of impurities; however the decrease in surface area beyond 2M HCl is due to structural changes and the decomposition of samples.

The properties of the acid activated clays are controlled by the following factors: acid concentration, temperature, treating time and dry acid/clay ratio, drying temperature of the clay, washing procedure (Díaz and De Souza Santos, 2001). Bhattacharyya and Sengupta (2001) activated kaolinite and montmorillonite by acid activation with 0.25M H₂SO₄ for 3h. On acid activation the surface area of kaolinite increased from 3 to 15m²g⁻¹, whereas the surface area of montmorillonite increased from 19 to 52m²g⁻¹. The adsorption of Fe (III) ions on montmorillonite was more than kaolinite and acid activation enhanced the activation capacity adsorbing more Fe (III) ions on their acid activated forms.

The high surface area of the clay particles after the acid activation is attributed to the reduction in the pore size of the particles (Venaruzzo et al., 2002). The surface area of the clays increases to a large extent if acid activation is followed by thermal activation (Khenifi et al., 2007). The adsorption of two acidic dyes

namely, Bezanyl red and Nylomine green, on natural and acid activated bentonite is examined by Benguella and Yacouta-Nour (2009). The activation of natural bentonite is carried out using 0.1M H₂SO₄. The surface area of acid activated bentonite (56m²g⁻¹) was much higher than natural bentonite (23m²g⁻¹). The increased amount of dye adsorbed on acid activated bentonite over natural bentonite shows that acid activation enhanced the adsorption capacity of bentonite (Benguella and Yacouta-Nour, 2009). Özcan and Özcan (2004) have successfully adsorbed acidic dyes, namely Acid red 57 (AR57) and Acid blue 294 (AB294), on H₂SO₄ acid activated bentonite.

Yildiz et al. (2004) analysed the effect of acid activation on surface properties of bentonite. Acid activation was carried out by treating bentonite with H₂SO₄ (0.2M – 4M). It has been reported that the surface area generally increased with an increase in acid concentration and maximum surface area attained by samples treated with 2M acid and decreased thereafter. The increase in surface area at a low concentration of acid is attributed to the cation exchange (i.e. replacement of exchangeable cations by H⁺ ions and the removal of impurities). The value of maximum BET specific surface area was 240m²g⁻¹. Christidis et al. (1997) observed a 4-5 fold increase in the surface area of acid activated Milos and Chios bentonite of Greece compared to the raw bentonite. The results showed that acid activation largely depends on acid strength and time: at longer residence time lower concentration of acid can attain the same maximum surface area as samples that were treated with higher acid concentration for shorter durations. Eren and

Afsin (2009) studied the adsorption of a basic dye, Crystal violet, to analyse the ability of bentonite to remove large cations. They tested the adsorption on raw and acid activated bentonite. Their results showed that an acid to clay ratio of 0.2 (w/w) is sufficient to considerably increase the surface area and adsorption capacity of bentonite for Crystal violet.

The properties of the clay mineral can be changed greatly when acid activated clays are combined with alkylammonium intercalations (Kooli et al., 2009). Even though bentonite is widely used for acid activation, the modification of only Ca^+ -bentonite was reported in the literature. The Na^+ -bentonite is a water swelling clay and there is no insight to acid activation of these clays (Díaz and De Souza Santos, 2001; Beragaya et al., 2006). The adsorption of Congo red on Ca-bentonite has been studied by Lian et al. (2009) who found that more than 90% of dye removal can be attained by 0.2g of bentonite for an initial dye concentration of 100 mgL^{-1} . Önal and Sarıkaya (2007) acid activated bentonite with H_2SO_4 and found that with an increase in acid concentration the crystallinity of Ca-bentonite deteriorated. The decrease in the dissolution of cations followed the order Ca^{2+} , Na^+ , Mg^{2+} , $\text{Fe}^{2+,3+}$ and Al^{3+} .

The acid activation increases the surface area as well as acid sites (Yang et al., 2006). The catalytic properties of clays largely depend on the surface acidity in terms of strength and number of acid sites (Tyagi et al., 2006). The increase in surface area of acid activated clays is attributed to the decomposition of smectite

structure. The increase in acid concentration and temperature enhances the decomposition rate of smectites increasing the surface area of bentonite correspondingly (Babaki et al., 2008).

A comparative study of the effect of acid activation with H₂SO₄ and HCl has been reported by Pushpaletha et al. (2005). The results revealed that modification of clay by sulphuric acid was proven to be more efficient than hydrochloric acid. The activation was carried out over a concentration range from 0.35 to 10N. The maximum conversion of benzene was obtained by samples treated at 1.5N for both acid and significant increase in conversion on acid activated bentonites has been observed compared to raw bentonite. Kara et al. (2003) analysed the effect of HNO₃, HCl and H₂SO₄ on the modification of sepiolite. The surface area evaluation revealed that surface area of sepiolite increased on acid activation and followed the order H₂SO₄ > HCl > HNO₃. Furthermore, the results showed that acid activation followed by thermal activation drastically increases the surface area.

2.7.5.2 Advantages of Acid Activation

Acid activation is a simple process to enhance the adsorption capacities of clays (Faur-Brasquet et al., 2002). It has been proved by several researchers that bentonite can be a promising adsorbent for the removal of Congo red (Bulut et al, 2008).

2.7.5.3 Applications of Acid Activated Clays

Acid activated clays require smaller amounts of cationic surfactants compared to natural clays. These acid activated clays can be used as base material for modification with cationic surfactants to prepare organoclays (Kooli et al., 2009). The acid activated clays can also be used for formulating clay-polymer-nanocomposites including rubbers, plastics, coatings and paints (Steudel et al., 2009) with higher structural strength (Roelofs and Berben, 2006).

The manufacturing of rubber materials generally require highly expensive reinforcing and structuring fumed silicas. Fumed silicas can be replaced by natural clay minerals due to the possession of similar SiO_4 units and OH group. The natural clay minerals are non-reinforcing and they need to be modified to make them suitable for rubber composites. Acid activation is most commonly employed method for modification of clay minerals to develop the reinforcing properties (Dai and Huang, 1991). The acid activated clays can be widely employed in many industrial processes, as a cheap source of protons (Beragaya et al., 2006).

Acid activated bentonite is widely used in sulphur production and in the manufacturing of detergents (Christidis et al., 1997).

Acid activated clays can be used as adsorbent and catalyst. It can also be used for manufacturing carbonless paper and pillared clays (Önal and Sarıkaya, 2007).

2.8 Conclusions

This chapter briefly reviewed the chemical composition of dyes related industrial applications and the toxic impacts of the dye effluent discharged by dyeing industries. A detailed account about all the available techniques for dye removal techniques is provided. The advantages and disadvantages of current dye removal technique are summarized and discussed. Adsorption is one of the most effective techniques for dye removal. Unfortunately the use of adsorption for dye removal is restricted due to high cost and regeneration difficulties of activated carbon, which is a widely used adsorbent for industrial adsorption processes. This limitation highlights the need for low-cost adsorbents. It has been found that clays have the potential to replace activated carbons.

This chapter focused on the various low-cost adsorbents that have been proved to successfully remove dyes. Clays have high potential for dye removal; however the application of clays is confined to the treatment of basic dyes due to the presence of net negative charges on their surface. Hence there is need for modification of clays to enhance their surface area and adsorption properties. Furthermore, this chapter also described various techniques for the modification of the surface area and adsorption properties of clays, therefore, enhancing adsorption capacity and specificity. The evidence to date strongly supports the possibility of thermal and acid activation for the modification of bentonite, which is a target adsorbent and will be investigated in detail in this study.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

3.1.1 Bentonite

The Australian clay mineral, sodium bentonite, called Active Gel 150 used in the study was obtained from Unimin Australia Limited. This sodium bentonite has high montmorillonite and low grift content. This sodium bentonite was used as received for modification without any further purification. The chemical composition of sodium bentonite provided by supplier is given in the Table 3.1:

Table 3.1: Chemical composition of sodium bentonite

Constituent	Composition
SiO ₂	56%
Al ₂ O ₃	16%
Fe ₂ O ₃	4.6%
CaO	0.9%
K ₂ O	0.4%
MgO	3.3%
Na ₂ O	2.9%
H ₂ O	10%
LOI	5.7%
Average particle size	75µm
Density	1.0gcm ⁻³
The cation exchange capacity	95mequiv.(100g) ⁻¹

3.1.2 Congo Red

The anionic dye, Congo red, used in the study was obtained from Labchem Ajax Finechem Australia and was used as received without any purification. The chemical formula of Congo red is $C_{33}H_{22}N_6Na_2O_6S_2$ with Color Index 22120. The molecular weight of Congo red is 696.7gmol^{-1} . Congo red, a diazo dye, was used as a surrogate indicator to simulate industrial wastewater in order to evaluate the adsorption capacity of raw and modified bentonites used in the study. Congo red is a diazo dye and is prepared by coupling tetrazotised benzidine with two molecules of naphthionic acid. The IUPAC name of Congo red is [1-naphthalene 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.

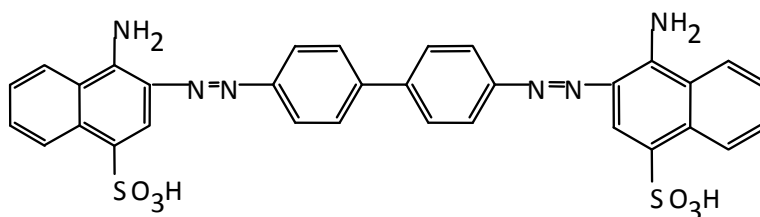


Figure 3.1 Chemical structure of Congo red

The sodium salt of Congo red is responsible for dyeing cotton full red and is the first synthetic dye capable of directly dyeing cotton (Pukrait et al., 2007). The color

of Congo red changes from red to blue in the presence of inorganic acids. The change of color is due to the resonance between charged canonical structures (Finar, 1986). The red color is stable in the pH range of 5-10 (Pukrait et al., 2007).

The maximum absorbance of Congo red on a UV-vis spectrophotometer is recorded at 496.5nm (Vimonses et al., 2009). The stock solution of Congo red was prepared by dissolving known quantity of Congo red powder in double-ionized water obtained from Barnstead nanopure Diamond Water ion exchange system with 18.2M Ω . The successive dilutions were made to obtain the working solution of desired concentrations.

3.2 Modification and Activation of Raw Bentonite

3.2.1 Thermal Activation

The physical modification of raw bentonite was performed by thermal activation. The preparation of thermal activated bentonite was carried out by calcination of raw bentonite in Muffle Furnace shown in Figure 3.2. The thermal activation was performed over a range of temperature from 50 °C to 500 °C (50, 100, 200, 300, 400 and 500°C). For thermal activation of bentonite, 10g of bentonite was taken in a crucible. This given amount of bentonite was placed in the Muffle Furnace. Then the temperature of the Muffle Furnace was set to the desired temperature, for example 50°C. The temperature was allowed to rise steadily to the desired

temperature in 5min. After the desired temperature was reached the samples were maintained at the set temperature and were heated for predetermined time varying from 10min. to 2h (10min, 20min, 40min, 1h, 1.2h, 1.4h, 2h).When the heating was complete the samples were taken out of the Muffle Furnace and cooled in the desiccator for 2h.



Figure 3.2 Muffle furnace used for thermal activation of bentonite

After that the samples were stored in air-tight plastic bottles in a desiccator for further use. Similar experiments were carried out for different temperatures and times. Figure 3.3 shows thw thermal activated bentonite at 100°C and 500°C.



Figure 3.3 Bentonite modified by TA at 100°C and 500°C for 20 min

3.2.2 Acid Activation

The acid activation of bentonite was carried out in a rotary shaker (Ratek OM 15 orbital) with temperature and agitation control. Raw bentonite was treated with HCl solution of varying concentrations (0.05, 0.075, 0.1, 0.25 and 0.5M) and at different temperatures (30, 60 and 80°C). The acid to clay ratio was fixed at 1:10 i.e. 10g of bentonite was treated with 100ml of known concentration of HCl solution. Agitation was applied by Ratek OM15 orbital, rotary shaker, at 180rpm. The reaction was carried out for 3h.

Stock solution of 5M HCl was prepared. This stock solution was diluted to make a working solution of HCl of varying concentrations, 0.05, 0.075, 0.1, 0.25 and 0.5M. 100ml of HCl solution of known concentration was taken in a shaker flask to which 10g of raw bentonite was added. The shaker flask was then kept in the rotary shaker and the temperature was maintained (for example 30°C and similar

experiments were conducted for all acid concentrations and at all temperatures). Agitation was applied during 3h. After 3h the reaction was terminated with addition of large amount of double-ionized water obtained from Barnstead nanopure Diamond Water ion exchange system with 18.2M Ω .

The acidified product was then washed several times with double-ionized water. The solution was then centrifuged in Model J-21C centrifuge at 8000rpm for 15min. After each wash Cl⁻ ions were detected in the supernatant, using silver acetate solution. The washing was continued until the supernatant was free of Cl⁻ ions and a pH of 5 was reached. The final sample was centrifuged with Allegra X-12 centrifuge at 3750 rpm for 10min. This centrifuge was used for the centrifugation of the final sample to have a flat and even layer of bentonite in the centrifuge tubes so that uniform drying of acid activated bentonite could be achieved.



Figure 3.4 Bentonite modified by AA at 30°C for 3h with acid concentration of 0.075M, 0.1M and 0.5M.

The final sample was then dried in oven at 55°C for 12h and then stored in air-tight plastic bottles in desiccator for further use. Figure 3.4 shows the bentonite modified by AA at 30°C for 3h with acid concentration of 0.075M, 0.1M and 0.5M.

3.2.3 Acid and Thermal Activation

The acid and thermal activation of bentonite is a two step procedure. In the first step bentonite was acid activated by treating it with HCl acid and in the second step the acid activated bentonite was further subjected to thermal activation. The acid activation of bentonite was performed by a similar method as explained in section 3.2.1.

The acid activation of bentonite was carried out over a concentration range from 0.05, 0.075, 0.1, 0.25 and 0.5M of HCl. 10g of bentonite was treated with 100ml of known concentration of acid. The reaction temperature was fixed at 30°C and the agitation was applied during 3h. Then the reaction was terminated after 3h with addition of large amount of double-ionized water obtained from Barnstead nanopure Diamond Water ion exchange system with 18.2MΩ. The samples were exhaustively washed until free of Cl⁻ ions and pH of 5 is maintained. The acid activated samples were centrifuged and dried in oven for 12h. The acid activated bentonite was then subjected to thermal activated by calcination at 100°C for 20min in a Muffle furnace. The contents were then cooled in a dessicator and stored in air-tight plastic bottles for further use.

3.3 Characterization of Modified Bentonite

The effect of modification on the surface properties of clay was analysed using various characterization tools, including Brannuer-Emmet-Teller (BET) method, Fourier transform infra red spectroscopy (FTIR) and scanning electron microscopy (SEM). A brief description of these tools is discussed below.

3.3.1 Surface Area and Pore Size Evaluation

The specific surface areas of thermal activated bentonite, acid activated bentonite and a combination of acid and thermal activated clay were estimated using BET method. The pore width was determined using BJH method. The sample tubes were loaded with 0.3g of modified bentonite samples. The samples were then degassed under vacuum at $378\pm 1\text{K}$ for 12h in Vacuum Prep 061 sample degas system prior to surface area measurements. The surface area and pore width determinations were based on isotherms of adsorption and desorption of nitrogen at 77K using Micrometrics gas adsorption analyzer (Gemini VII).

3.3.2 Fourier Transform Infra Red Spectroscopy

FTIR spectroscopy was carried out to analyze the effect the acid attack and the change that have taken place in the structure of bentonite as a result of modification by AA and ATA. The infra red (IR) spectra of RB and bentonite modified by AA and ATA were obtained. The spectra were recorded in the range from $4000\text{-}400\text{cm}^{-1}$ using Nicolet 6700 FT-IR with Smart orbit Attenuated Total

Reflectance (ATR) accessory. The ATR is fitted with Diamond crystal on powders that can be analyzed without the formation of a pellet with potassium bromide which is required with other standard FT-IR equipments. The modified bentonites were dried prior to the analysis. The infra red spectra of raw and modified bentonites were obtained in the powder form by placing the samples on the Diamond crystal to obtain FTIR spectra.

3.3.3 Scanning Electron Microscopy

Bentonite samples were examined under scanning electron microscopy (SEM) to analyze the morphological and surface characteristics. The SEM was carried out using a Philips XL30 Scanning Electron Microscope at accelerating voltage of 15kV, beam size 3.0, working distance 10 and magnification of 8000. The samples were coated with carbon under vacuum before analysis to prevent the accumulation of static electric charge on the surface of particles. Several microscope images were taken for raw and modified bentonite samples.

3.4 Experimental Set up and Procedure

Adsorption of CR on raw and modified bentonite was carried out in a batch system. The batch technique was selected due to its simplicity and reliability. The effect of various operational parameters such as contact time, initial dye concentration, pH and temperature has been investigated. The experimental procedure followed for the investigation of the operational parameters is

discussed below. The contents in the flasks were agitated in a rotary shaker (Ratek OM 15 orbital) as shown in Figure 3.5.



Figure 3.5 Image of rotary shaker used for dye adsorption experiments and clay modification

The agitation speed was fixed at 150rpm and the temperature was maintained at 30°C. The agitation was carried out for 24h to ensure that the equilibrium is reached unless otherwise stated as in the case of the study of contact time. The samples were then centrifuged in Eppendorf Centrifuge 5415R (Germany) at 13200rpm for 20min. to separate the dye solution from the adsorbent. Figure 3.6 shows the centrifuge used for the separation of dye from supernatant.



Figure 3.6 Eppendorf Centrifuge 5415R

The dye concentration in the supernatant was determined by UV-vis spectrophotometer. (model γ , Helios, UK) as shown in Figure 3.7.



Figure 3.7 UV-vis spectrophotometer (model γ , Helios, UK)

3.4.1 Effect of Contact Time

The study of the effect of contact time on the adsorption of Congo red on raw and modified bentonite was carried out. 20mg of adsorbent was added to 50ml dye solution of initial concentration of 100mgL^{-1} . The contents in the flask were agitated in the rotary shaker. This process of agitation was carried out for all the four samples for varied time ranging from 2h to 30 h. The flasks were taken out of shaker at predetermined time intervals. The dye concentration in the supernatant was measured.

3.4.2 Effect of Initial Dye Concentration

The equilibrium data of adsorption of Congo red on raw bentonite and the bentonite modified by TA, AA and ATA was obtained to investigate the effect of initial dye concentration on CR adsorption. The effect of initial dye concentration was studied over a concentration range from 100mgL^{-1} to 1000mgL^{-1} . 20mg of adsorbent was added to 50ml dye solution of predetermined initial dye concentrations. The contents in the flasks were agitated. After 24h the dye concentration in the supernatant was determined by UV-vis spectrophotometer.

3.4.3 Effect of Adsorbent Dosage

To study the effect of adsorbent dosage the amount of adsorbent was varied from 2 to 20gL^{-1} . A known amount of adsorbent was added to 50ml dye solution of initial concentrations of 100mgL^{-1} . The contents in the flasks were agitated. The

samples were then centrifuged and the dye concentration of the supernatant was determined. Similar experiments were performed for all the adsorbents (i.e RB and bentonite modified by TA, AA and ATA).

3.4.4 Effect of pH

The effect of pH on the CR adsorption on RB and bentonite modified by TA, AA and ATA was studied. The pH of Congo red solution of initial concentration of 100mgL^{-1} was adjusted with 0.1M HNO_3 and 0.1M NaOH . A known amount of adsorbent was added to the Congo red solution of desired pH value. The pH of the initial dye solution was maintained at 3, 5, 7, 9 and 11. The samples were then centrifuged and the dye concentration of the supernatant was determined.

3.4.5 Effect of Temperature

The amount of dye adsorbed on clay was determined at 25, 30, 40, 50 and 60°C to investigate the effect of temperature. A known amount of adsorbent was added to 50ml dye solution with initial dye concentration of 100mgL^{-1} . The contents in the flasks were agitated for 24h, after which they were centrifuged and the concentration of dye in the supernatant was determined.

3.5 Isothermal and Kinetic Study

The adsorption isotherms have been evaluated to analyze the equilibrium data. The effect of the contact time on the adsorption of Congo red has been analyzed by evaluating the kinetic data by pseudo-first order and pseudo-second order kinetic models.

3.5.1 Adsorption Isotherms

Adsorption isotherm is the equilibrium relationship between the concentration in the liquid phase and the concentration in the adsorbent phase in the adsorbent particles at a given temperature (Treybal, 1981). The experimental data obtained are analyzed by adsorption isotherms to describe the adsorption of dye on clay. In the present study, Langmuir and Freundlich models were used to analyze the data which are widely used in solid-liquid adsorption systems.

3.5.1.1 Langmuir Isotherm

Langmuir adsorption isotherm was studied by Langmuir in 1918 and is the earliest of the kinetic groups of theory of adsorption (Langmuir, 1918). Langmuir adsorption isotherm is based on the assumption that the molecules of the adsorbate form a monolayer on the surface of the adsorbent. Adjacent adsorbed molecules do not interact, i. e., the adsorption of adsorbate at a particular site is independent whether the neighboring sites are adsorbed or not. Langmuir isotherm is widely used and can be represented as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

where q_e is the amount of dye per unit mass of adsorbent at equilibrium (mgg^{-1}), q_m is the maximum amount of dye adsorbed per unit mass of adsorbent for the formation of complete monolayer on the surface of adsorbent (mgg^{-1}), K_L is

Langmuir constant related to energy of adsorption (Lmg^{-1}). Langmuir constant can be estimated from the linear plot of C_e/q_e versus C_e .

3.5.1.2 Freundlich Isotherm

Freundlich adsorption isotherm is applicable for heterogeneous systems and involves formation of multilayers. Freundlich isotherm can be represented as:

$$q_e = kC_e^{1/n}$$

where k and n are the Freundlich constant. K is a measure of amount of adsorption and n is a measure of the heterogeneity of the adsorption energy across the surface. The value of k and n can be obtained from the slope and intercept of a linear plot of $\log q_e$ versus $\log C_e$.

3.5.2 Adsorption Kinetics

The kinetics of adsorption of Congo red on raw and modified bentonite has been evaluated. The experimental data were examined by pseudo-first-order kinetics, pseudo-second-order kinetics and intraparticle diffusion to understand the dynamics of adsorption process.

3.5.2.1 Pseudo-first order model

The pseudo-first-order kinetic model also known as the Lagergren kinetic equation is widely employed to understand the kinetic behaviour of the system (Ho, 2004).

It is given by the equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

where q_e and q_t are the amounts of dye adsorbed at equilibrium and at time t (mgg^{-1}), k_1 is the pseudo first order rate constant (min^{-1}).

3.5.2.2 Pseudo-second order model

The pseudo-second-order kinetic model is given by the equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where, q_t and q_e are the amount of dye adsorbed at equilibrium and at time t . k_2 is the equilibrium rate constant of pseudo-second-order model ($\text{gmol}^{-1}\text{min}^{-1}$). 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).

3.6 Analysis Procedure

3.6.1 Sampling Procedure

The samples were withdrawn from the rotary shaker after 24h when the equilibrium is reached apart from the study of contact time where the flasks were removed at predetermined intervals for the determination of the dye

concentration. The contents in the flask were centrifuged and the concentration in the supernatant was determined by UV-vis spectrophotometer.

The concentration of the dye in the supernatant is determined by UV-visible spectrophotometer. The concentration of CR in supernatant was measured at maximum absorbance of 496.5nm (Vimonses et al., 2009). The absorbance concentration profile was obtained by plotting the calibration curve between absorbance and dye concentration. The absorbance for each sample given by UV-visible spectrophotometer was converted using calibration factor obtained from the calibration curve to calculate the final dye concentration.

3.6.2 Amount of Dye Adsorbed

The amount of dye adsorbed on the surface of adsorbent at time t can be estimated from the mass balance equation:

$$q_e = (C_i - C_e) \frac{V}{m}$$

Where q_e is the amount of dye adsorbed per unit mass of adsorbent (mgg^{-1}), C_i is the initial dye concentration (mgL^{-1}), C_e is the equilibrium dye concentration (mgL^{-1}), V is the volume of dye solution (mL) and m is the mass of bentonite (g).

The final dye concentration has been calculated in the previous section and the initial dye concentration is predetermined. Initial dye concentration in all experiments is fixed at 100mgL^{-1} except in the study of the effect of initial dye

concentration. In case of the study of initial dye concentration the concentration range is varied from 100 mgL^{-1} to 1000 mgL^{-1} .

3.7 Regeneration of Modified Bentonite

The cost of adsorption process primarily depends on the cost of adsorbent and its reusability. In this study the regeneration of bentonite modified by ATA, AA and TA was carried out by heating the adsorbent at 50°C for 12h, followed by calcination at 100°C for 20min. The purpose of regeneration at very low temperature was carried out to regenerate the adsorbent with simple and economical method.

CHAPTER 4

PHYSICOCHEMICAL MODIFICATION AND CHARACTERISATION OF AUSTRALIAN BENTONITE

4.1 Introduction

Clays are finding increasing application in wastewater treatment as adsorbents due to their low-cost and good intrinsic adsorption characteristics, such as high adsorption capacity and large surface area. There are large numbers of clay minerals such as kaolin (Nandi et al., 2009), montmorillonite (Damardji et al., 2009 and Yan et al., 2007), bentonite (Özcan et al., 2005), clinoptilolite (Li and Bowman 1997), smectite (Díaz and Santos et al., 2001), sepiolite (Kara et al., 2003) and zeolite (Vimonses et al., 2009) that are widely used for the cost – effective removal of chemical pollutants from wastewater. Among all these clays, bentonite is one of the most widely used due to its abundant availability and good adsorption characteristics (Christidis et al., 1997). Bentonite possesses a net negative charge on its surface and would naturally induce an electrostatic attraction for cationic compounds that are present in wastewater. On the contrary, the bentonite could prohibit its close interaction with anionic compounds. Adsorption capacity

and selectivity of natural and or raw bentonite can be limited. Thus, a systematic surface modification of bentonite is essential for the removal of anionic compounds from wastewater since most of the dissolved chemical pollutants are negatively charged.

There are various physical and chemical methods available for the modification of clays. These include acid activation (Steudel et al., 2009), treatment with cationic surfactants (He et al., 2006), clay-rubber composite (Dai and Huang, 1991), thermal treatment (Al-Asheh et al., 2003), polymer addition, pillaring by different types of poly(hydroxo metal) cations, intraparticle and interparticle polymerization, dehydroxylation and calcination, delamination and reaggregation of smectites, and lyophilisation, ultrasound and plasma (Paiva et al., 2008) adsorption and ion exchange with inorganic and organic cations, binding of inorganic and organic anions (mainly at the edges) and grafting of organic compounds (Liu, 2007). Among these, acid activation is one of the most commonly used modification techniques because it is a simple and low-cost process (Jovanovic et al., 1990).

Dyes are extensively used in many manufacturing industries like textile, cosmetics, pulp and paper, paints, pharmaceutical, carpet and printing (Damardji et al., 2009). Many dye materials are toxic and biological non-degradable (Unuabonah et al., 2008) due to their chemical structure and the presence of aromatic ring in their structure which is hard to break. Azo dyes are widely used

in textile industries. Azo dyes contain one or more azo group with aromatic rings and sulfonate groups attached to these rings. Under anaerobic conditions azo dyes can be transformed into more hazardous substances (Song et al., 2009). The removal of dye from wastewater before discharging it to the mainstream is essential. If discharged into water without treating they can cause allergy, dermatitis, skin irritation and mutation in human bodies (Özcan et al., 2005). The dye at even 0.005ppm in water is highly visible (Unuabonah et al., 2008) and can affect the photosynthesis process (Özcan et al., 2007).

Recently, the adsorption of Congo red using three Australian clay minerals namely; sodium bentonite, kaolin and zeolite has been studied by Vimonses et al (2009). In these studies, they have revealed that sodium bentonite showed the best adsorption performance and capacity to remove CR. As a continuation to this previous work, sodium bentonite has been chosen for subsequent modification study, which is aimed to enhance its adsorption capacity. The focus of the study was to devise an economical method for modification of raw Australian bentinite clay. Clays is widely used as an adsorbent due to low-cost but in most cases the modification techniques are rather expensive thereby adding to the overall cost of the adsorbent. With this in consideration bentonite was modified with a series of thermo-physical and chemical methods, which includes sole thermal activation (TA), acid activation (AA) and a combination of acid and thermal activation (ATA). The characterization of modified clays is vital to reveal the changes that the modification process has brought in the physical structure and chemical

properties of a clay mineral. In the present study, the characterization of bentonite is performed by analyzing the surface area of bentonite activated by TA, AA and ATA by Brauner-Emmet-Teller (BET) method. The scanning electron microscopy (SEM) was carried out to reveal the morphological changes in the modified bentonite. To analyse the effect of acid attack the modified bentonite was evaluated by Fourier transform infrared spectroscopy (FTIR).

Results and Discussion

4.2 Thermal Activated Bentonite

4.2.1 Characterisation of Thermal Activated Bentonite

4.2.1.1 *Surface Area*

The calcination of clays at high temperatures can alter the surface properties of clays (Al-Asheh et al., 2003). However the changes in structure and composition upon heating can be variable, depending on the physical properties of the clays and the heating regime (Beragaya et al., 2006). The thermal activation of Australian raw bentonite was carried out over a temperature range from 50°C to 500°C for a period of 20min. To analyze the effect of thermal activation on the surface area of bentonite the BET surface area of bentonite modified by TA was evaluated. The BET specific surface area for all of the TA samples is shown in Figure 4.1 and the corresponding values are reported in Table 4.2.

The results reveal that surface area increased with an increase in the temperature upto 100°C and then gradually decreased beyond 100°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. Excessive heating may lead to irreversible collapse of structure therefore thermal activation of bentonite has to be carried out in a particular range of temperature.

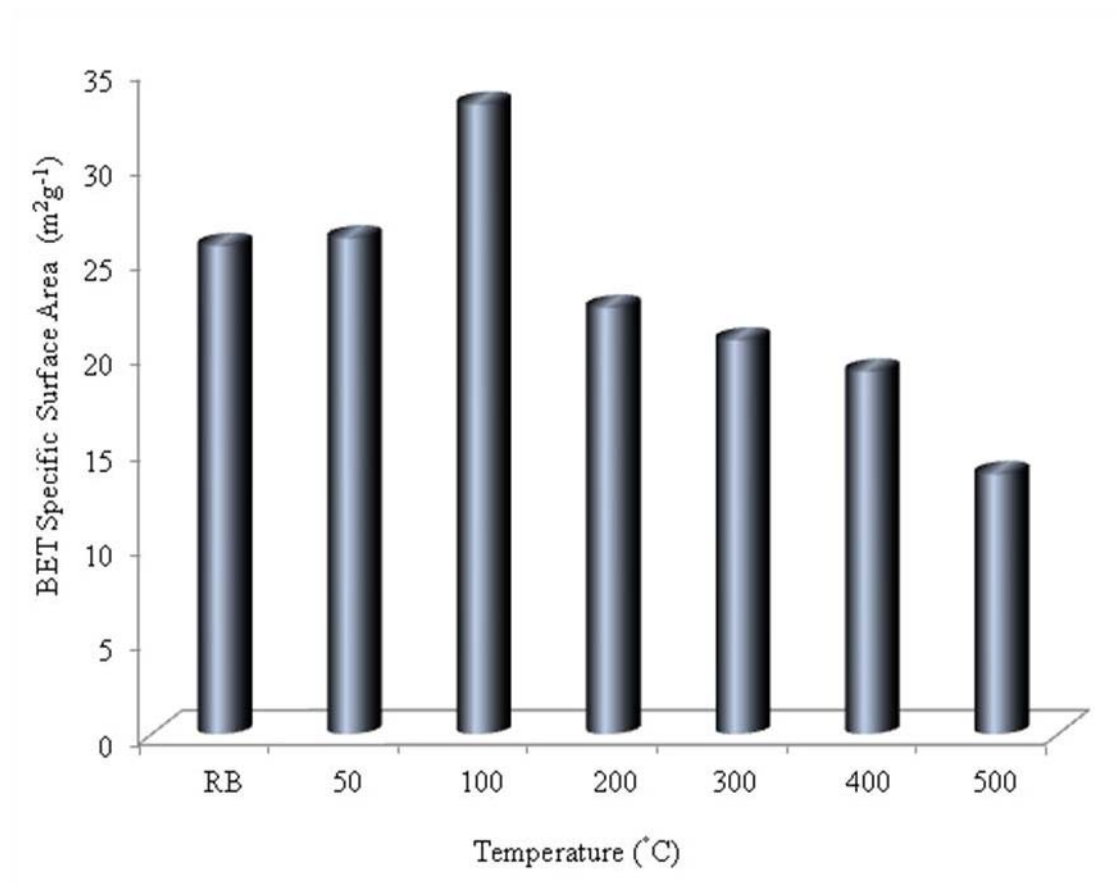


Figure 4.1 BET specific surface area of bentonite modified by TA.

In the present study the surface area decreased beyond 100°C. The decrease in surface area with increasing temperature is attributed to the collapse of interlayer

spaces (Beragaya et al., 2006). This collapse of interlayer spaces brings particles closer to one another and as a result surface area decreases (Chorom and Rengasamy, 1996). The heating at 500°C may damage the clay structure, resulting in decrease in the surface area. More than 20% increase in surface area was observed at 100°C (33.15 m²g⁻¹) compared to raw bentonite (25.70 m²g⁻¹). Similar results have been reported by Önal and Sarıkaya (2007). They examined the thermal activation of bentonite in the temperature range of 100°C to 1300°C and observed that the surface area increased with increasing temperature and then decreased at a temperature over 400°C.

4.2.1.2 Pore Size

Clay minerals have porous structure and the number and size of pores are variable. Specific feature of clay which can differ from one clay to another and is subject to the origin. They can even differ on the same types of clay minerals itself (Stefanova et al., 1996). The complete characterization of clay structure requires detailed analysis of pore size. The classification of pores of clays on the basis of their size is given in Table 4.1 (Jovanavić and Jonaćković, 1991).

Table 4.1: Pore size classification of clay minerals

Pores	Pore size
Micropores	< 2nm
Mesopores	> 2nm <
Macropores	> 50nm

The macropores and the mesopores originate from interactions between the particles, but micropores arise from randomly piled up layers within a particle (Beragaya et al., 2006). The adsorption properties of a solid depend largely on the micropores and mesopores, whereas macropores have negligible effect on adsorption properties (Babaki et al., 2008). Furthermore, porosity of clay can be affected by the adsorbed and hydrated water that existed in the clay. Thermal activation is a common thermo-physical method applied to remove these water molecules (Beragaya et al., 2006).

The initial stage of thermal activation is dehydration, which is a reversible process. The adsorbed and hydrated water and the impurities attached to the surface of clay can be removed in the dehydration stage (Önal et al., 2007). The external surface and mesopores are the first to undergo a change on thermal activation, resulting in the decrease of average pore size initially. The second stage of thermal activation is known as dehydroxylation which is an irreversible process. Further increase in temperature above dehydration alters both the macro and mesoporosity of bentonite showing an increase in the average pore size (Beragaya et al., 2006). Heating above the dehydroxylation temperature collapses the structure completely due to destruction of the layered structure of the clays.

Calcination may involve movement of octahedral cations within the octahedral sheet. However, the changes in texture of bentonite after calcinations are attributed to the exchange of cations in the interlayers (Aytas et al., 2009). The

average pore size of raw bentonite and bentonite modified by thermal activation is shown in Table 4.2.

Table 4.2: BET specific surface area and average pore size of TA bentonite

Temperature (°C)	BET Surface Area	Pore Width (Å)
RB	25.70 ± 0.13	50.28 ± 0.27
50	27.10 ± 0.29	46.13 ± 0.05
100	33.15 ± 0.18	41.12 ± 0.11
200	28.12 ± 0.53	48.19 ± 0.42
300	26.73 ± 0.10	51.65 ± 0.22
400	22.44 ± 0.08	50.95 ± 0.45
500	13.68 ± 0.31	56.73 ± 0.66

The measured average pore size indicates that the pore size first reduced as temperature increased. This is due to the removal of adsorbed water and formation of meso and micropores. Further increase in temperature beyond 100°C resulted in enlarging in the average pore size as the water molecules in the interlayer spaces are removed, and the interlayer spaces collapse. The particles come closer to one another and start forming aggregates. This results in the transformation of micro and mesopores into macropores, and the increase in average pore size. The thermal activation at a high temperature results in the change in structure of the clays. Bojemueller et al. (2000) stated that at high temperatures the edges of the layers are attacked. The destruction of the edges

results in the release of aluminum or hydroxyaluminum cations. Moreover the destruction of edges also results in the increase of formation of mesopores. The collapse of interlayer spaces first transforms three layered structure of clay to two layered and then to one layered clay (Beragaya et al., 2006). As a result, clay mineral loses its originality, forming new phases, such as mullite, cristobalite and feldspars with different composition and properties than the parent clay mineral (Ritherdon et al., 2003).

4.2.1.3 Thermal Analysis

Vimonses et al. (2009) studied the effect of heating on the thermal stability of bentonite. Figure 4.2 shows the differential thermal analysis (DTA) profile of bentonite. The DTA of bentonite was carried out to analyze the effect of heating on the surface and structural properties of bentonite. The thermogravimetric (TG) analysis was also performed to estimate the mass of water evolved corresponding to the weight loss.

The results reveal that the dehydration stage corresponding to the removal of adsorbed and hydrated water can be seen at 85°C. This is the first endothermic peak on DTA plot and the corresponding derivative weight loss on TG plot. It could be seen that the maxima of the DTA curve occurs at 127°C. The removal of adsorbed and hydrated water provides additional adsorption sites and the increase in surface area was observed.

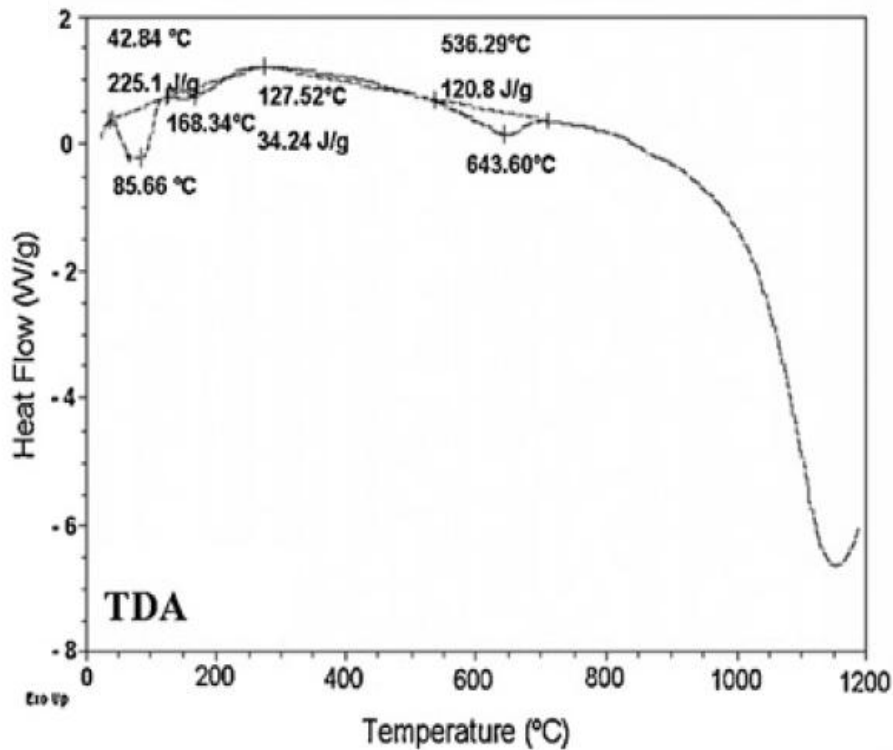


Figure 4.2 Differential thermal analysis profile of sodium bentonite
(adapted from Vimonses et al., (2009))

Further heating indicates the transition from dehydration stage to dehydroxylation stage. The second endothermic peak appears at 640°C, showing the maximum exothermic breaking point at 985°C. Heating beyond these temperatures results in collapsing the interlayer spaces, and consequently rupturing the clay structure. This structure rupture can cause morphology changes of the clay minerals, which is supported by the decrease in surface area at high temperatures, as discussed in 4.2.1.1. The DTA plot also suggests that the thermal activation of bentonite should be carefully carried out in the temperature range between 85°C and 640°C.

Heating above the dehydroxilation stage may cause irreversible damage to the structure of bentonite.

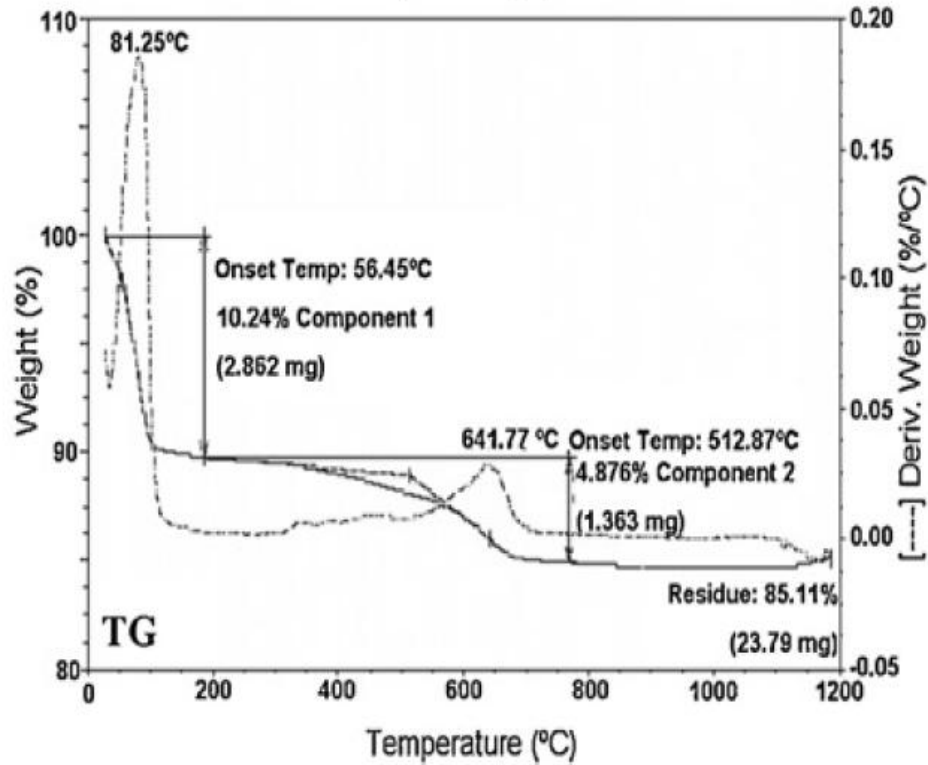
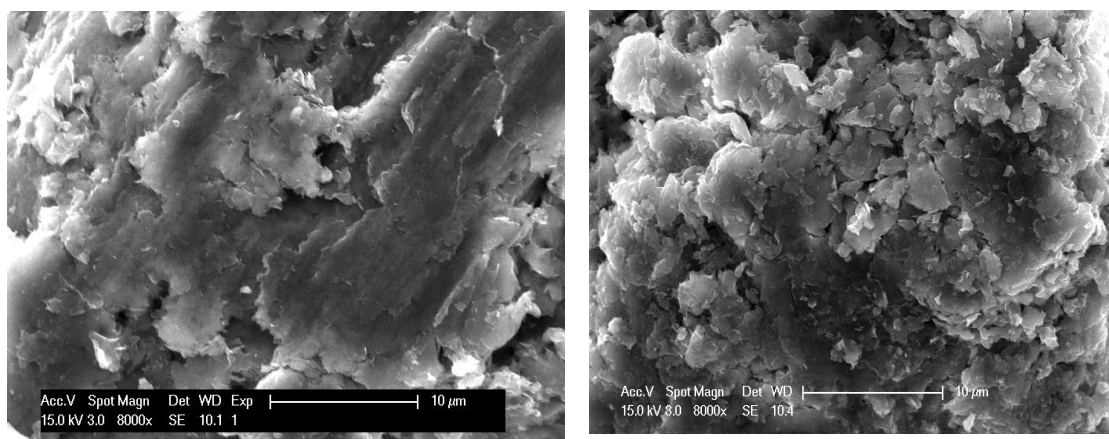


Figure 4.3 Thermogravimetric profile of sodium bentonite (adapted from Vimonses et al., (2009))

The total mass loss of 15% is observed in the temperature range of 50°C to 750°C as shown in Figure 4.3. The weight loss in the dehydration stage was 10% in the temperature range of 50 to 200°C and further heating with increase in temperature shows 4% weight loss in the temperature range of 200 to 750°C.

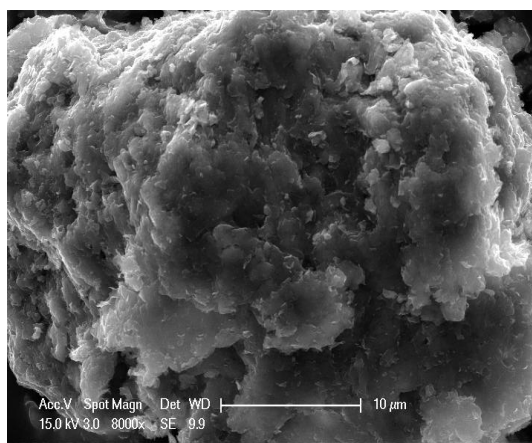
4.2.1.4 Surface Morphology

The SEM of raw bentonite and bentonite modified by TA was carried out to assess the effect of heating on the surface morphology of bentonite. The surface of raw bentonite appears to be smooth due to closely packed flakes in contrast to the ragged appearance of bentonite modified by TA. Thermal activation at 100°C shows more porous structure compared to RB as is evident from Figure 4.4.



(a) Raw Bentonite

(b) 100°C



(c) 500°C

Figure 4.4 SEM images of raw and thermal activated bentonite

These results are also in accordance with the measured BET specific surface areas of bentonite modified by TA. The surface area increased with the increase in temperature, leading to a maximum surface area corresponding to 100°C. Heating beyond 100°C resulted in the gradual decrease in surface area. The SEM image of bentonite modified by TA indicates that the interlayer spaces may have collapsed resulting in more tightly bound structure with reduction in porous structure at 500°C.

4.2.2 Adsorption of Congo red on Thermal Activated Bentonite

To investigate the effect of thermal activation on the adsorption properties of bentonite, the adsorption of CR on bentonite modified by TA has been analyzed. The CR adsorption on TA bentonite increased with an increase in activation temperature, as shown in Figure 4.5. The increase in CR adsorption is attributed to the enlarged specific surface area. The removal of bound water from interlayer spaces and from the surface may have opened the pores that provide additional adsorption sites for CR. The maximum CR adsorption occurred on bentonite which was activated at 100°C, corresponding to the maximum specific surface area calculated by BET at this temperature. Similar results have been reported by Bojemueller et al (2001) for the adsorption of metolachor on thermal activated bentonite. Their results revealed that the adsorption of metolachor increased with increase in calcinations temperature due to enhanced adsorption sites and surface

area. Further the exposure of aluminum ions at the edges facilitated the adsorption of metolachor.

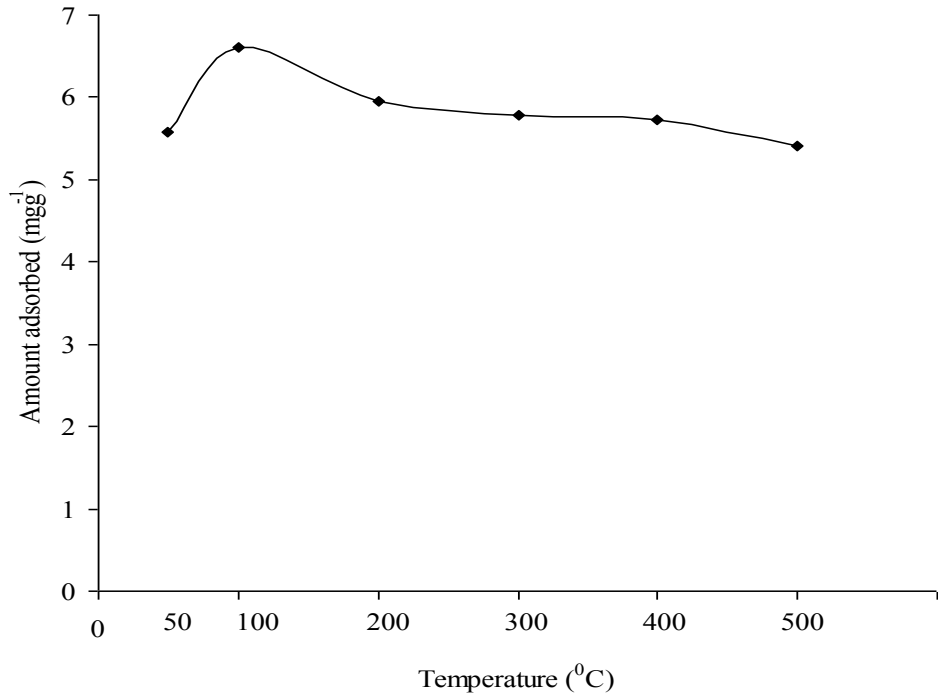


Figure 4.5 Effect of thermal activation on adsorption of Congo red (initial dye concentration 100mgL⁻¹, adsorbent dosage 1g, error bar indicates standard deviation of three replicated at each temperature, SD ± 0.19)

The CR adsorption decreased on the bentonite samples activated in the temperature range from 200°C to 500°C. This decrease in CR adsorption is due to the decrease in surface area which resulted in the decrease in the availability of adsorption sites affecting the adsorption capacity of bentonite modified by TA. Similar results have been reported by Aytas et al. (2009) who studied the

adsorption of Uranium (VI) on thermal activated bentonite. It could be inferred from the results that thermal activation of bentonite at 100°C for 20min. can enhance the adsorption capability of bentonite by 15% in comparison to raw bentonite and can be used as an economical method of activation.

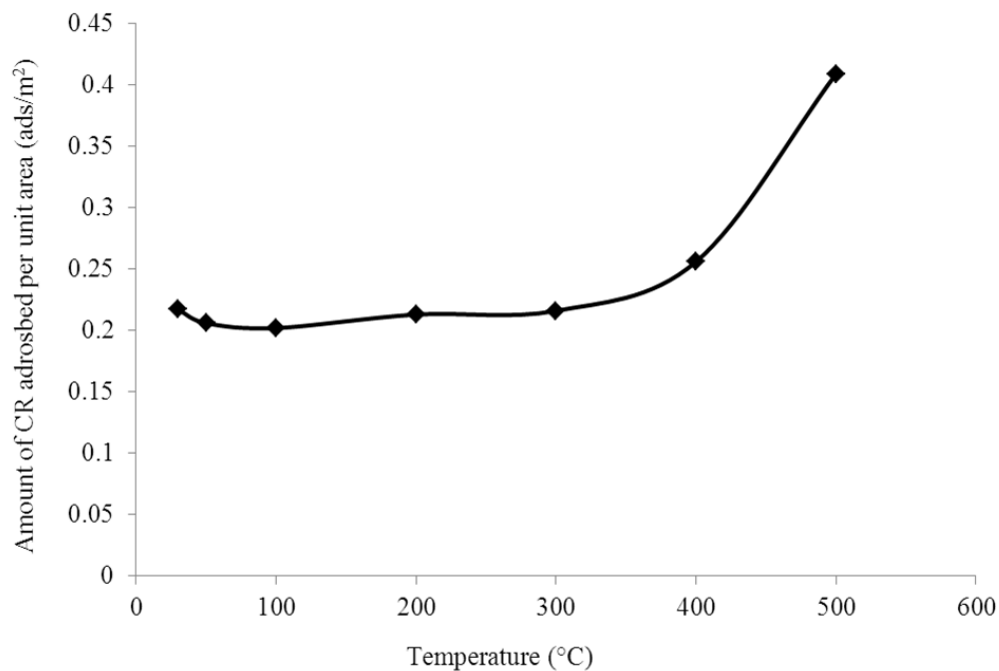


Figure 4.6 Effect of Thermal Activation on the adsorption of Congo red per unit area.

The amount of dye adsorbed per unit area is plotted in Figure 4.6. The comparison of Figure 4.6 and the corresponding values of surface area in Table 4.2 reveal that the amount of dye adsorbed per square meter is decreasing as the surface area increases. The amount of dye adsorbed at maximum area is least as there are large numbers of sites available. As the surface area starts decreasing after 100°C the amount of dye adsorbed per unit area starts increasing.

4.2.3 Effect of Heating Time on Adsorption Capacity of Thermal Activated Bentonite

To analyze the effect of heating time, the thermal activation of bentonite was carried out for different periods of time ranging from 20min. to 2h. Figure 4.7 shows that CR adsorption on thermal activated bentonite increased with an increase in heating time at all temperature ranges. This increase is attributed to the removal of physisorbed water and impurities present in the clay. The maximum CR adsorption was achieved with heating time of 1h 40 min. after which it decreased. The results indicate that apart from temperature, heating time also influences the surface and adsorption capacity of bentonite. If the heating is continued over the applicable range it may result in the destruction of the structure of clay. In this study, the decrease in adsorption beyond 1h 40 min was attributed to the collapse of interlayer spaces due to the removal of water present in the interlayer spaces. Although, the increase in heating time from 20min to 1h40min contributed only a 4% increase in adsorption as shown in Figure 4.6. Therefore, from an economical point of view it was considered that 20 min. be the sufficient time for thermal activation of bentonite.

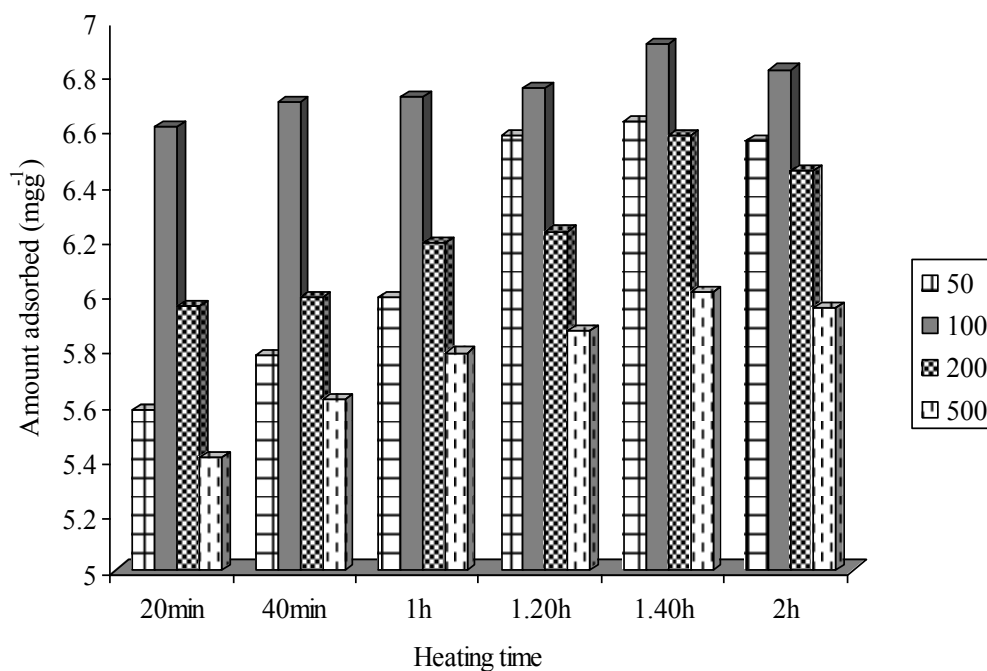


Figure 4.7 Effect of heating time on CR adsorption on TA bentonite (initial dye concentration 100mgL^{-1} , adsorbent dosage 1g , error bar indicates standard deviation of three replicated at each temperature, $\text{SD} \pm 0.27$)

4.3 Acid Activated Bentonite

4.3.1 Characterisation of Acid Activated Bentonite

4.3.1.1 Surface Area

The acid activation of bentonite was carried out by treating it with HCl over a concentration range from 0.05M to 0.5M . Generally, the surface area of AA bentonite increases with increase in acid concentration until a maximum surface area is reached after which it gradually decreases (Pushpaletha et al. 2005). In the

present investigation, the surface area increased with an increase in acid concentration from 0.05M to 0.1M. A maximum surface area of acid activated bentonite obtained with 0.1M HCl at 30°C as shown in Figure 4.8.

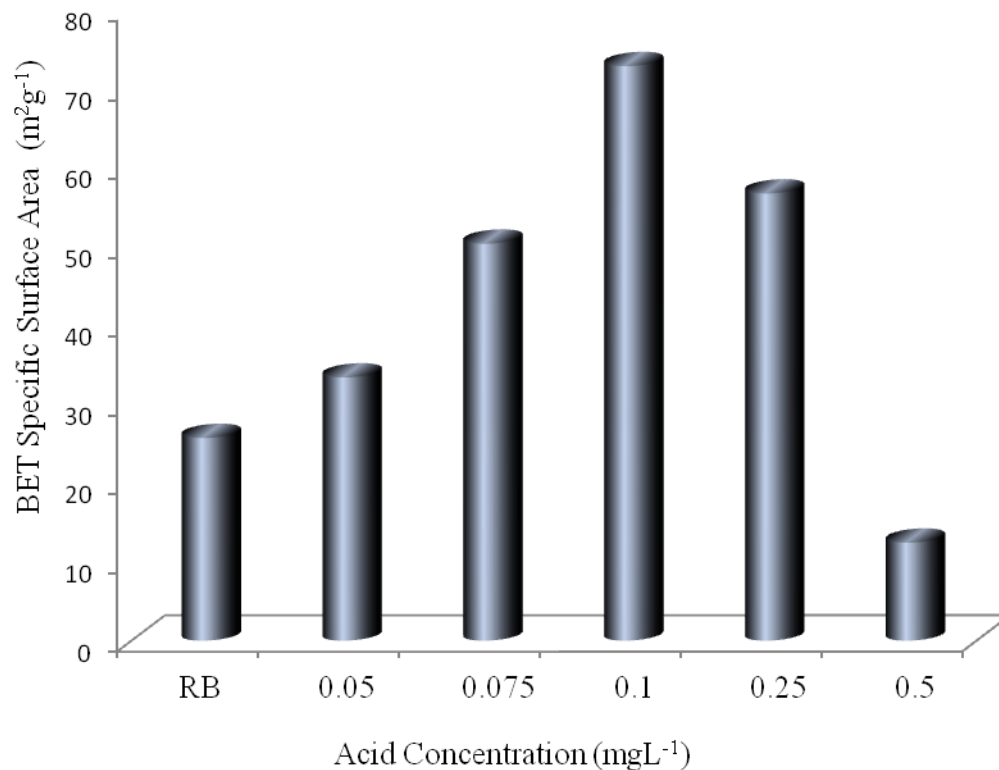


Figure 4.8 BET specific surface area of bentonite modified by AA at 30°C at different acid concentrations

The corresponding values are given in Table 4.3. This increase in surface area is attributed to the removal of impurities, replacement of exchangeable cations (K^+ , Na^+ , Ca^{2+}) with hydrogen ions and leaching of Al^{3+} , Fe^{3+} and Mg^{2+} from the octahedral and tetrahedral sites in bentonite which exposes the edges of platelets (Tsai et al., 2007).

Further increase in acid concentration beyond 0.1M HCl showed a decrease in surface area. The decrease in surface area at higher acid concentrations is attributed to the deeper penetration of acid into the voids and excessive leaching of Al^{3+} , Fe^{3+} and Mg^{2+} , resulting in the collapse of layered structure and close packing of particles (Korichi et al., 2009). The results reveal that acid activation of bentonite with 0.1M HCl at 30°C can be employed as an economical technique for modification of bentonite to enhance its surface properties and adsorption capacity.

4.3.1.2 Pore Size

To obtain the complete characterization of bentonite modified by AA the average pore size of various acid activated bentonites was evaluated and is provided in Table 4.3. The results depicts that the pore size decreased with increase in acid concentration of acid activated bentonite up to 0.1M, and further increase in acid concentration results in an increase in pore size.

Table 4.3: BET specific surface area and average pore size of AA bentonite

Acid Conc.	BET Surface Area (m^2g^{-1})	Pore Width (\AA)
0.05	33.37 ± 0.45	49.36 ± 0.39
0.075	50.34 ± 0.67	48.89 ± 0.27
0.1	72.86 ± 0.33	42.08 ± 0.17
0.25	56.71 ± 0.35	46.17 ± 0.54
0.5	10.42 ± 0.16	53.78 ± 0.31

The initial decrease in pore size is attributed to the removal of impurities and replacement of exchangeable cations by hydrogen ions which are smaller in size than the exchangeable cations (Korichi et al., 2009). This decrease is also attributed to unoccupied octahedral and tetrahedral spaces left by the leaching of Mg^{2+} , Fe^{3+} and Al^{3+} by acid (Babaki et al., 2008).

The increase in pore size beyond 0.1M HCl is due to the collapse of interlayer spaces. As the interlayer spaces collapses the particles come closer to one another and combine, resulting in the decrease in the number of the micropores. The empty spaces lead to increasing pore size, and consequently transforming micropores into mesopores. Further increase in the size of empty spaces results in the disappearance of mesopores at some locations due to disintegration of the crystal structure (Chritidis et al., 1997). This disappearance of mesopores causes a significant decrease in surface area. Similar results have been reported in other studies (Jovanavić et al., 1991 and Yildiz et al., 2004). The average pore size of the AB (0.1M HCl) is 42.08Å which lies in the mesopore region.

4.3.1.3 Effect of Acid Attack on Bentonite

The FTIR spectra of acid activated bentonite are carried out in the range from 4000-400 cm^{-1} to investigate the effect of acid activation on the raw bentonite. The changes in the functional groups provide the indication of the changes occurred during acid activation. FTIR spectra for raw bentonite and the bentonite modified

by AA at activation temperature of 30°C were shown in Figure 4.9 to understand the effect of acid activation on the structure of bentonite.

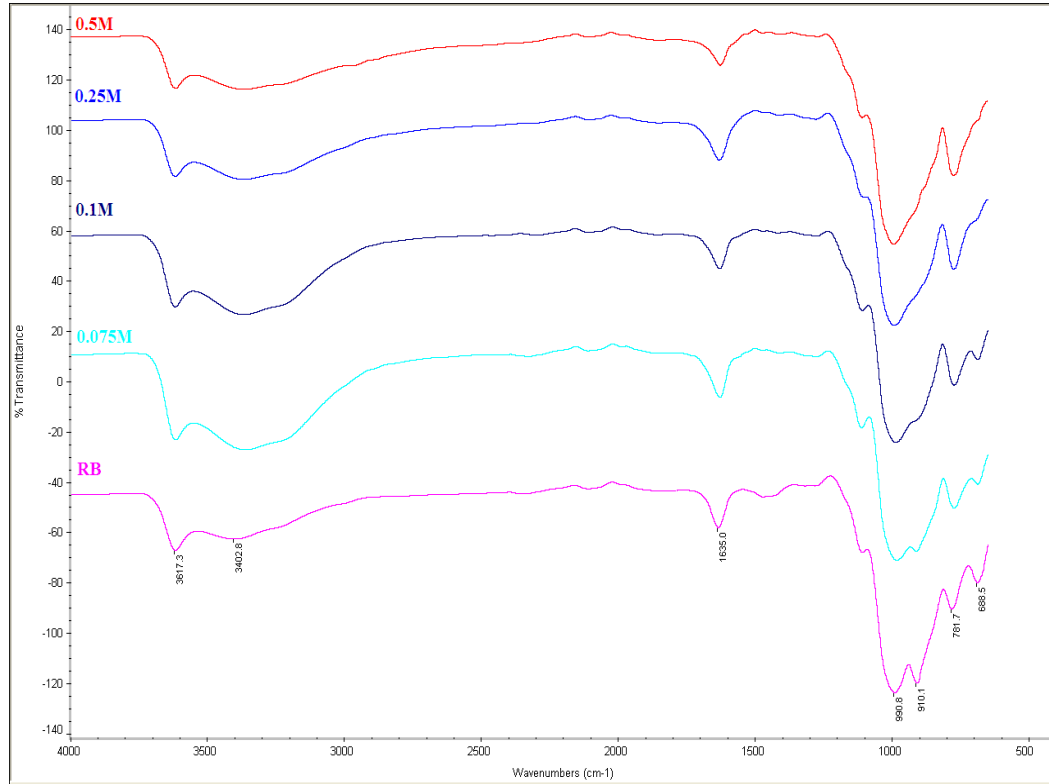


Figure 4.9 FTIR spectra RB and bentonite modified by AA at different acid concentrations

During acid activation of clay the protons penetrate into the clay layers attacking the OH groups causing the alteration in the adsorption bands attributed to the OH vibrations and octahedral cations. The intensity of stretching bands observed at 3617.3cm^{-1} (Al-OH-Al along with the Al-Mg-OH stretching vibrations) decreases with increase in acid concentration (Özcan et al., 2005). The increase in the severity of acid treatment resulted in the decrease of the peaks of the bands

associated with the adsorbed water at 3405.7 (H-O-H stretching) and 1634.6 cm^{-1} (H-O-H bending). The peak of Si-O-Si band at 988.1 cm^{-1} remained unchanged with the intensity of treatment, similar results have been reported by Christidis et al. (1997). The bands at 906.6 cm^{-1} disappeared with the increase in acid strength due to the increased substitution of Al^{2+} ions by Fe^{3+} ions. The transformation of the tetrahedral sheet was found at 781 cm^{-1} . The acid activation leads to the formation amorphous silica, indicated by the increased intensity of the peak, which may be exposing more adsorption sites (Komandel et al., 1990). The intensity of band at 688.1 cm^{-1} (Al-OH-Si bending) decreased with the increase in acid concentration signifying the partial dissolution of aluminum ions present in the octahedral sheet of bentonite.

4.3.1.4 Effect of Activation Temperature

The acid activation of bentonite was carried out at 30°C, 60°C and 80°C to analyze the effect of activation temperature on the properties of acid activated clays. The time of reaction was kept constant to 3 h. Figure 4.10 shows the FTIR of 0.1M HCl acid activated samples at three reaction temperatures. The increase in activation temperature resulted in the deeper penetration of protons into the clay layers. The increase in activation temperature resulted in a decrease in the intensity of peaks at 3617.3 cm^{-1} (Al-OH-Al along with the Al-Mg-OH stretching vibrations), 3405.7 cm^{-1} (H-O-H stretching) and 1634.6 cm^{-1} (H-O-H bending)

(Özcan et al., 2005). The peak of Si-O-Si band at 988.1cm^{-1} remains unchanged (Christidis et al. 1997).

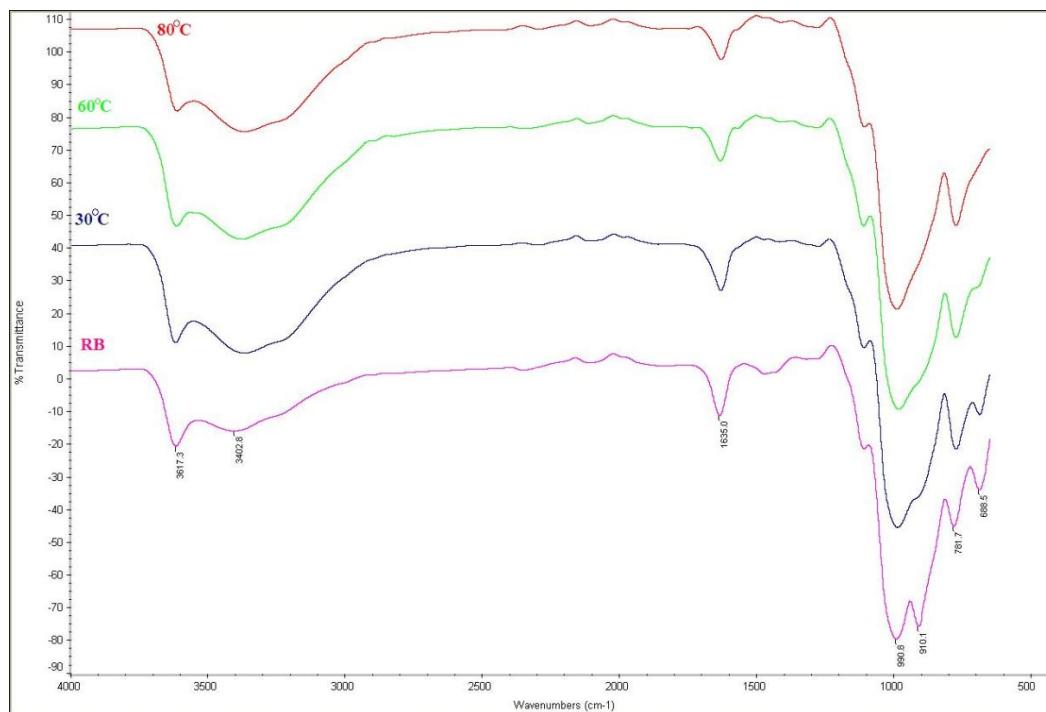
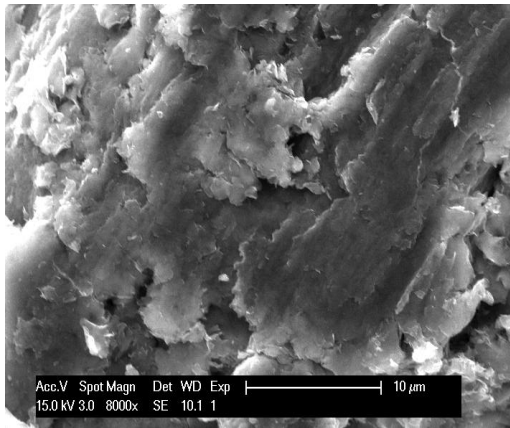


Figure 4.10 FTIR spectra RB and 0.1M HCl AA bentonite treated at different temperatures

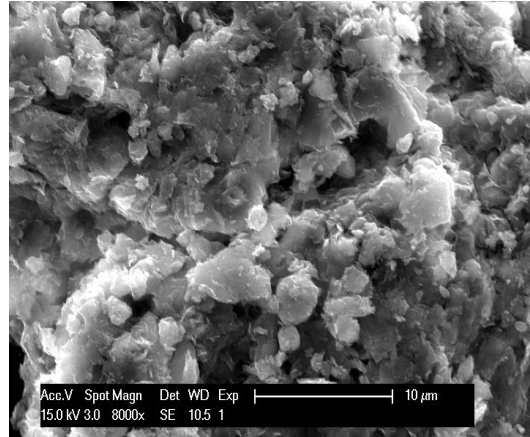
The bands at 906.6cm^{-1} disappeared with the increase in temperature. The intensity of the peak increases at 781cm^{-1} indicates the alteration of tetrahedral sheet (Komandel et al., 1990). The intensity of band at 688.1cm^{-1} (Al-OH-Si bending) decreased with the increase in temperature, showing the dissolution of Al ions that present in the octahedral sheet of bentonite. It is evident from FTIR results that keeping acid concentration and time constant, the increase in temperatures results in the disintegration of structure.

4.3.1.5 Surface Morphology

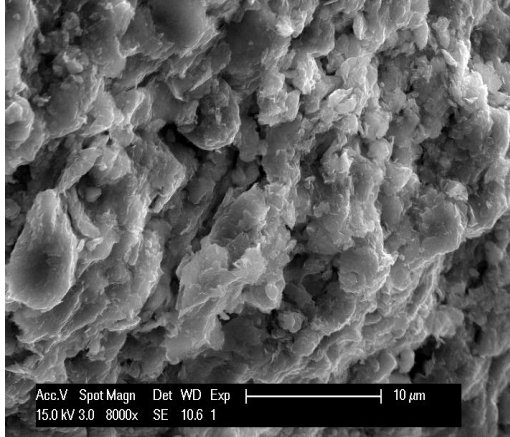
The scanning electron microscopy (SEM) of bentonite modified by acid activation was performed to analyze the changes in the surface morphology of modified bentonite.



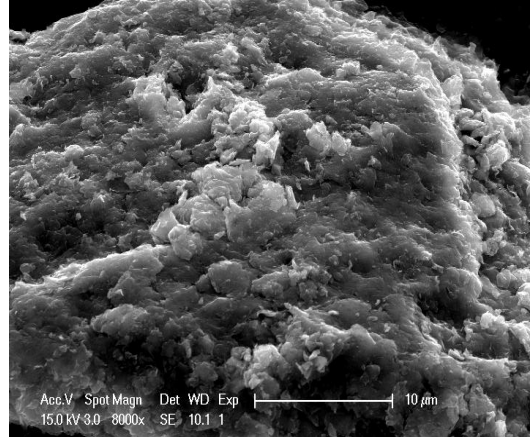
(a) Raw Bentonite



(b) 0.075M HCl



(c) 0.1M HCl



(d) 0.5M HCl

Figure 4.11 SEM images of Acid Activated Bentonite

The leaching of cations on acid activation creates voids in the bentonite making the clay surface more porous. At acid concentration of 0.075M clumps of uneven

surface can be seen along with some flat flakes of low porosity. With the increase in acid concentration to 0.1M the surface becomes highly porous with even distribution of pores. Further increase in acid concentration reduced the porosity rendering clay surface rather flat.

4.3.2 Adsorption of Congo Red on Acid Activated Bentonite

The influence of acid activation on the adsorption capacity of bentonite was investigated by the adsorption of Congo red with initial dye concentration of 100mgL^{-1} on AAB (acid activated bentonite).

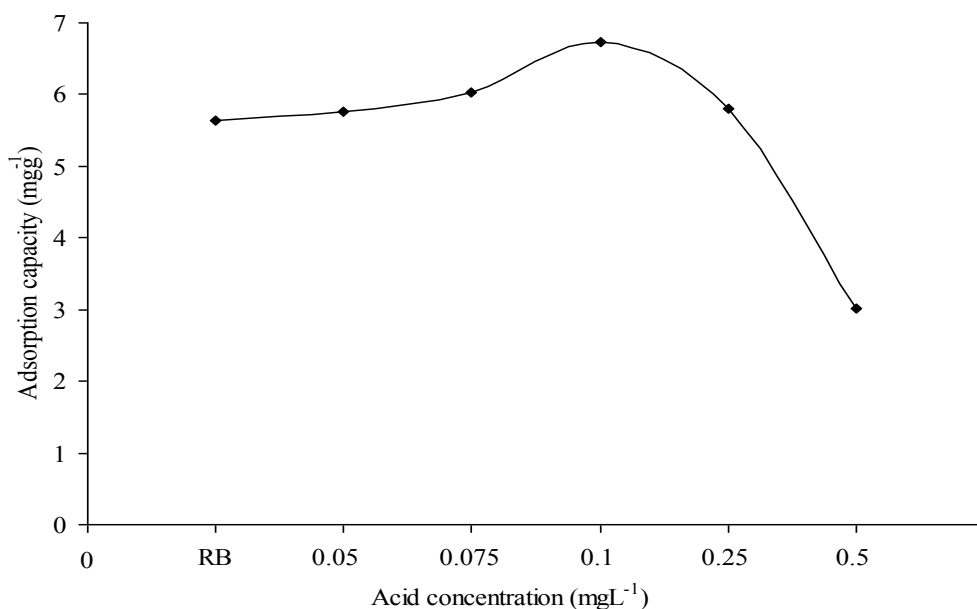


Figure 4.12 Effect of acid activation on the adsorption of CR on bentonite modified by AA at different acid concentration (initial dye concentration 100mgL^{-1} , adsorbent dosage 1g , error bar indicates standard deviation of three replicated at each acid concentration, $\text{SD} \pm 0.31$)

It is evident from Figure 4.12 that CR adsorption increased with an increase in acid concentration until 0.1M HCl. This increase in the adsorption capacity of bentonite modified by acid activation is due to an increase in surface area. Further increase in acid concentration caused excessive leaching of cations resulting in collapse of structure and decrease in surface area. Thus at higher acid concentrations there are less adsorption sites available for Congo red and therefore showed lower adsorption of Congo red.

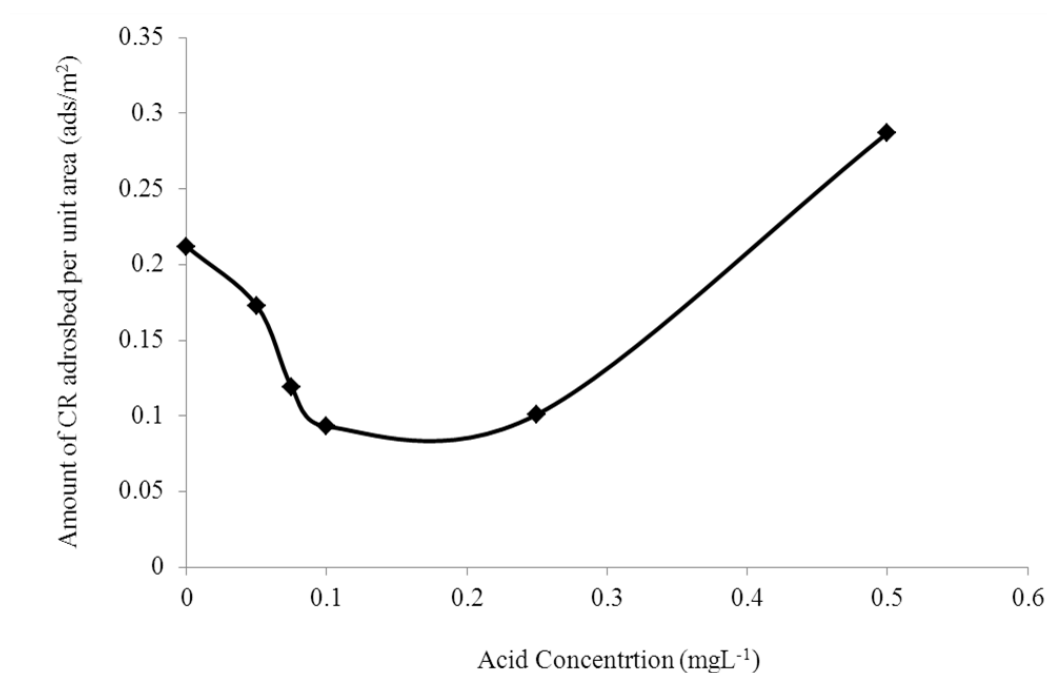


Figure 4.13 Effect of acid activation on the adsorption of Congo red on acid activated bentonite per unit area

It is evident from Figure 4.13 that as the acid concentration increases the amount of congo red adsorbed per unit area first decreases and then increases. The

adsorption of congo red per unit area decreases as the surface area increase due to available of vacant adsorption sites. However, the adsorption of congo red per unit area on bentonite modified by acid increases as the surface area decreases.

4.3.3 Effect of Activation Temperature on Adsorption of Congo Red

The acid activation of bentonite was carried out at different temperatures (30°C, 60°C and 80°C) with HCl over a concentration range from 0.05M to 0.5M to examine the effect of temperature on the adsorption properties of bentonite modified by acid activation. The adsorption of Congo red at all temperatures increased with the increase in acid concentration. However keeping the time constant the increase in activation temperature resulted in a decrease in the amount of dye adsorbed as is evident from Figure 4.14. This decrease in the amount of dye adsorbed is attributed to the deeper penetration of the acid molecules which results in the collapse of structure. At a given acid concentration, the increase in activation temperature corresponds to a shorter time required to achieve the maximum surface area. Babaki et al., (2007) have developed a relationship between the temperature and the optimum time required. They performed the acid activation of bentonite by sulfuric acid. The results revealed that as the activation temperature increased, the time required to achieve the maximum surface area decreased.

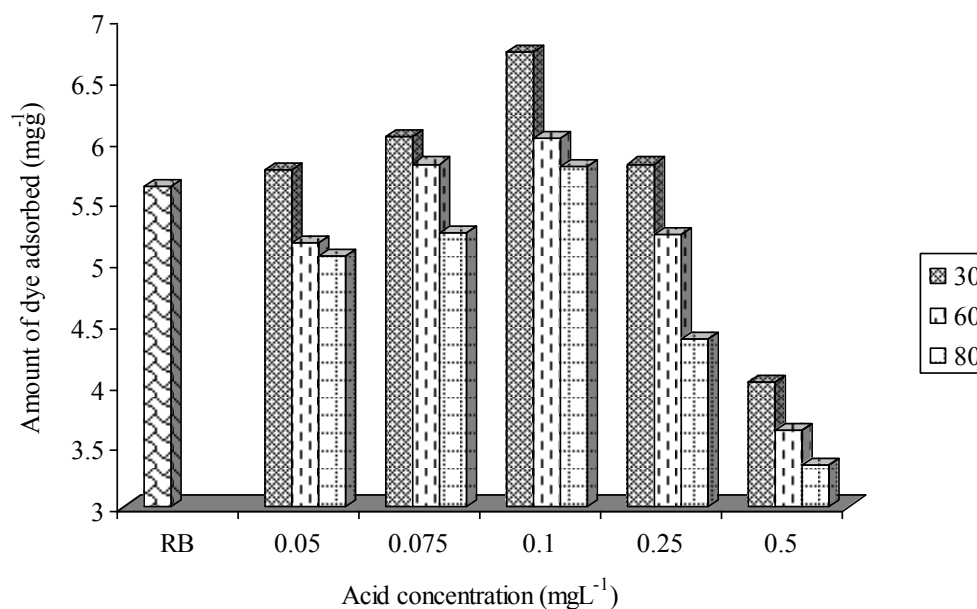


Figure 4.14 Effect of activation temperature on the adsorption capacity of bentonite modified by AA (initial dye concentration 100mgL⁻¹, adsorbent dosage 1g, error bar indicates standard deviation of three replicated at each acid concentration, SD \pm 0.064)

4.4 Acid and Thermal Activated Bentonite

4.4.1 Characterisation of Acid and Thermal Activated Bentonite

4.4.1.1 Surface Area

The surface properties of acid activated clays can be enhanced further if acid activation is followed by thermal activation (Beragaya et al., 2006). In the present study the surface area of bentonite modified by AA was recorded as 72.86m²g⁻¹ (0.1M HCl). The surface area increased to 84.12m²g⁻¹ (0.1M HCl) when acid activation was followed by thermal activation as can be seen in Figure 4.15.

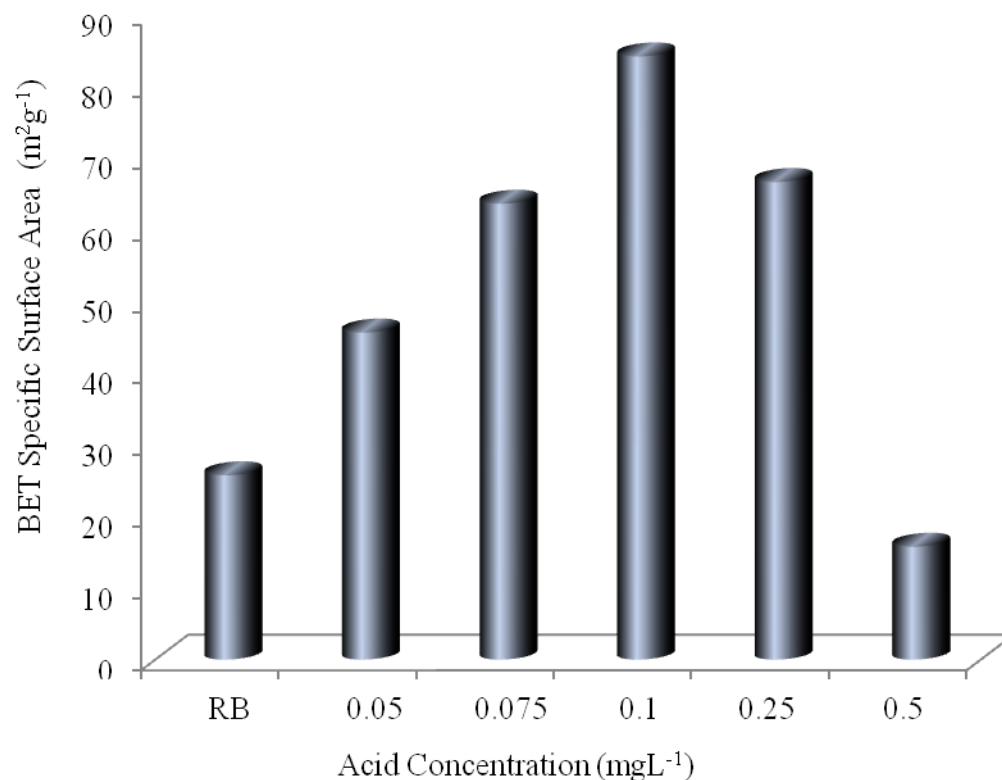


Figure 4.15 BET specific surface area of bentonite modified by ATA at different acid concentrations

The acid activation of bentonite carried out by other researchers and their corresponding increase in surface area is presented in Table 4.4. This increase in surface area is attributed to the removal of molecules that were already present in the clay and those that were attached during acid activation and washing (Bhattacharaya and Sen Gupta 2006).

Table 4.4 Surface area of various acid activated bentonites

Surface Area Raw Bentonite (m ² g ⁻¹)	Surface Area Modified Bentonite (m ² g ⁻¹)	Increase in Surface Area (%)	Acid Conc. (M)	Reference
29.23	165.8	82.37	2M HCl	Korichi et al., 2009
50	250	80	2M HCl	Christidis et al., (1997)
50	200	75	2M HCl	Christidis et al., (1997)
52	184	71.74	2M HCl	Jovanavić and Jonačković, (1991)
25.7	84.12	69.45	0.1M HCl	<i>Present study</i>
~80	240.9	66.79	2M H ₂ SO ₄	Yildiz et al., 2004
71.95	109.8	34.47	5N HCl	Koyuncu (2008)
52	76	31.58	0.5M HCl	Jovanavić and Jonačković, (1991)

4.4.1.2 Pore Size

The pore size analysis of acid and thermal activated bentonite has been carried out to understand the variation in pore size of raw bentonite on modification with acid and thermal activation. The measured average pore size values are listed in Table 4.5. The analyses revealed that the pore size first decreased with increase in acid concentration and then increased with increase in acid concentration. The mechanism of change in pore size is similar to that of acid activation. However,

an additional step of thermal activation removed the adsorbed and hydrated water. This mechanism creates new pores and provides more adsorption sites facilitating higher adsorption of dyes on modified bentonite. The average pore size of the ATB (0.1M HCl) is 38.916Å indicating mesopore region.

Table 4.5: BET specific surface area and the average pore size of ATA bentonite

Acid Conc.	BET Surface Area (m ² g ⁻¹)	Pore Width (Å)
RB	25.70 ± 0.18	50.28 ± 0.04
0.05	45.61 ± 0.06	48.57 ± 0.15
0.075	63.58 ± 0.01	46.63 ± 0.07
0.1	84.12 ± 0.14	38.92 ± 0.09
0.25	66.61 ± 0.07	44.12 ± 0.12
0.5	15.73 ± 0.28	56.13 ± 0.31

4.4.1.3 Effect of Acid Attack on Bentonite

Figure 4.16 shows the FTIR spectra for raw bentonite and bentonite modified by ATA at different acid concentrations. The FTIR spectra of bentonite modified by ATA is similar to AB as discussed in section 4.3.1.2 with a significant decrease in peaks at 3617.3cm⁻¹ (Al-OH-Al alongwith the Al-Mg-OH stretching vibrations). The decrease in the intensity of peaks has also been observed in the bands associated with the adsorbed water at 3405.7 (H-O-H stretching) and 1634.6 cm⁻¹

(H-O-H bending) due to loss of adsorbed water at high temperatures. The peak of Si-O-Si band at 988.1 cm^{-1} remains unchanged with the intensity of treatment.

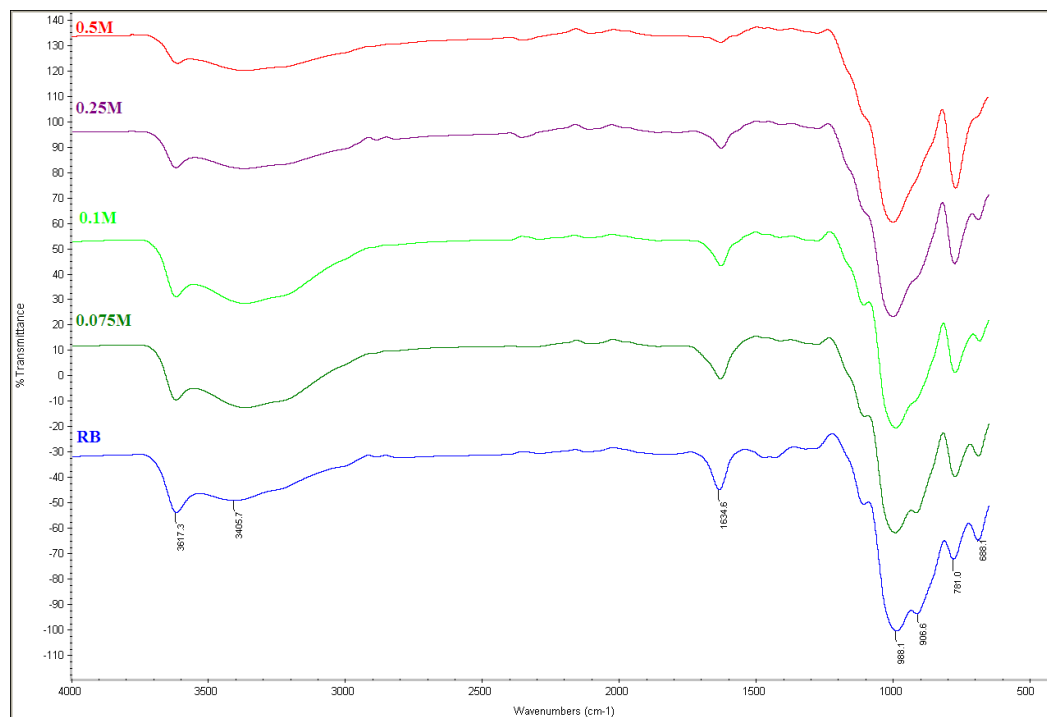


Figure 4.16 FTIR spectra of RB and bentonite modified by ATA at different acid concentrations

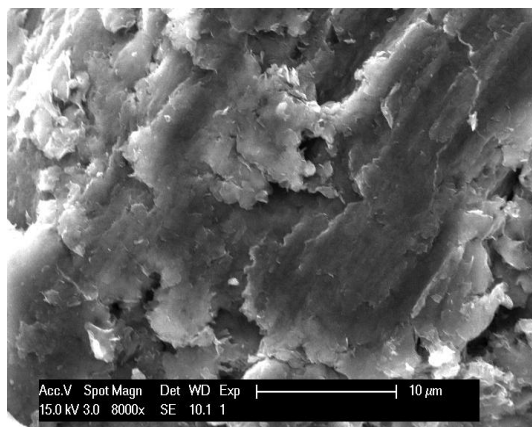
The bands at 906.6 cm^{-1} disappeared with the increase in acid strength due to the increased substitution of aluminium ions by iron ions. The transformation of the tetrahedral sheet has been observed at 781 cm^{-1} . The acid activation leads to the formation amorphous silica, indicated by the increased intensity of the peak, which may be exposing more adsorption sites (Komandel et al 1990). The intensity of band at 688.1 cm^{-1} (Al-OH-Si bending) decreased with the increase in

acid concentration signifying the partial dissolution of aluminum ions present in the octahedral sheet of bentonite.

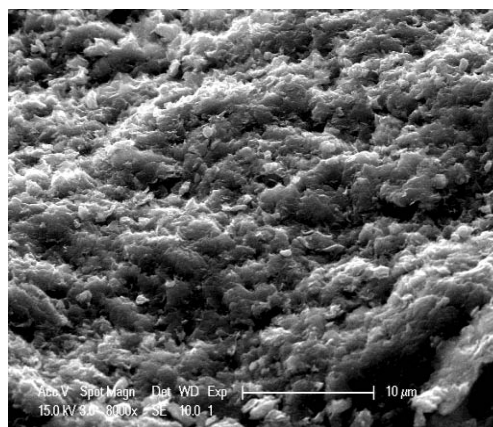
4.4.1.4 Surface Morphology

The surface morphology of the modified bentonite was analysed by scanning electron microscopy (SEM) to evaluate the effect of acid and thermal activation on raw bentonite. Figure 4.17 show that the surface morphology of raw bentonite has undertaken significant changes on acid and thermal activation. The edges of the platelets are first to be exposed to acid attack. The formation of smaller pores takes place as the impurities are removed and the exchangeable cations are replaced by H^+ ions. These physio-chemical reactions alter the morphology of the clay as the pores open up and the clay surface appears to be more porous and homogeneous. The SEM images reveal that after the thermal activation of acid activated bentonite at 0.075M HCl the clay has become more porous.

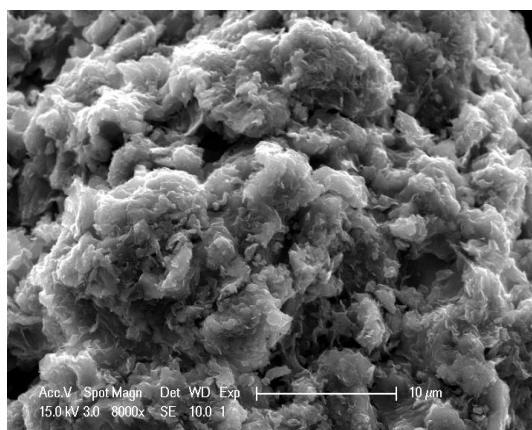
Further increase in severity of acid treatment that is the bentonite modified by 0.1M HCl followed by thermal activation exhibit highly porous structure. This was also evident from the increase in surface area. The acid activation followed by thermal activation provides more porous clay than the acid activated clay due to the removal of any water that was already present in the clay and that was adsorbed during washing of acid activated clay.



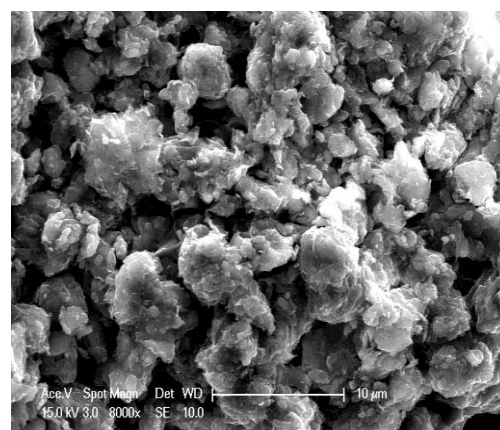
(a) Raw Bentonite



(b) 0.075M HCl



(c) 0.1M HCl



(d) 0.075M HCl

Figure 4.17 SEM images of bentonite modified by ATA at different acid concentrations

4.4.2 Adsorption of Congo Red on Bentonite Modified by Acid and Thermal Activations

The adsorption of CR with initial concentration of 100 mgL^{-1} on ATA bentonite was analyzed to evaluate the effect of acid and thermal activation on the adsorption capability of bentonite. The CR adsorption on ATA bentonite

increased with the increase in severity of acid treatment. Adsorption profile results are shown in Figure 4.18.

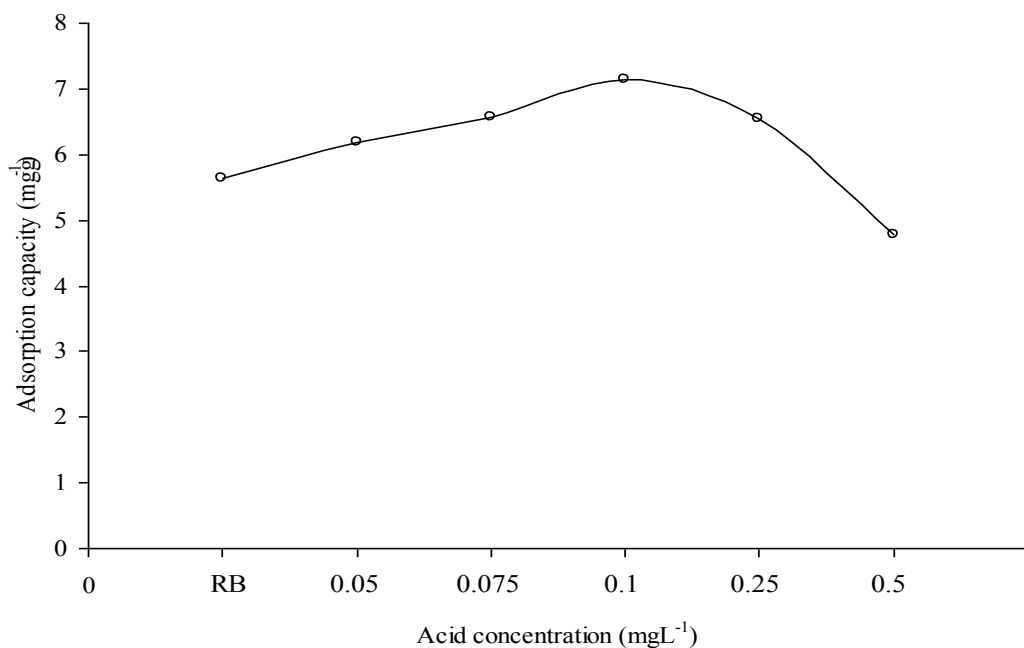


Figure 4.18 Effect of modification of bentonite by ATA on adsorption of Congo red (initial dye concentration 100mgL⁻¹, adsorbent dosage 1g, error bar indicates standard deviation of three replicated at each temperature, SD \pm 0.22)

The increase in CR adsorption is due to increase in surface area and availability of additional adsorption sites. The maximum amount of Congo red was adsorbed on 0.1M HCl activated bentonite. The increase in acid concentration beyond 0.1M HCl results in excessive leaching of cations and the collapse of interlayer spaces. The surface area of bentonite modified by acid activation beyond 0.1M HCl

followed by thermal activation decreased, affecting the adsorption capacity of ATA bentonite. Therefore, CR adsorption on the ATA bentonite beyond 0.1M HCl decreased.

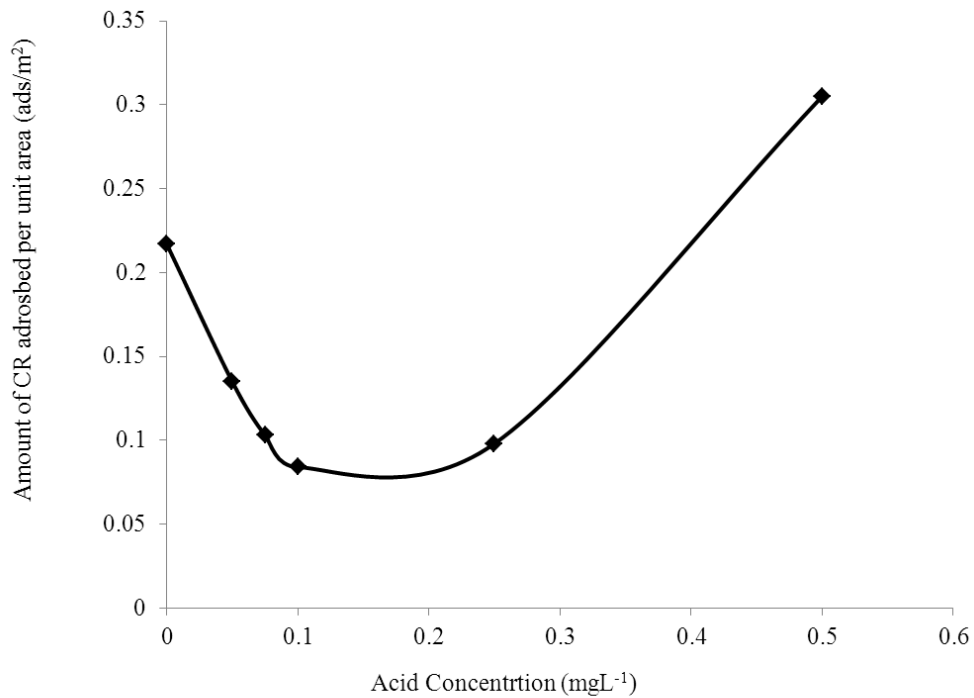


Figure 4.19 Effect of modification of bentonite acid and thermal methods on the adsorption of congo red on modified bentonite per unit area

The adsorption of congo red on modified bentonite per unit area in Figure 4.19 shows a similar variation as shown by bentonite modified by thermal or acid treatment. The adsorption per unit area first decreases with increase in acid concentration due to increase in surface area and availability of large number of

adsorption sites. As the severity on acid treatment increased the surface area decreased thereby showing higher adsorption of congo red per unit area.

4.5 Comparison of Adsorption Efficiency of Modified Bentonites

Table 4.6 provides the comparison of modification parameters, changes in surface properties and the adsorption capacities of raw bentonite and bentonite modified by TA, AA and ATA. The comparison of the adsorption efficiencies of the bentonite modified by TA, AA and ATA reveals that the CR adsorption follows the order shown below.

$$ATA > AA > TA > RB$$

Table 4.6 Comparison of modified bentonites

	ATA	AA	TA	RB
Acid Conc.	0.1M HCl	0.1M HCl		
Temperature for AA	30 ⁰ C	30 ⁰ C		
Temperature	100 ⁰ C <i>(thermal activation)</i>		100 ⁰ C	
Treatment Time	3h 20min	3h	20min	
Surface Area (m ² g ⁻¹)	84.12	72.86	33.15	25.70
Pore Width (Å)	38.92	40.08	41.12	50.28
Adsorption Capacity (mgg ⁻¹)	7.13	6.83	6.61	5.63

The maximum adsorption of Congo red was achieved on acid and thermal activated bentonite as is depicted in Figure 4.20. The maximal adsorption is attributed to the highest surface area among all the activated samples. The adsorption capacity of bentonite modified by ATA increased with an increase in acid concentration. However, the improved adsorption capacity in comparison to bentonite modified by AA is due to the removal of hydrated and adsorbed water that was already present in the clay and that attached during the washing of acid activated bentonite.

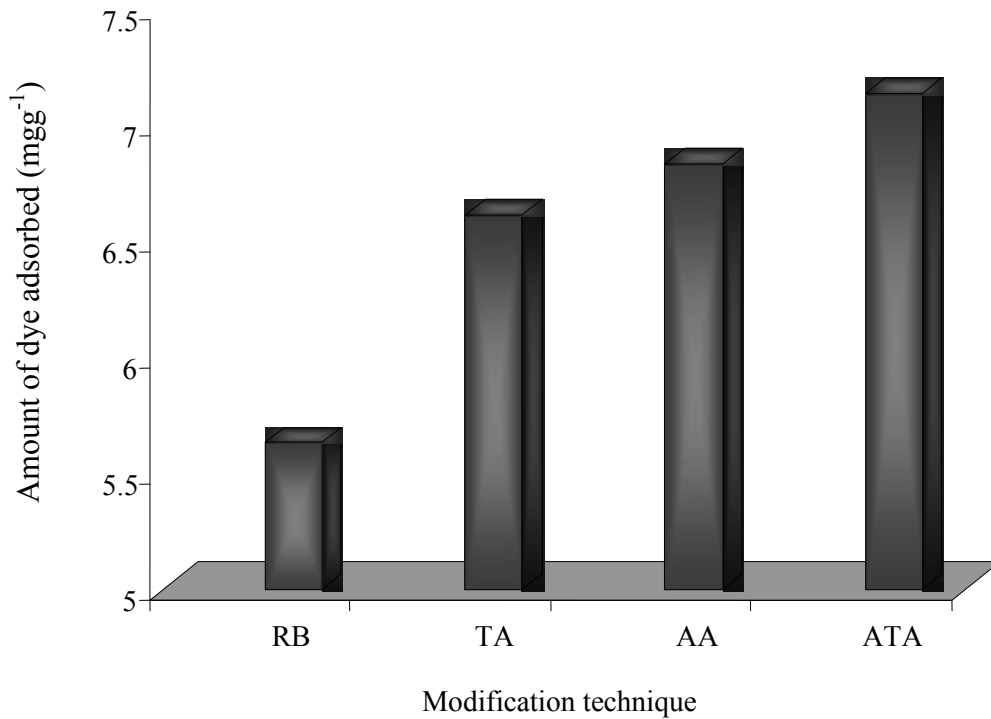


Figure 4.20 Effect of modification technique on the adsorption capacity of bentonite

4.6 Conclusions

The modification of Australian sodium bentonite was carried out by thermal activation, acid activation and combined acid and thermal activation processes. The results reveal that thermal activation of bentonite (TA) at 100⁰C for 20 min exhibited more than 20% increase in surface area. However an increase in activation temperature beyond 100⁰C expressed a decrease in surface area due to degeneration of the crystal structure.

Acid activation of bentonite indicated that surface area of raw bentonite increased with an increase in acid concentration up to 0.1M HCl due to removal of impurities and opening up of closed pores. Further increase in acid concentration caused excessive leaching of cations leading to collapse of interlayer spaces causing a drop in surface area. A maximum of about 65% increase in surface area is observed.

The activation of bentonite with a combined acid and thermal activation (ATA) demonstrated that if acid activation is followed by thermal activation the surface area can be enhanced significantly. The surface area of bentonite modified by AA was improved by roughly 15% on thermal activation. Overall ~70% increase in surface area was observed for bentonite modified by ATA in comparison to RB. The adsorption capacity of raw bentonite was also enhanced on activation and

followed the order: ATA > AA > TA > RB. The overall adsorption capability of bentonite modified by ATA was augmented by more than 20%.

From the experimental results of the current study it is evident that bentonite modified by ATA (0.1M HCl) for 3h followed by thermal activation at 100⁰C can significantly enhance the surface and adsorption properties of raw bentonite. The bentonite is a widely available and abundant natural mineral, and can be a low cost adsorbent for water and wastewater treatment. Results from this study revealed that the activation of bentonite with acid at a lower concentration of 0.1M HCl and thermal activation at relatively low temperature could be a cost-effective modification method to enhance adsorption capacity and applicability of bentonite.

CHAPTER 5

ADSORPTION PERFORMANCE AND KINETICS OF MODIFIED BENTONITE

5.1 Introduction

The effluent discharged by textile industries contains large amounts of dyes which are high in color and presence of even very small amount of dye is highly visible and can be very toxic. The synthetic dyes are generally non-biodegradable and difficult to remove, thus affect the human and the aquatic life (Bulut et al., 2008). Various physical, chemical and biological methods have been employed for the treatment of dyes, including coagulation, flocculation, precipitation (Pandit and Basu, 2002), ozonation (Khadhraoui et al., 2009), oxidation (Jagatap and Ramaswamy, 2006), photocatalysis (Kabra et al., 2004), and ultrasound irradiation (Song et al., 2009). All these methods have some drawbacks, such as high operating cost, sludge production and complexity of the treatment processes. Adsorption is a widely used technique for the removal of dyes due to economical and environmentally friendly reasons (Jiuhui, 2008). The cost of removal of dyes by adsorption lies mainly in the cost of adsorbent and regeneration of adsorbent. Activated carbon is the most widely used adsorbent due to its high surface area and adsorption capacity, but the use of activated carbon is becoming restricted

due to its high cost and regeneration difficulties. Many low-cost adsorbents are developed worldwide to replace activated carbon. Generally these low-cost adsorbents have a small surface area and a low adsorption capacity. Previous studies stated that the adsorption capability of the adsorbents can be enhanced by modification of these adsorbents via physical and chemical processes. Clays are one of the most widely used low-cost adsorbent due to its availability in abundance and excellent adsorption capacity. Among clay minerals, bentonite is one of the most extensively used adsorbent.

Modification of bentonite is vital for the adsorption of anionic dyes, as the net negative charge on the dye and clay surface provoke charge repulsion and thus, resulting in a lower degree of interaction/adsorption (Özcan et al., 2004). Thermal activation, acid activation and combined acid and thermal activation are some of the mostly applied modification methods. The effect of these modifications on the surface properties of bentonite was discussed in detail in Chapter 4. This chapter focuses on the analysis of the effect of operating parameters, such as initial dye concentration, adsorbent dosage, contact time and temperature, on the removal of Congo red using modified bentonites. The adsorption data will be evaluated by fitting with Langmuir and Freundlich adsorption isotherms. The pseudo-first order and pseudo-second order kinetics model will be investigated to understand the kinetics of adsorption. The mechanism of adsorption is analyzed by intra particle diffusion model.

Results and Discussion

5.2 Effect of Contact Time

The effect of contact time on the amount of Congo red adsorbed on bentonite modified by ATA, AA and TA has been experimentally investigated in CR solution at 100mgL^{-1} initial dye concentration.

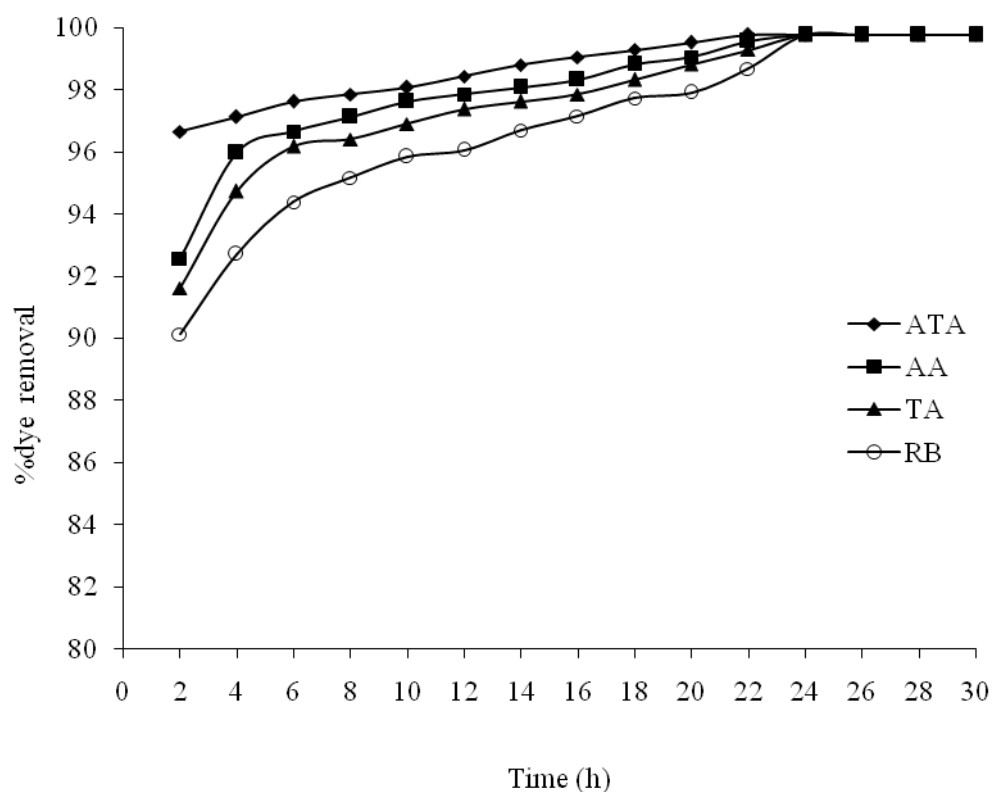


Figure 5.1 Effect of contact time on adsorption of Congo red (initial dye concentration 100mgL^{-1} , adsorbent dosage 1g, error bar indicates standard deviation of three replicated at each temperature, $\text{SD} \pm 0.11, 0.42, 0.26, 0.61$ for bentonite modified by ATA, AA, TA, and raw bentonite, respectively)

It has been observed that the CR adsorption increased with an increase in contact time. Figure 5.1 shows that nearly 100% of dye removal was attained in 22h for the bentonite modified by ATA and 24h for the bentonite modified by AA and TA. The adsorption rate was very high during early adsorption period. A CR removal of 96.65%, 92.75% and 91.62% was obtained within first 2h using the bentonite modified by ATA, AA and TA, respectively. The relatively high removal of dye initially is attributed to the availability of 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.

5.3 Effect of Initial Dye Concentration

The effect of initial dye concentration on the CR adsorption on raw bentonite and the bentonite modified by ATA, AA and TA was examined over a concentration range from 100mgL^{-1} to 1000mgL^{-1} . Figure 5.2 shows, that initial CR concentration plays a vital role in the uptake of dye by the adsorbents. The CR adsorption on all the bentonite samples increased with an increase in initial dye concentration. The maximum adsorption of 68.07mgg^{-1} for 1000mgL^{-1} of initial CR was obtained by the bentonite modified by ATA. The CR adsorption capacity by modified bentonites appeared to follow an order as:

$$\text{ATA} > \text{AA} > \text{TA} > \text{RB}$$

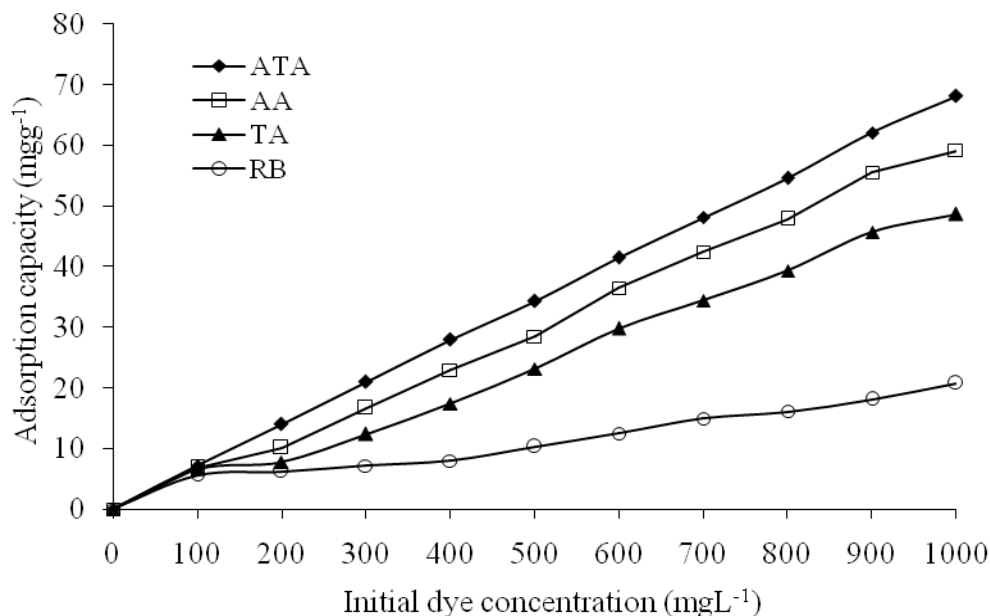


Figure 5.2 Effect of initial dye concentration on CR adsorption (adsorbent dosage 1g, error bar indicates standard deviation of three replicated at each temperature, SD \pm 0.09, 0.23, 0.03, 0.19 for bentonite modified by ATA, AA, TA and raw bentonite, respectively)

The increase in adsorption with the increase in CR concentration is due to the driving force that initial concentration provides to overcome the mass transfer resistance between the aqueous and solid phases. The adsorption rate was high at early adsorption period due to availability of large number of vacant site which increased the concentration gradient between the adsorbate in the solution and adsorbate on the adsorbent surface (Zohra et al., 2008). As the CR adsorption on all of the bentonite samples is increasing with increase in acid concentration suggesting that there is no formation of monolayer on the surface of the adsorbents. The steady increase in the adsorption with the increase in initial dye

concentration indicates that the adsorbents have very high potential for the removal of Congo red. Gonzalez –Pradas et al (1997) have reported similar results for the adsorption of atrazine on acid activated bentonite.

5.4 Effect of Adsorbent Dosage

The effect of amount of adsorbent ranging from 2gL^{-1} to 20gL^{-1} on dye removal was investigated in bottle tests using initial CR concentration of 100mgL^{-1} . The results are shown in Figure 5.3.

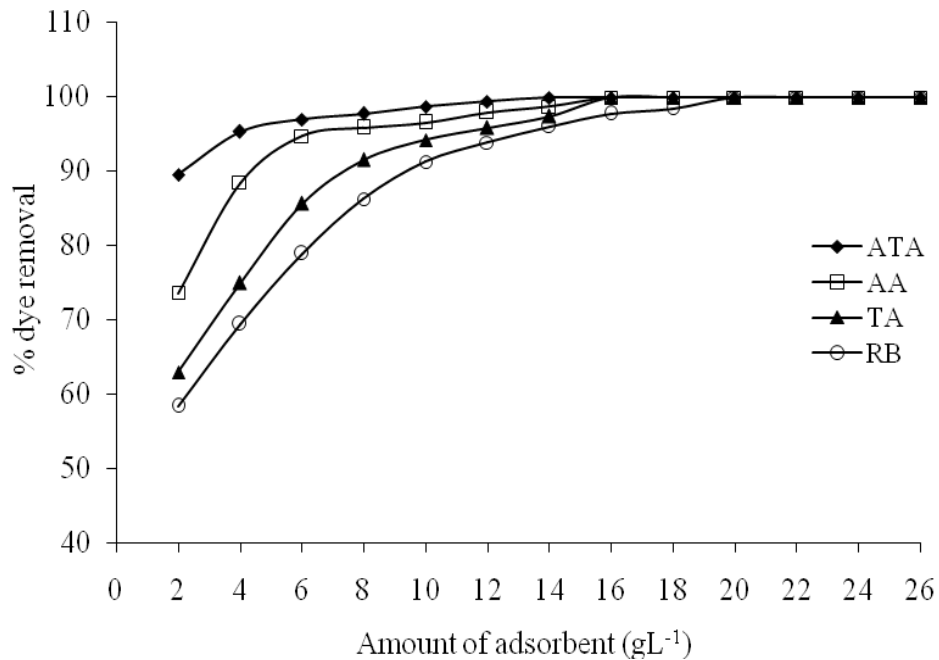


Figure 5.3 Effect of adsorbent dosage on the removal of Congo red (initial dye concentration 100mgL^{-1} , error bar indicates standard deviation of three replicated at each temperature, $\text{SD} \pm 0.37, 0.04, 0.18, 0.14$ for ATA, AA, TA and raw bentonite, respectively)

The percentage of CR removal by bentonite modified by ATA increased as the adsorbent dosage increased, which varied from 90% to nearly 100%. The CR adsorption increased gradually upto 14 gL^{-1} of clay dosage. A further increase in bentonite dosage beyond 14 gL^{-1} exhibited no extra improvement in dye removal due to attainment of equilibrium between the adsorbate and adsorbent (Chaari et al., 2008) under the current experimental condition. Thus, the adsorbent dosage was set to 14 gL^{-1} for the following experiments.

Compared to the bentonite modified by ATA, an equilibrium adsorption appeared to be achieved upto 16 gL^{-1} when the bentonite was modified by AA and TA. The percentage of CR removal with the increase in adsorbent dosage for the bentonite modified by AA and TA increased from 74% and 63%, respectively, to nearly 100%. The adsorption increased from 58% and nearly 100% removal of CR was achieved by 20g of bentonite for 1L of solution. The increase in CR adsorption with the increase in adsorbent dosage is attributed to increase in surface area of micropores and the increase in availability of vacant adsorption sites (Khenifi et al., 2007).

5.5 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 acids 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. The change of color is due to the resonance between charged canonical structures (Beragaya et al., 2006). The chemical structure of bentonite varies with the variation in pH. The natural bentonite is basic in nature and bears a net negative charge on its surface as the pH reduces in the presence of inorganic acids. The transformation in the clay structure takes place, building up net positive charge on the clay surface. The influence of pH on the CR adsorption was studied by varying the initial pH values of CR solution from 3 to 11. The results are shown in Figure 5.4, in which adsorption conditions were set up at an agitation speed of 150rpm, temperature 30°C and initial dye concentration 100mgL⁻¹ for 24h.

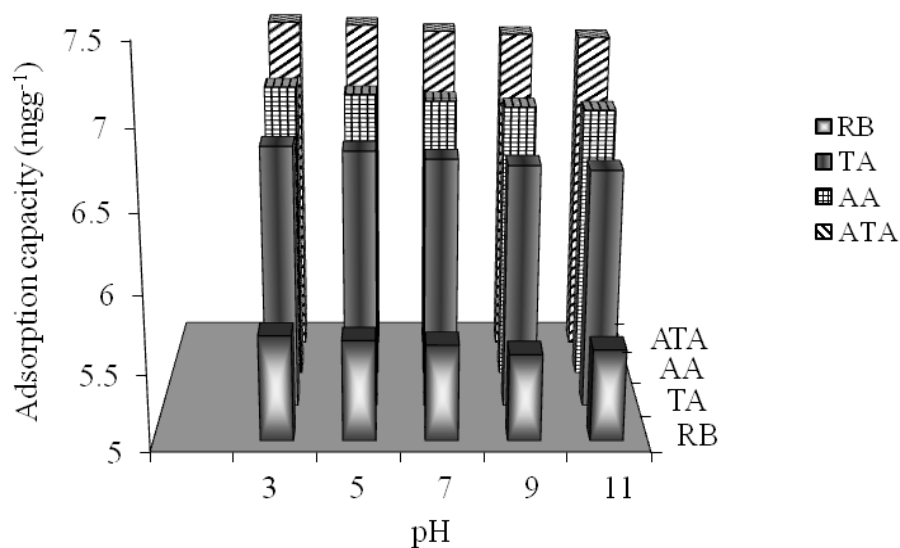


Figure 5.4 Effect of pH on the adsorption of Congo red (initial dye concentration 100mgL⁻¹, error bar indicates standard deviation of three replicated at each temperature, SD ± 0.008, 0.02, 0.02, 0.04 for ATA, AA, TA and RB respectively)

The pH changes appeared to have little impact on the CR adsorption performance by the bentonite modified by AA. Only slight decrease in the amount of dye adsorbed was found as the pH increased. This slight decrease in CR adsorption may be attributed to the repulsion between the anionic dye molecules and negatively charged clay particles (Acemioğlu et al., 2004). The results reveal that the effect of pH on the adsorption of CR is not significant. This may be due to the alkaline nature of bentonite that neutralizes the acidic pH of the CR solution.

5.6 Effect of Temperature

The effect of temperature on the CR adsorption on raw bentonite and bentonite modified by ATA, AA and TA was investigated using initial dye concentration of 100mgL^{-1} at 25, 30, 40, 50 and 60°C . The Gibbs energy, ΔG^0 , is calculated from the given equations:

$$\Delta G^0 = \Delta H^0 - T \Delta S^0$$

$$\Delta G^0 = -RT \ln K_c$$

K_c represents the ability of the adsorbent to retain the adsorbate and extent of movement of the adsorbate within the solution (Lian et al., 2009). The value of K_c can be deduced from

$$K_c = \frac{q_e}{C_e}$$

where q_e is the equilibrium concentration of dye adsorbed and C_e is the equilibrium concentration of dye in the solution.

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

The values of ΔH^0 and ΔS^0 can be obtained from the slope and intercept of a linear plot between $\ln K_c$ and $1/T$. A slight decrease in the CR adsorption on bentonite modified by ATA, AA and TA was observed with an increase in temperature, as shown in Figure 5.5. This decrease in CR adsorption indicates that preferential adsorption may occur at a low temperature.

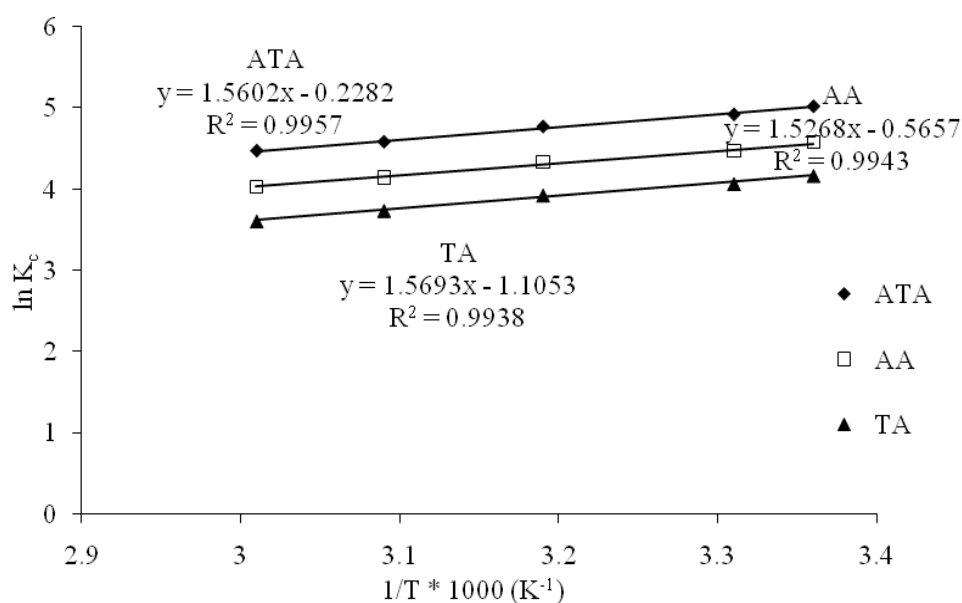


Figure 5.5 Effect of temperature on CR adsorption (initial dye concentration 100mgL^{-1} , error bar indicates standard deviation of three replicated at each temperature, SD $\pm 0.07, 0.01, 0.03, 0.16$ for ATA, AA, TA and RB respectively)

The enthalpy of bentonite modified by ATA is higher than bentonite modified by AA indicating that the dye molecules are held more strongly by bentonite

modified by ATA. The negative values of enthalpy indicate that the process is exothermic. The change in enthalpy lies between -20 to 40kJmol⁻¹ confirming physisorption. At higher values from -400 to -80kJmol⁻¹ chemisorption becomes predominant (Lian et al., 2009). Similar results have been reported by Vimonses et al (2009) and Chatterjee et al. (2007). They stated that the decrease in adsorption with increasing temperature is a result of poor interaction between the dye and bentonite as hydrogen bonds and Van der Waals interaction are not strong. The thermodynamic parameters for CR adsorption on bentonite modified by ATA, AA and TA are recorded in Table 5.1. The spontaneity and feasibility of the adsorption process is indicated by the negative values of Gibbs energy.

Table 5.1 Thermodynamic parameters for CR adsorption on modified bentonite at different temperatures

Adsorbent	ΔG° (kJmol ⁻¹)					ΔH° (kJmol ⁻¹)	ΔS° (Jmol ⁻¹ K ⁻¹)
	25°C	30°C	40°C	50°C	60°C		
ATA	-12.437	-12.394	-12.413	-12.299	-12.375	-12.97	-1.89
AA	-11.323	-11.260	-11.267	-11.117	-11.157	-12.69	-4.71
TA	-10.331	-10.253	-10.227	-10.043	-10.049	-13.05	-9.18

The negative values of entropy indicate the decrease in the randomness at the adsorbent and solution interface. This further indicates that CR adsorption onto bentonite modified by ATA, AA and TA does not result in any noticeable changes

in the internal structure of the adsorbent. These results are comparable to those reported by Özcan et al., 2004 for the adsorption of AR57 on acid activated bentonite. The decrease in entropy implies the positive affinity of the adsorbents towards the CR adsorption (Bhattacharyya and Gupta, 2006).

5.7 Adsorption Isotherms

The mechanism of adsorption could be determined by evaluating the equilibrium data also known as adsorption data obtained from the experiments. An equilibrium relationship between the amounts of dye adsorbed on the surface of an adsorbent could be established through adsorption isotherms (Bulut et al., 2008). In the present study, both Langmuir and Freundlich isotherm models have been used to examine the adsorption data.

5.7.1 Langmuir Isotherm

The basic assumption of Langmuir model is that the formation of monolayer takes place on the surface of the adsorbent indicating that only one dye molecule could be adsorbed on one adsorption site and the intermolecular forces decrease with the distance. It is also assumed that the adsorbent surfaces is homogeneous in character and possess identical and energetically equivalent adsorption sites. The Langmuir model is given by the following equation;

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}$$

where C_e is the equilibrium concentration of the dye (mgL^{-1}), q_e is the amount of dye adsorbed per unit of bentonite (mg), q_m the Langmuir constant for adsorption capacity (mgg^{-1}) and K_L is the Langmuir constant for energy of adsorption (Lg^{-1}). The values of q_m and K_L can be obtained from Figure 5.6 from the slopes and intercept of the linear plot of C_e/q_e versus C_e and are listed in the Table 5.2 along with the values of R^2 .

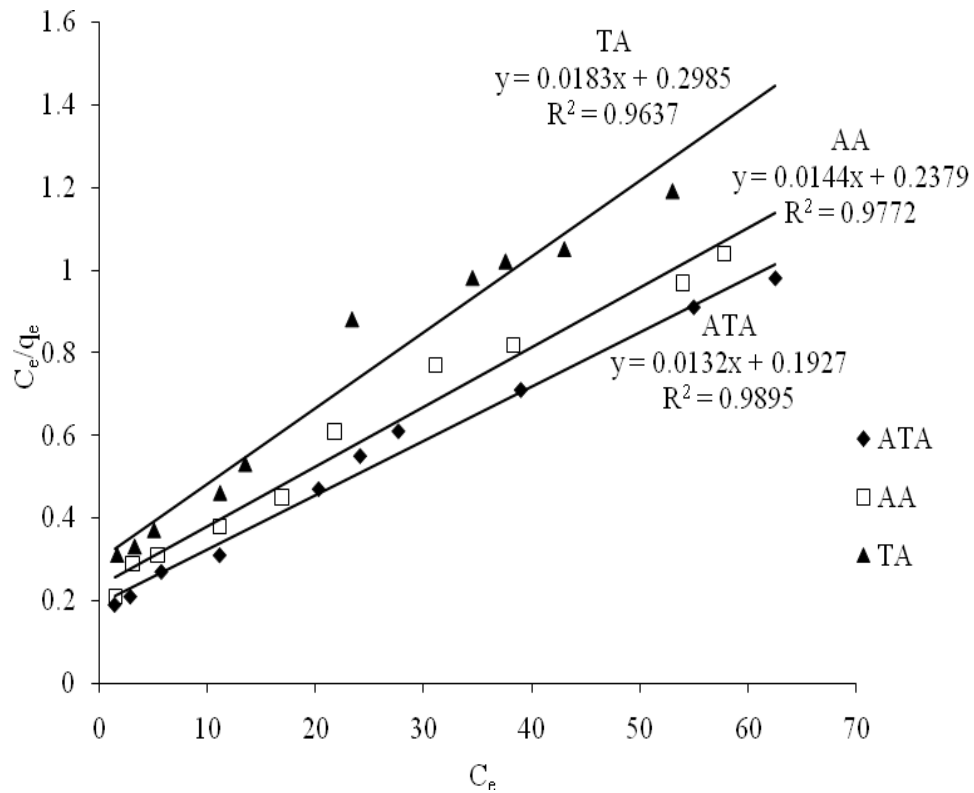


Figure 5.6 Langmuir adsorption isotherms for CR adsorption (linear)

The isotherm is linear over the entire concentration range and shows a reasonable fit to the adsorption data.

Table 5.2 Langmuir adsorption isotherm constants

Adsorbent	q_m	K_L	R^2	χ^2
ATA	75.75	0.068	0.98	4.56
AA	69.44	0.060	0.97	3.74
TA	54.64	0.061	0.96	4.71

The favourability and feasibility of adsorption process can be determined by the separation factor R_L in the analysis of data by Langmuir isotherm. It is given by the following equation.

$$R_L = \frac{1}{1 + K_L C_i}$$

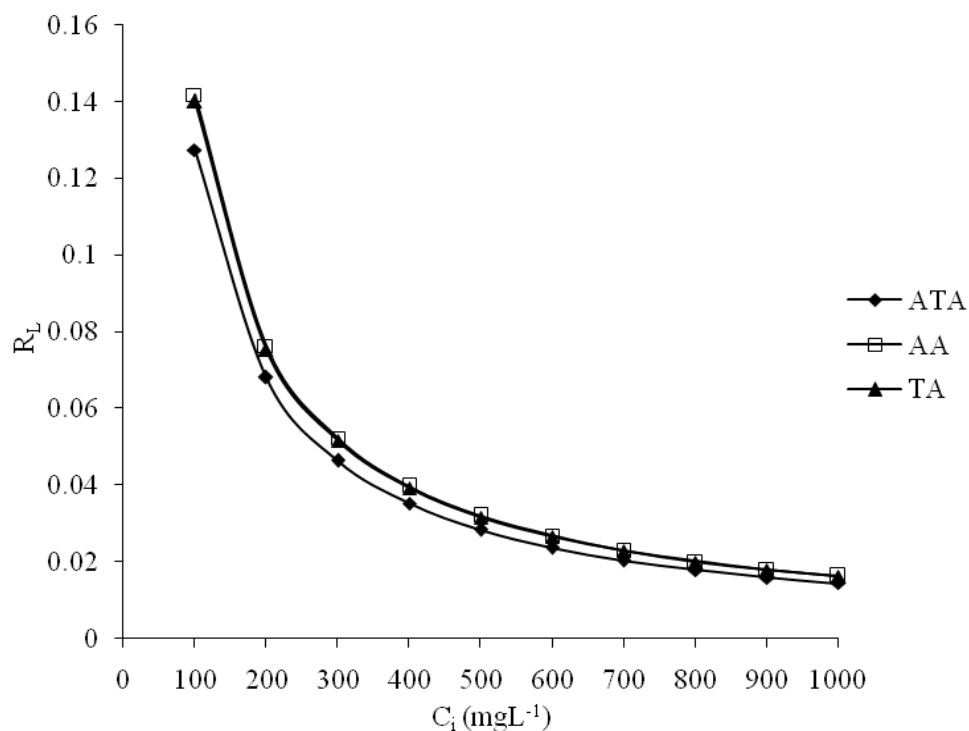


Figure 5.7 Plot of separation factor versus initial dye concentration

The shape of the isotherm depends on the value of R_L as follows: The isotherm is unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or reversible ($R_L = 0$). In the present study the value of R_L in all the cases lies between 0 and 1 indicating that CR adsorption modified bentonites is favourable. Figure 5.7 demonstrates the change in separation factor with initial dye concentration for various adsorbents.

5.7.2 Freundlich Isotherm

The Freundlich model is applicable to heterogeneous systems and it involves the formation of multilayers. The Freundlich adsorption isotherm is given by:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e$$

where k_f and n are the Freundlich constants and represent the adsorption capacity and measure of heterogeneity, respectively.

The values of k_f and n can be obtained from the slope and intercept of linear plot of q_e versus C_e (Figure 5.8) and the values are given in Table 5.3. The favourability 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 favourable.

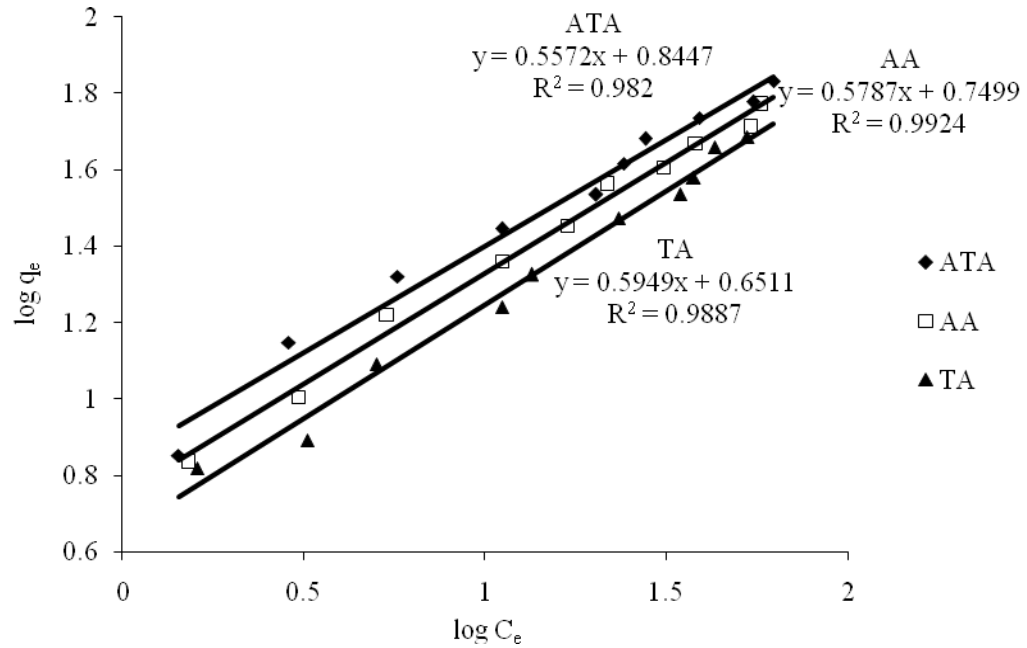


Figure 5.8 Freundlich adsorption isotherms for CR adsorption (linear)

Table 5.3 Freundlich adsorption isotherm constants

Adsorbent	k_f	n	R^2	χ^2
ATA	6.99	1.79	0.9820	1.87
TA	5.62	1.73	0.9924	1.02
TA	4.48	1.68	0.9887	0.89

The comparison of the values of correlation coefficient R^2 from Table 5.4 indicates that Freundlich isotherm model yields a better fit to the experimental adsorption data than Langmuir adsorption isotherm. This indicates that the surface of bentonite is heterogeneous in character.

Table 5.4 Comparison of correlation coefficients of Langmuir and Freundlich Models

Adsorbent	Langmuir Model R ²	Freundlich Model R ²
ATA	0.9895	0.9820
AA	0.9772	0.9924
TA	0.9637	0.9887

The evaluation of adsorption data from the linear form model as calculated above sometimes does not provide the satisfactory results as the linear equations may provide multilinear plots. Therefore, to overcome this limitation the adsorption data has also been evaluated by non-linear equation as given below:

5.7.3 Non-linear Langmuir Adsorption Isotherm Model

The non-linear expression of Langmuir adsorption isotherm was given by the following equation

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

The non-linear Langmuir adsorption isotherm is presented in Figure 5.9. The calculated values of q_e are not in agreement with the experimental values. This is further confirmed by lower values of correlation coefficient R² recorded in Table

5.4 suggesting that Langmuir adsorption isotherm does not provide a satisfactory fit to the experimental data for CR adsorption.

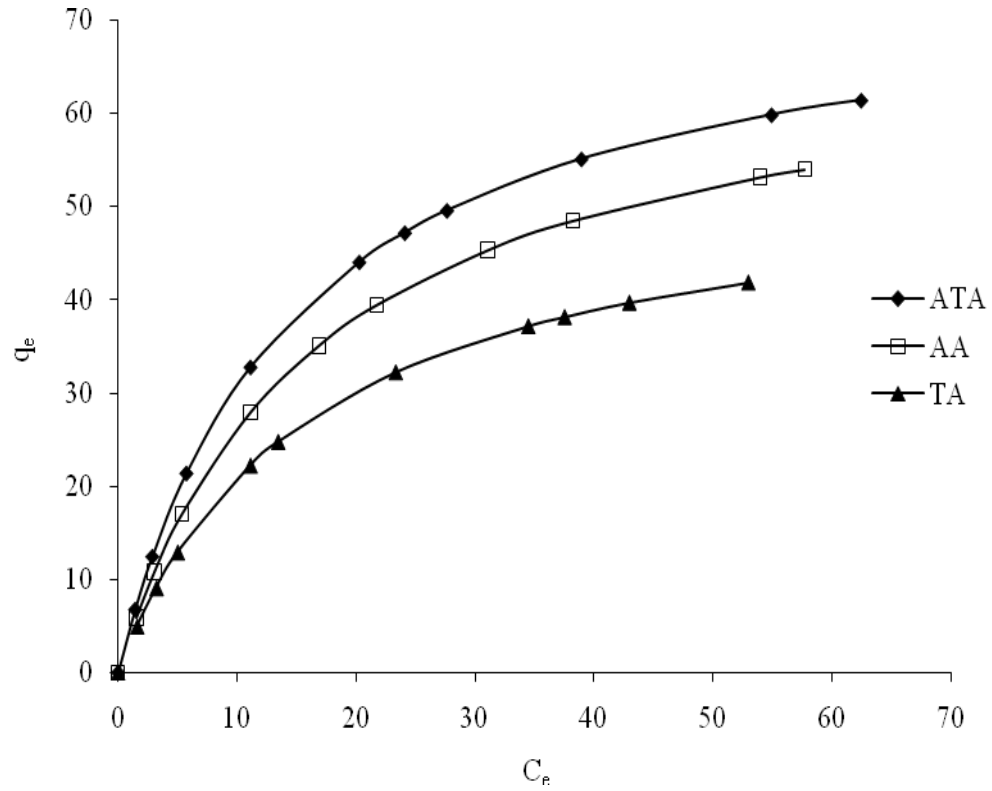


Figure 5.9 Langmuir adsorption isotherms (non-linear)

5.7.4 *Non-linear Freundlich Adsorption Isotherm Model*

The non-linear form of Freundlich adsorption isotherm is represented by the following equation

$$q_e = k_f C_e^{1/n}$$

To test the fit of Freundlich model to equilibrium data and to verify the results obtained from the linear expression, the non-linear calculations were made. Figure 5.10 shows the non-linear plot of Freundlich model.

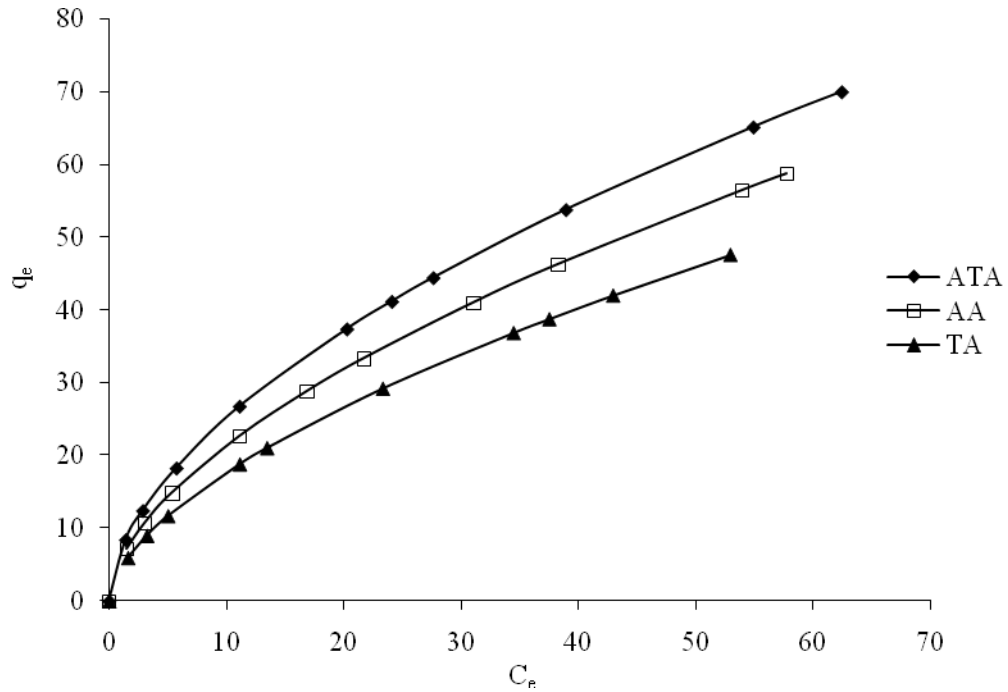


Figure 5.10 Freundlich adsorption isotherms (non-linear)

The Freundlich model in both linear and non-linear form yields a better fit to experimental data. The high values of correlation coefficient R^2 suggest the applicability of Freundlich model to the adsorption process.

Furthermore, to prevent the any errors in results obtained from the linearisation of models the chi-square error function was calculated. Chi-square (χ^2) is the sum of squares of differences between the experimental data and data predicted by the

models, with each squared difference divided by the corresponding data obtained by calculating from models (Ho et al., 2004).

$$\chi^2 = \sum \left[\frac{(q_e - q_m)^2}{q_m} \right]$$

The calculated values χ^2 recorded in Tables 5.2 and 5.3 reveal that the Freundlich model provides a better fit to the experimental data as indicated by the values of χ^2 . The χ^2 values of Langmuir model are relatively large making it unfit for the given experimental data. These results are analogous to those obtained from the linear expressions of the models. All these results suggest that there is no formation of the monolayer of Congo red on the adsorbent surface.

5.8 Adsorption Kinetics

The effect of contact time on the adsorption of CR on bentonite modified by ATA, AA and TA was studied. The CR adsorption increased with increase in contact time. The maximum amount of dye was adsorbed at 22h for bentonite modified by ATA and 24h for bentonite modified by AA and TA. The experimental data were examined by pseudo-first-order kinetics, pseudo-second-order kinetics and intraparticle diffusion to understand the dynamics of adsorption process.

5.8.1 Pseudo-First Order Model

The pseudo-first-order kinetic model also known as the Lagergren kinetic equation is widely employed to understand the kinetic behaviour of the system (Ho, 2004). It is given by the equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

where q_e and q_t are the amounts of dye adsorbed at equilibrium and at time t (mgg^{-1}), k_1 is the pseudo first order rate constant (min^{-1}). The values of k_1 and q_e are calculated from Figure 5.11 from the slope and intercept of plots of $1/q_t$ versus $1/t$ respectively.

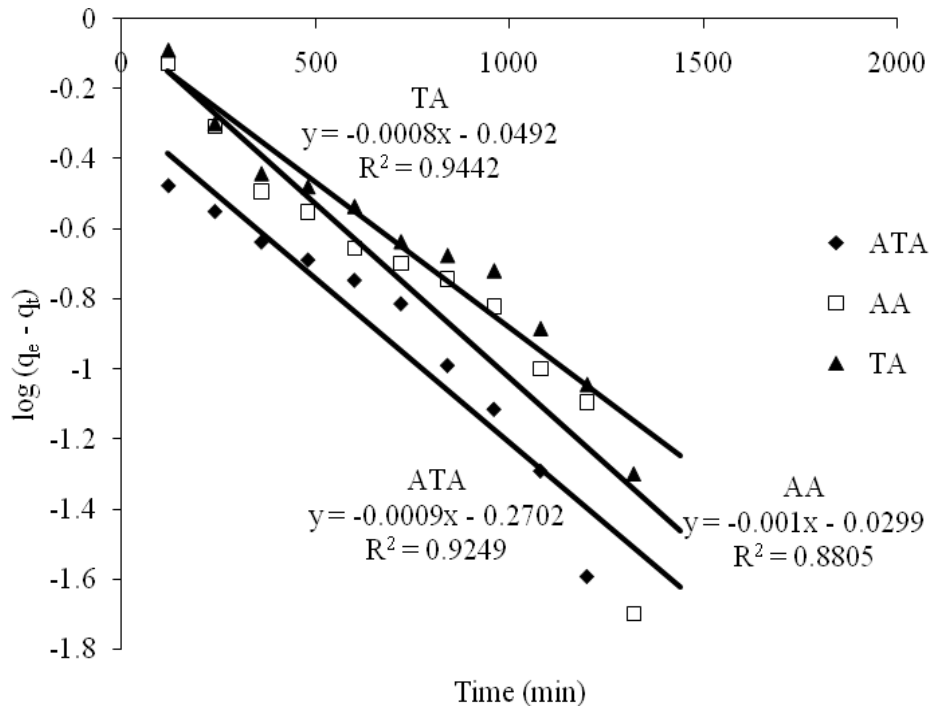


Figure 5.11 Pseudo-first order kinetics for the adsorption of Congo red

The calculated values of q_e as shown in Table 5.5 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.

Table 5.5: Pseudo first order constants

Adsorbent	k_1	$q_{e(\text{experimental})}$	$q_{e(\text{calculated})}$	R^2	χ^2
ATA	0.003	7.13	1.863	0.9249	356.74
AA	0.033	6.73	1.102	0.8805	575.87
TA	0.016	6.61	1.118	0.9442	385.52

5.8.2 Pseudo-Second Order Model

The pseudo-second-order kinetic model is given by the equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where, q_t and q_e are the amount of dye adsorbed at equilibrium and at time t . k_2 is the equilibrium rate constant of pseudo-second-order model ($\text{g mol}^{-1} \text{min}^{-1}$). The value of k_2 and q_e can be obtained from the slope and intercept of plot of t/q_t versus t (Figure 5.12). The values of the rate constants, maximum amount adsorbed and the correlation coefficients are given in the Table 5.6.

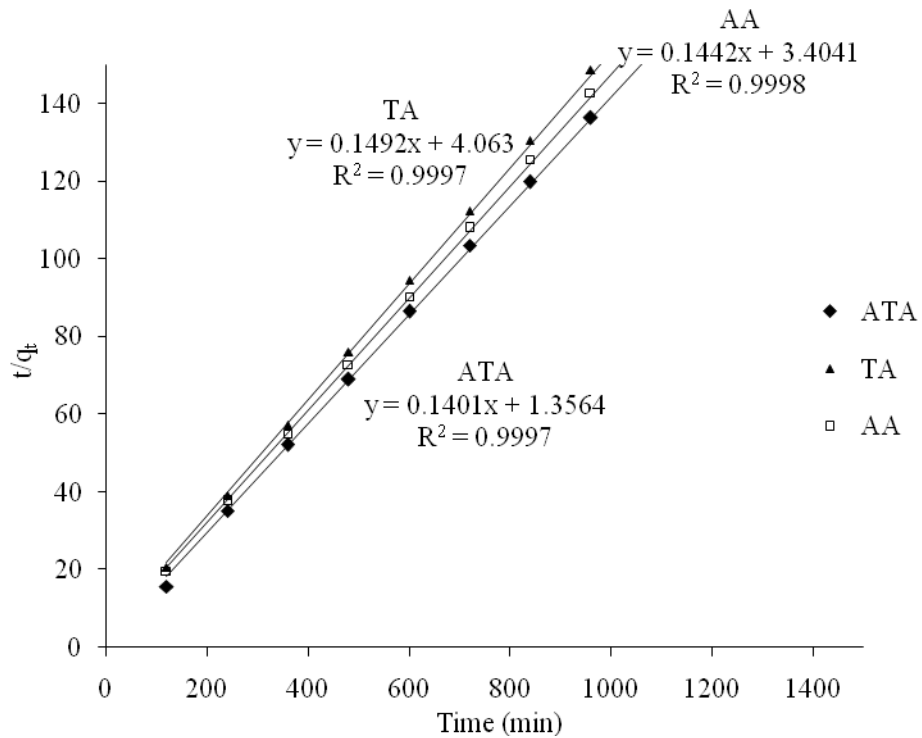


Figure 5.12 Pseudo-second order kinetics for the CR adsorption (linear)

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 q_e 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, 2004 and Vimonses et al., 2009). The plot of t/q_t versus t is linear showing that chemisorption is the main rate controlling step of the adsorption process.

Table 5.6 Pseudo second order constants for linear expression

Adsorbent	$q_{e(experimental)}$	k_2	$q_{e(calculated)}$	R^2
ATA	7.13	0.0145	7.14	0.9997
AA	6.73	0.0061	6.93	0.9998
TA	6.61	0.0055	6.70	0.9997

As discussed in the previous section the kinetic models were also analyzed by the non-linear expressions to avoid the bias results generated by the linearization of the equations. The non-linear calculations for pseudo-second order kinetics were performed using the following equation (Unuabonah et al., 2008):

$$q_t = \frac{t}{\left[\left(\frac{1}{h} \right) + \left(\frac{t}{q_e} \right) \right]}$$

where h is the initial sorption rate and can be calculated as $q_t/t \rightarrow 0$

$$h = k_2 q_e^2$$

Figure 5.13 depicts the non-linear plot of pseudo-second order kinetics and agrees well with the experimental data which is also confirmed by high values of correlation coefficient R^2 in contrast to pseudo-first order kinetics.

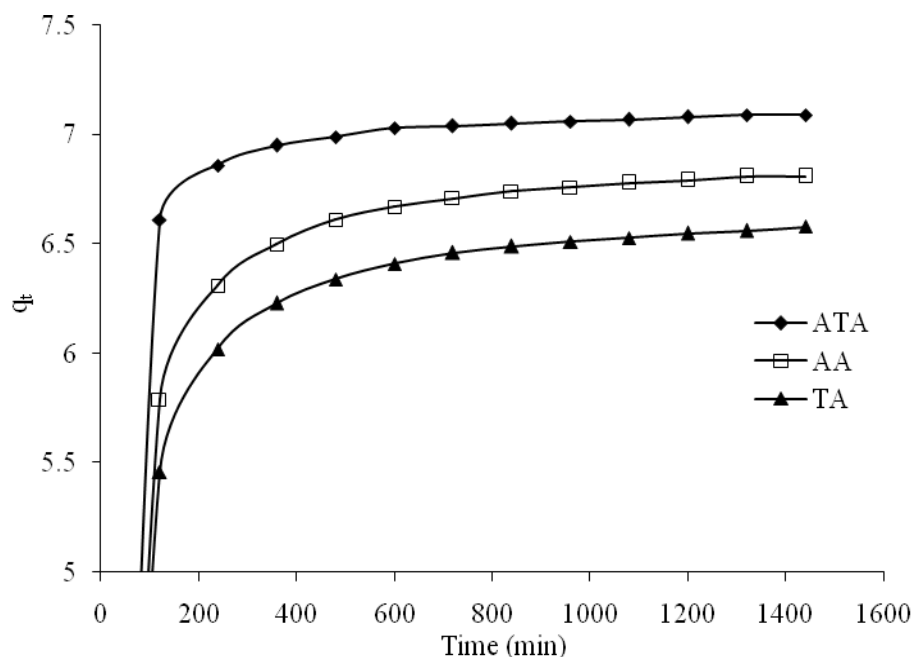


Figure 5.13 Pseudo-second order kinetics for adsorption of Congo red (non-linear)

The comparison of the error function Chi-square for pseudo-first order kinetics and pseudo second order kinetics are listed in Table 5.5 and 5.7 and small values of χ^2 indicate that adsorption kinetics follow pseudo-second model. On the other hand, the error function is very large and moreover the pseudo first order kinetic curves does not fit with the experimental data.

Table 5.7 Pseudo second order constants for non-linear expression

Adsorbent	H	χ^2
ATA	0.739	0.059
AA	0.294	0.208
TA	0.246	0.275

5.8.3 Intraparticle Diffusion Model

The evaluation of the diffusion mechanism is not possible from pseudo first order and second order kinetic model. The intraparticle diffusion can be determined by the following equation (Weber et al., 1963):

$$q_t = k_p t^{1/2} + C$$

where k_p is the intraparticle rate constant ($\text{gmol}^{-1}\text{min}^{-1/2}$) and C is the intercept. The intraparticle diffusion model implies that the plot of q_t versus $t^{1/2}$ should be linear.

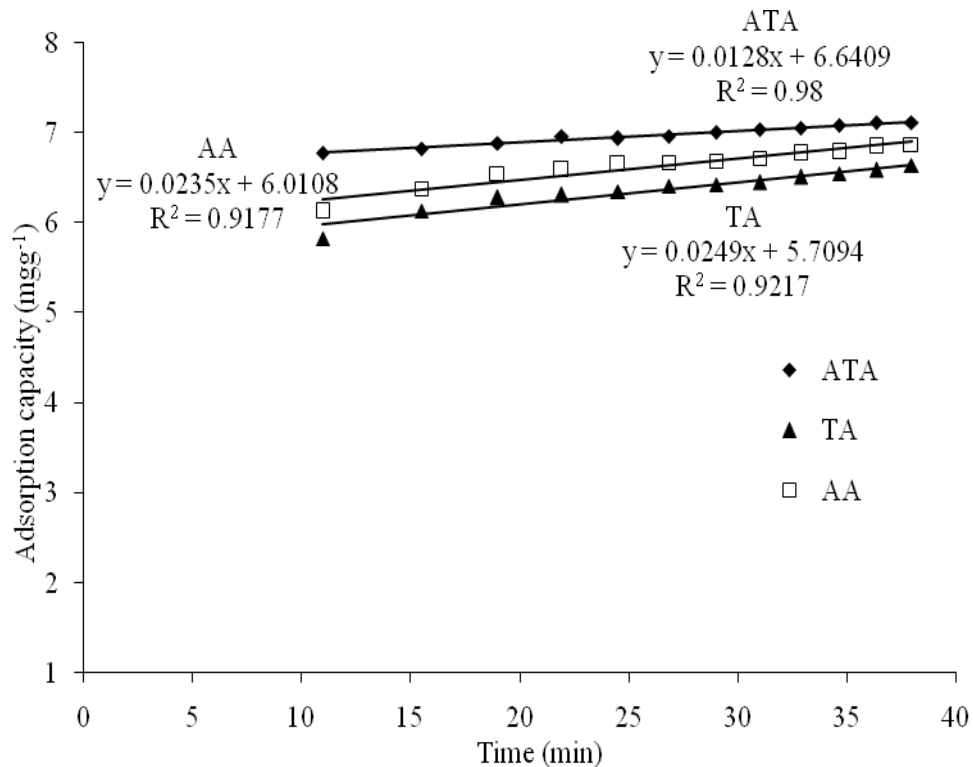


Figure 5.14 Intraparticle diffusion model for the adsorption of Congo red

Furthermore, the intraparticle diffusion is the controlling step if the lines pass through the origin otherwise some degree of boundary layer control exists and the extent of thickness of boundary layer can be examined from the values of intercept. The larger the value of intercept is, the greater the effect of boundary layer can be (Özcan et al., 2005). Similar results have been reported by Vimonese et al., (2009) and Özcan et al., (2005) It is evident from Figure 5.14 that apart from intraparticle diffusion other processes may also control the adsorption process, as the lines do not passing through the origin and all the processes may occur simultaneously. The decrease in the maximum adsorption capacity is observed from the bentonite modified by ATA to TA. Table 5.8 shows values of the intraparticle diffusion constants.

Table 5.8 Intraparticle diffusion constants

Adsorbent	k_p	R^2
ATA	0.0128	0.980
AA	0.0235	0.918
TA	0.0249	0.922

5.9 Regeneration and Reusability of Modified Bentonite

The cost of adsorption process primarily depends on the cost of adsorbent and its reusability. In this study the regeneration of bentonite modified by ATA, AA and TA was carried out by heating the adsorbent at 50⁰C for 12h, followed by

calcination at 100 °C for 20min. It can be seen in Figure 5.15 that the adsorption capacity of the adsorbent decreased with an increase in number of runs on an adsorbent.

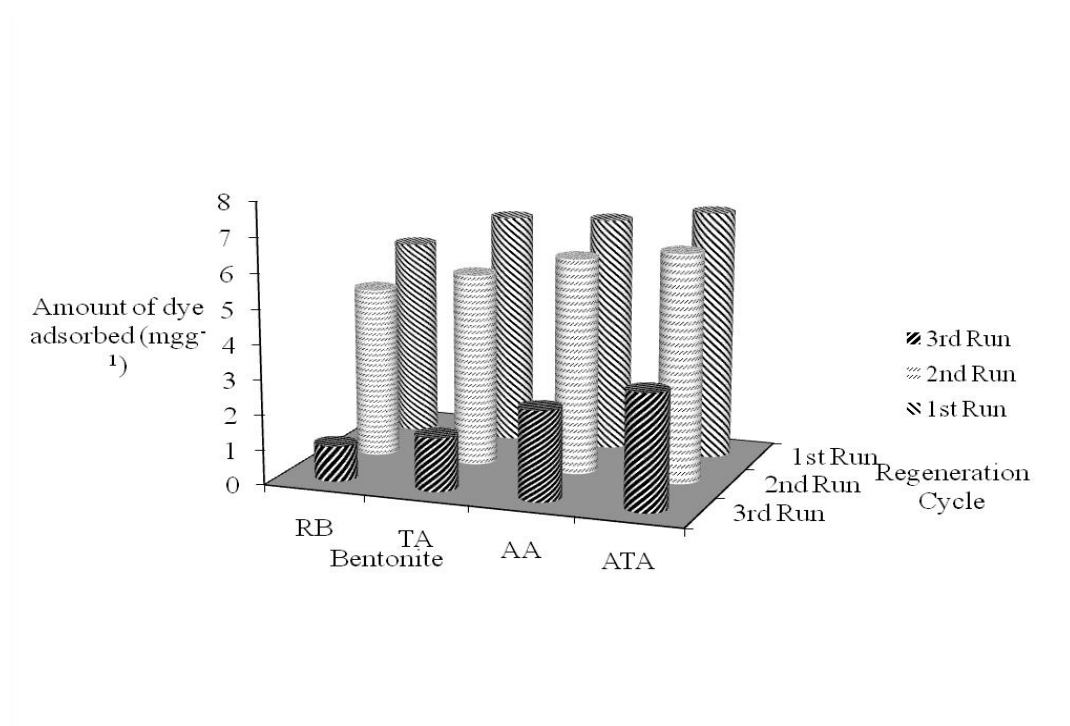


Figure 5.15 Life cycle of raw and modified bentonite

This decrease in the CR adsorption suggests that the availability of the number of adsorption sites for CR decreases with the increase in number of runs on the adsorbent. Furthermore, the results show that the adsorption in the second run occurred only on the adsorption sites which were created due to the removal of water from the surface and the interlayers. It is evident from the results that only about 8% decrease in the adsorbents efficiency between the first and the second run was found for the bentonite modified by ATA and AA. However, significant

reduction of adsorption capacity was given if the modified bentonites were further used after the second run.

5.10 Conclusions

The CR adsorption on modified bentonites has been studied. The experimental results indicate that bentonite modified by ATA has the highest adsorption capability for synthetic dye in comparison to the raw bentonite and bentonite modified by AA and TA. The CR adsorption over a concentration range of 100 – 1000 mgL⁻¹ was evaluated and increase in CR adsorption was observed with the increase in initial dye concentration. The percentage of CR removal increased, corresponding to an increase in the amount of adsorbent up to a maximal level, and thereafter remained constant. The effect of pH on the CR adsorption on modified bentonites was not significant. The adsorption capacity decreased slightly with the increase in temperature. The evaluation of thermodynamic parameters, i.e. the negative values of Gibbs energy and enthalpy, revealed that the adsorption process is spontaneous and exothermic.

The equilibrium data were analyzed using Langmuir and Freundlich adsorption isotherms. Freundlich isotherm yielded a better fit to the adsorption data, signifying that the CR does not form a monolayer on the adsorbent and rather follows multilayer adsorption. The kinetics of CR adsorption on modified bentonites was evaluated by pseudo first order kinetics and pseudo second order

kinetics. The pseudo second order model exhibited the best correlation for the experimental data. The intraparticle diffusion model was also studied to understand the mechanism of adsorption. The results showed that intraparticle diffusion is not the only process controlling the CR adsorption on bentonite modified by ATA, AA and TA.

The results of the present study indicate that bentonite modified by ATA can be successfully employed for the removal of CR over a wide concentration range. Moreover, bentonite modified by ATA has the potential to replace the high cost adsorbents such as activated carbon; as bentonite is a low-cost adsorbent and is plentiful. The modification of bentonite with acid and thermal activation is an economical method to enhance its adsorption properties.

CHAPTER 6

CONCLUSIONS

6.1 Introduction

The treatment of dyes and other toxic pollutants discharged by the industries has become a major problem internationally due to stability and non-biodegradability of these compounds. Adsorption is one of the most preferred techniques for the removal of dyes and other pollutants from wastewater because of the simplicity of the method and the economical feasibility. Activated carbon is the most widely used adsorbent that delivers successful results. However, its high cost and regeneration difficulty are the major issues that limit the use of activated carbon in developing countries.

The adsorption of dyes on clay which is a natural and widely available adsorbent is a valid and confirmed method. One of the key technical problems associated with the use of natural clays is that they have low adsorption capacity compared with activated carbon. Among clays, bentonite shows high efficacy for the removal of dye. The presence of permanent net negative charges on the surface of bentonite makes it unfavorable for the adsorption of cationic dyes. Thus, the surface of bentonite has to be modified to extend its range of applicability from cationic dyes to anionic dyes. There are various methods available for the

modification of the physical structure and chemical properties of bentonites. The modification of bentonite by cationic surfactants involves high cost of surfactants. On the other hand, modification by addition of polymers is a very complex method.

The objective of this research was to search a simple and low-cost method to modify the physical and chemical properties of the bentonite, and to enhance the adsorption capacity in adsorption process for wastewater treatment. As bentonite is a natural and low-cost adsorbent, thus the focus of the study was to identify a modification technique which is economically viable and at the same time enhance the surface and adsorption properties of bentonite. To achieve this goal the modification of bentonite was carried out by thermal treatment and acid activation, and by a combination of thermal and acid activation. The study also focused on the applicability of these modified bentonites for the removal of anionic dye, Congo red, from wastewater. The CR removal was evaluated to investigate the performance of modified bentonites for removal of anionic dye which is very stable and highly non-biodegradable due to the presence of aromatic ring.

6.2 Major Achievements

6.2.1 Development of Thermal Activated Bentonite

To enhance the adsorption capacity of bentonite by thermal treatment, a known amount of bentonite was heated over a temperature range from 50°C to 500°C

with variation in heating time from 20 min to 2 h in order to find the optimum temperature and time required for the modification process. It has been found that the surface area and adsorption capacity of bentonite increased with an increase in temperature upto 100°C and thereafter it started decreasing, indicating that a temperature over 100°C does not necessarily improve the properties of the adsorbent. The heat treatment at 100°C resulted in 20% increase in surface area and the adsorption capacity was improved by 15% in comparison with the raw bentonite.

6.2.2 Synthesis of Acid Activated Bentonite

The acid activation of raw bentonite was carried out to investigate the effect of acid treatment on the physical structure and chemical properties of bentonite. The acid activation of bentonite was performed over a concentration range from 0.05M to 0.5M HCl. The reaction temperature for acid activation was varied at 30°C, 60°C and 80°C to analyze the effect of temperature on the modification of bentonite by acid activation. The results indicate that the surface area and adsorption capacity of bentonite increased initially with an increase in acid concentration until 0.1M HCl. Further increase in acid activation showed a gradual decrease in surface area and adsorption capacity. Similarly, an increase in activation temperature demonstrated a decrease in surface area and adsorption capacity as the time was kept constant at 3h. The surface area and adsorption

capacity of acid activated bentonite were improved by 65% and 18%, respectively, compared with raw bentonite.

6.2.3 Impact of Heat Treatment on Acid Activated Bentonite

The heating treatment of the bentonite after the acid activation was examined in this study. The acid activated clays were subjected to heat treatment at 100°C for 20 min. It was found that the heating treatment could enhance the surface area and the adsorption capacities of acid activated clays. The maximum surface area and adsorption capacity was delivered by 0.1M HCl activated clay at 30°C for 3h, followed by thermal treatment at 100°C for 20min. The bentonite that was acid activated followed by thermal treatment showed overall three fold increase in surface area compared to raw bentonite. However in comparison to bentonite modified by AA an increase in surface area after thermal treatment was 11%. The CR adsorption on bentonite modified by ATA manifested 21% increase when compared to raw bentonite. This is one of the few studies that have focused on the modification of Australian bentonites and their application to adsorption of dyes.

6.2.4 Analyzing the Effect of Operating Parameters on Congo Red Adsorption

In this study the bentonite modified by ATA, AA and TA were evaluated for their adsorption capacity by adsorption of an anionic dye, Congo red. The effect of

various operating parameters, such as, contact time, initial dye concentration, adsorbent dosage, pH and temperature was estimated. It has been evident from the results that the CR adsorption increased with the increase in contact time. The adsorption rate was very high initially. Within the first 2h the CR removal obtained 96.65%, 92.75% and 91.62% using the bentonite modified by ATA, AA and TA, respectively.

The CR adsorption increased with the increase in initial dye concentration. There was no plateau observed in the curves for CR adsorption on bentonite modified by ATA, AA and TA, indicating that these bentonites have very high potential for the adsorption of anionic dyes. The steady increase in the CR adsorption with the increase in initial dye concentration further signifies that there is no formation of monolayer of CR on the surface of adsorbent.

The dosage of adsorbent used plays a vital role in the adsorption of any pollutant. In the present study the CR adsorption increased with the increase in adsorbent dosage. Nearly 100% of dye removal was achieved by 14gL^{-1} of bentonite modified by ATA and 16gL^{-1} of bentonite modified by AA and TA. The change in initial pH of the dye solution did not display a significant change in the CR adsorption on bentonite modified by ATA, AA and TA. This is attributed to the alkaline nature of bentonite that may have neutralized the acidic pH of the CR solution.

In this study, the reaction temperature has been varied from 25 to 60°C to explore the effect of temperature on the CR adsorption on bentonite modified by ATA, AA and TA. It was found that CR adsorption decreased slightly with the increase in temperature for all bentonite samples. The adsorption process is spontaneous and feasible as indicated by the negative values of Gibbs energy. Furthermore, the decrease in entropy implies the positive affinity of all the bentonite samples towards adsorption of CR.

6.2.5 Evaluation of Adsorption Isotherms, Kinetics and Mechanism

The equilibrium data were examined by two well known adsorption isotherm models, namely, Langmuir and Freundlich isotherm models. 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. The results are also supported by high values of correlation coefficient and low values of error function for Freundlich isotherm.

The pseudo first-order and pseudo second-order kinetics model were used to interpret the kinetics of CR adsorption on bentonite modified by ATA, AA and TA. The equilibrium data did not follow pseudo first-order kinetics as the calculated values of amount of CR adsorbed, q_e , were much lower than the experimental values. The maximum adsorption capacities, q_e , calculated from the pseudo second order model are in accordance with the experimental values which

imply that the adsorption obeys pseudo second-order kinetics and is also verified by higher values of correlation coefficient and lower values of error function.

The intraparticle diffusion model was applied to understand the mechanism of CR adsorption on bentonite modified by ATA, AA and TA. From the experimental results it was determined that intraparticle diffusion is not the only rate controlling step and other processes may also be occurring simultaneously.

6.2.6 Reusability of the Modified Bentonite

The regeneration of bentonite modified by ATA, AA and TA was performed by heating the used adsorbent at 50°C for 12h followed by calcination at 100°C for 20min. The adsorption capacity of the adsorbents decreased with increase in number of runs carried out on an adsorbent. It is evident from the results that for bentonite modified by ATA and AA the decrease in efficiency of the adsorbents between the first and the second run is only about 8%, however further use of the adsorbent significantly affects the adsorption capacity.

6.3 Summary

This project has successfully achieved its objective of modification of Australian raw bentonite to enhance its surface area and adsorption capacity. The noteworthy findings of the research are: (1) modification of Australian raw bentonite by a simple and economical method (2) effective application of the modified

bentonites for the adsorption of an anionic dye. The modified adsorbents in this study have comparable surface area to the raw bentonite and those which were obtained with the application of lower acid concentrations. It is also noteworthy that the performance of modified bentonites for the adsorption of anionic dyes from wastewater is improved markedly due to steady increase in the adsorption capacity. Thus, modification of Australian bentonite by acid and thermal activation can be a viable technique to enhance the surface area and adsorption properties.

6.4 Future Direction

6.4.1 Assessing the Applicability of Bentonite Modified by Acid and Thermal Activation

In this study the bentonite modified by ATA, AA and TA were applied to the removal of anionic dye CR. However to assess the range of applicability of these modified bentonites other organic and inorganic pollutants which pose serious problems in wastewater treatment need to be tested. These modified bentonites have high surface area and being a natural adsorbent they are low-cost. Moreover the modification by inorganic acids is also simple and economical. Therefore it is expected that the use of these adsorbents can replace the most widely used adsorbent, activated carbon, and can revolutionize the water treatment in near future.

6.4.2 Scale-up of Batch Process to Continuous Process

The scale up of batch adsorption process of dyes on bentonite modified by ATA, AA and TA to a continuous process is vitally important for its practicality on the commercial scale. The use of these bentonite samples in continuous process can provide an estimate of its usability at industrial scale. The study for various parameters, such as flow rate, aeration rate and reusability is essential to analyze the capacity of these bentonites for the removal of dyes and other pollutants in wastewater.

6.4.3 Further Optimization of the Activation Process

In the present study the reaction time for the acid activation of bentonite was kept constant at 3h. However contact time largely affects the properties of the natural bentonite on acid activation. Furthermore the clay to acid ratio can also be varied to find the optimum clay to acid ratio required for the desirable properties of bentonite. The reactivity of the bentonite also varies with the type of acid used. The activation of bentonite can also be carried out with sulfuric acid and nitric acid and changes in the surface and chemical properties can be analysed.

6.4.4 Cost Analysis

The complete cost analysis of the process will be very beneficial. The cost analysis should include the cost of raw material, cost of treatment and operating

cost. It should also include the amount of congo red required for desired separation and handling and disposal of sludge. The cost involved should be compared with the improvement in the performance of the adsorbent.

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