School of Chemical and Petroleum Engineering

Department of Chemical Engineering

Development and Characterization of Biomass Based Novel Adsorbent in the Removal of Congo Red Dye by Adsorption

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Declaration

To the best of my knowledge, I declare this thesis contains no material that have been published or written previously by any person except where due references and acknowledgment have been made in the text.

Also, this thesis contains no material which has been accepted for the award of any other degree in any university.

Signature.............................

Date......................................

I dedicate this thesis to my parents

Abdul-Aziz Dawood & Layla Mohamed

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ACKNOWLEDGEMENTS

NOMENCLATURE

C_0 = Initial dye concentration, ppm (mg/L)

C_t = dye concentration at time t, ppm (mg/L)

D = Diffusion coefficient, (cm^2/sec)

ΔG^0 = Gibbs free energy change, (kJ/mole)

ΔH^0 = Enthalpy change, (kJ/mole)

ΔS^0 = Entropy change, (J/k mole)

k_1 = Pseudo-first-order rate constant (min^{-1})

k_2 = Pseudo-second-order rate constant, (mg/g.min)

K_F = Freundlich adsorption constant, (mg/g)

K_{id} = Intra-particle rate constant $(mg/g\ min^{0.5})$

M = Mass of adsorbent per unit volume (g/L)

m = Amount of adsorbent added in g

n = Freundlich constant

q_e = Amount of adsorbate per gram of adsorbent at equilibrium, (mg/g)

q_t = Amount of adsorbate per gram of adsorbent at any time, t

q_{max} = Maximum adsorption capacity (mg/g)

R^2 = Linear regression coefficient

R_L = Separation factor

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ABSTRACT

Wastewater effluents contain synthetic dyes which may cause a potential hazard to human beings and to aquatic life. Dye bearing effluents are normally not easily amenable for conventional biological wastewater treatment due to their synthetic origin, complex aromatic molecular structures which make them difficult to biodegrade. Adsorption is considered to be a very effective separation technique and it is widely used in wastewater and water treatment. Pine cone (*Pinus. Radiate*) is a natural low cost agricultural solid waste available worldwide. This research study showed that raw pine cone, acid treated pine cone and pine cone based activated carbon can be used as effective alternative low cost adsorbents for the removal of anionic dye Congo red from aqueous solutions. Also, CHNS analysis, SEM, FTIR, bulk density, BET surface area and particle size distribution were carried out to investigate the physical and chemical properties of the adsorbents. The amount of Congo red dye adsorption by raw and acid treated pine cone biomass was found to increase with increase in initial dye concentration, contact time, temperature but was found to decrease with increase in solution pH and amount of adsorbent. It was further observed that the adsorption was pH dependent and the maximum adsorption of 32.65 mg/g occurred at pH of 3.55 for an initial dye concentration of 20 ppm by raw pinecone, whereas for acid treated pine cone the maximum adsorption of 40.19 mg/g for the same experimental conditions. Freundlich isotherm model gave better fittings with experimental data than Langmuir model and the maximum adsorption capacity of raw pine cone biomass from Freundlich model was found to be 19.18 mg/g. Furthermore, pine cone based activated carbon was synthesized chemically at various concentrations of phosphoric acid and temperature profiles in a horizontal tube furnace. The adsorption mechanism and suitability of the adsorbent were developed based on isotherm and kinetic study under various physico-chemical process parameters. Furthermore, the amount of Congo red dye uptake on synthesized activated carbon was found to increase with an increase in initial dye concentration, temperature but decreased with increase in solution pH and amount of adsorbent. Also, Freundlich, Langmuir and Temkin isotherm models were fitted well with the experimental data. Langmuir maximum adsorption capacity (q_{max}) was found as

500 mg/g at a pH of 3.5. From the thermodynamic analysis, it was observed that the adsorption system was endothermic and physical processes in nature. The positive value of ΔS^0 indicated also greater stability of an adsorption process with no structural changes at the solid-liquid interface. Kinetic experiments clearly indicated that adsorption of Congo red on raw pine cone and pine cone based activated carbon were followed a multi-step processes: a rapid adsorption of dye onto the external surface followed by intra-particle diffusion into the interior of adsorbent which has also been confirmed by intra-particle diffusion model. Overall, the kinetic studies showed that the Congo red dye adsorption process followed pseudo-second order kinetics models and the adsorption was controlled by chemisorption process. Finally, it can be concluded that pine cone (*Pinus. radiate*) biomass is good and cheap precursor for the production of raw, acid modified and biomass based activated carbon adsorbents and their adsorption capacity is very much comparative with other adsorbents including commercial activated carbon in the removal of Congo red from aqueous solution.

1. CHAPTER ONE- INTRODUCTION

1.1 Background

Water is essential for life. According to U.S. Geological Survey 96.5% of earth's water is salt water thus not suitable for human consumption without further treatment. Only 3.5% of total water is considered to be fresh water (Greenlee et al., 2009). The fresh water is mainly made up of polar ice and water from underground sources and only 0.8% is accessible for human, agriculture and industry uses. The water demand doubles every 21 year worldwide due to the increase in the population and industrial activities and the decrease in rainfall (Toor, 2010). The fresh water from rivers, lakes, and aquifers to supply water to agriculture, industry and household sectors has increased rapidly in last century from 600 km^3 to more than 4000 km^3 per annum (Lundqvist, 2009). Thus it is estimated that by the year of 2025, approximately 60% of the total world population would live in regions potentially experiencing moderate to extreme water resource-based vulnerability (Kulshreshtha, 1998). It was been estimated that the industrial demand is about double the household requirements (Lundqvist, 2009). With the urbanization and industrialization, water is getting polluted day by day. One of the important classes of pollutant is dyes and once they enter into water bodies, it is no longer good and has harmful effect on ecosystem. Several industries such as dyestuff, textile, paper, printing, carpet, plastic, food and cosmetic industries are used dyes to produce colour their products. These dyes are always left in industrial waste and discharged into water body. Dyes are broadly classified into cationic, anionic and non-ionic dyes. The removal of anionic dyes is to be considered as the most challenging task as they are water soluble and produce very bright colours in water with acidic properties. Dye bearing effluents are normally not easily amenable for conventional biological wastewater treatment due to their synthetic origin, complex aromatic molecular structures and xenobiotic properties which make them difficult to biodegrade. It has been estimated that the total dye consumption in textile industry worldwide is more than 10,000 tonnes per year and about 10–15% of these dyes are released as effluents during the dyeing processes (Gómez et al., 2007; Gupta et al., 2013).

Synthetic dyes such as Congo red (CR) is known to form carcinogenic aromatic amines which are toxic and may cause direct harmful effect to the environment and human beings (Yaneva and Georgieva, 2012). Various technologies such as adsorption, coagulation/flocculation, advanced oxidation technologies, ozonation, membrane filtration, aerobic and anaerobic degradation are widely used for the treatment of dye-bearing wastewater. These technologies can be grouped into three categories: Physical, Chemical and Biological (Yagub et al., 2012). All of these methods have their own advantages and disadvantages. Adsorption process is a physiochemical separation method and it is reported to be the most effective and economical separation technique in the removal of dye-bearing wastewater. It is also considered to be a very effective separation technique in wastewater treatment in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances (Abd EI-Latif et al., 2010; Mohammad et al., 2010; Sen et al., 2011; Yao et al., 2009).

The removal of dye from aqueous phase by Commercial Activated Carbon (CAC) is very well established and successful technology. Commercial activated carbon is an extremely versatile material with a high pore volume and a large surface area. Due to its excellent adsorption capacity, it is widely used as an adsorbent in wastewater and gas treatment industries. However, due to its high cost and the difficulties associated with its disposal, researchers are engaged to search alternative adsorbents in the treatment of dye-bearing effluents. Natural materials, agriculture solid waste and biomass based activated carbon are considered to be interesting alternatives to commercial activated carbon (Salleh et al., 2011; Toor, 2010). The utilization of the large quantities of agriculture solid wastes adsorbents presents double benefits with wastewater treatment and solid waste management. Various cost effective alternative adsorbents are reported in the removal of textile dyes from wastewater such as eucalyptus wood (Mane and Vijay Babu, 2013), raw and modified papaya seed (Nasuha et al., 2011), *pinus sylvestris* L (Aksakal and Ucun, 2010), soy meal hull (Arami et al., 2006), organo-attapulgite (Chen and Zhao, 2009), garlic peel (Hameed and Ahmad, 2009), almond shell (Doulati Ardejani et al., 2008) and pine tree leaves (Deniz and Karaman, 2011).

Basically the selection of the precursor for the development of cost effective adsorbents depends on many factors. The precursor should be freely available, in-expensive and non-hazardous in nature. Pine cone (*P. radiate*) is native tree available in Australia. The ovulate cone is the well-known cone of the Pinus and other conifers. Large quantities of pine cones are produced annually as agricultural by-product throughout the world. These scale of this ovulate cone as cone biomass is a waste itself and can be used as an effective adsorbent. In this research study, Australian raw pine cone and acid modified pine cone are used to examine their applicability as effective and low cost sustainable adsorbents in the removal of toxic dye Congo red (CR) from aqueous solution. Pine cone biomass based activated carbon may also be utilized and used as an effective adsorbent in the removal of Congo red (CR) from aqueous solution by adsorption. Activated Carbon (AC) obtained from biomass has the advantage of offering an effective low cost replacement for non-renewable coal based granular activated carbon provided that they have similar or better adsorption efficiency. Therefore, researchers also successfully reported the synthesis of biomass activated carbon from various agriculture solid waste such as Myrtus communis & pomegranate (Ghaedi et al., 2012), date palm pits (Reddy et al., 2012), macadamia nut shells (Poinern et al., 2011) and Cattail (Shi et al., 2010), rice hulls (de Luna et al., 2013), date stone and pomelo skin (Foo and Hameed, 2011a; Foo and Hameed, 2011b) which are effectively used in the removal of dyes from aqueous solutions.

1. 2 The objectives and motivation of this research

The overall objective of this research work is to develop a cost effective and environmentally friendly pine cone based adsorbent and its applications in the removal of toxic anionic dye Congo red (CR) from its aqueous solution by adsorption. The effectiveness of synthesized biomass adsorbents has been justified by kinetics and isotherm mechanism, study under different physico- chemical process conditions. Therefore, the specific objectives of this research project are:

1. Preparation of raw pine cone and chemically modified pine cone biomass adsorbents.

2. Synthesisation of pine cone biomass based activated carbon powder through chemical activation with the use of phosphoric acid as an activation agent.

3. Characterisation of raw pine cone, chemically modified pine cone and biomass based activated carbon by using different analytical instruments such as Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR), BET, zeta potential, bulk density, CHNS-O analyser and Malvern particle size analyser.

4. Batch Kinetic dye adsorption study under various physico-chemical process conditions such as initial solution pH, initial adsorbent dose, initial dye concentration, contact time and initial solution temperature and to find out the optimim process parameters.

5. To identify the fundamental mechanism of dye adsorption by biomass, a systematic kinetic and isotherm study was undertaken.

6. To carry out dye adsorption kinetic study and to determine the applicability of kinetic model among pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion models.

7. To find out various kinetic design parameters from CR dye adsorption study.

8. To carry out CR dye adsorption isotherm study and to find out the applicability of isotherm model with optimum parameters among various isotherm models.

9. To evaluate the thermodynamics properties of the adsorption system such as Gibb's free energy change (ΔG^0), enthalpy change (ΔH^0) and change in entropy (ΔS^0).

These novel adsorbents have various significance applications in waste water and water treatment, oil and gas, food, chemical industries, solvent recovery, air pollution control and in hydrometallurgy industry for the recovery of gold and silver. Therefore, upon the successful completion of this project, it will help to synthesise economical, effective and environmentally friendly adsorbents. Also, these agricultural by-product waste pine cone have little value thus, it will reduce the cost of waste disposal and provide potentially inexpensive adsorbents comparing to the current industrial adsorbents

1. 3 Organisation of thesis

This thesis has been organized in seven chapters. Following the present introductory chapter, chapter two presents the literature review and current state of art in the removal of dye on dye removal from aqueous solution by various adsorbents. A critical analysis and research gap have been identified in this chapter. Chapter three outlines the preparation methods of the adsorbents and the other chemicals, experimental procedures and the basic description of different instruments used in this research study. Chapter four focuses on the removal of anionic dye Congo red from aqueous solution by raw and acid modified pine cone powders as well as examine the physical and chemical characterization of the adsorbents. Also, the theoretical and calculated results of thermodynamic, batch kinetic and isotherm adsorption studies are investigated to evaluate the effectiveness of the adsorption process. Chapter five outlines the production of pine cone biomass based activated carbon under different phosphoric acid concentrations and temperature profiles.

Chapter six focuses on the removal of anionic dye Congo red from aqueous solution by pine cone based activated carbon powder as well as examines the physical and chemical characterization of the adsorbent. Also, the theoretical and calculated results of thermodynamic, batch kinetic and isotherm adsorption studies are examined to evaluate the effectiveness of biomass based AC in the adsorption process. Finally, chapter seven summarises the outcomes of this research project. Also, it explains the research gaps associated with this research and future research direction /recommendations.

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2. CHAPTER TWO- LITERATURE REVIEW

2.1 Dyes sources and their classifications

Dyes are natural or synthetic organic compounds used in various industries. Dyes are used to colour various materials such as fibers, leathers, papers, plastics, foods etc. Prior to the year of 1856, natural dyes are extracted from plants, animals, insects and minerals sources. Natural dyes are such as Turmeric, Weld, Onion, Jackfruit etc are used in the early textile industry. The most common natural dyes used in textile industry are presented in Table.2.1 along with their scientific names and chemical structures. Due to the increase in population and industrial activities, natural dyes do not meet the industrial demand.

The first synthesis dye was discovered by William Henry Perkin in 1856. Chromophores and auxochromes components play important roles in the dye's molecules as Chromophores (OH, NH_2, NHR, NR_2, Cl and COOH) are responsible for the production of colours where auxochromes (NO_2, NO, N=N) enhance the affinity of the dye toward the fibers (Salleh et al., 2011). Synthetic dyes have a high visibility even at very low concentration in water. There is no single dye that can have a complete degree of fixation to fiber during dyeing and finishing processes (Pang and Abdullah, 2013). Dye based effluents are normally not amenable for conventional biological wastewater treatment due to their synthetic origin and complex molecular structures, thus decrease their ability to biodegrade. There are various types of dyes used in textile, paper, rubber ,food and paint industries such as acid dyes, reactive dyes, basic dyes, azo dyes, direct dyes, vat dyes and disperse dyes (Demirbas, 2009). All dyes are water soluble except disperse dyes and vat dyes. All dyes contain traces of metals such as copper, zinc, lead, chromium and cobalt in their aqueous solution except vat and disperse dyes. Dye bearing effluents from these industries are characterized by its high colour, organic content and hazardous as well. It is estimated that more than 100,000 commercial dyes are known with an annual production of more than $7x10^5$ tonnes per year (Gupta et al., 2013).

The total dye consumption in textile industry worldwide is more than 10,000 tonnes per year and approximately 100 tonnes per year of dyes are discharged into water streams (Gupta et al., 2013). These effluents can cause potential pollutants to human beings and to aquatic life. Dyes are broadly classified into cationic, anionic and non-ionic dyes. Anionic dyes include various dyes' groups such as acid dyes, reactive dyes, azo dyes and direct dyes while cationic dyes are the basic dyes. A summary of dye's classifications and their applications is presented in Table.2.2.

Table 2.1. The common natural dyes used in textile industry (Shahid et al., 2013)

Natural dyes	Scientific names	Chemical structure
Turmeric	Curcuma Longa	
Weld	Reseda Luteola	
Eucalyptus	Eucalyptus globules	
Cutch	Acacia Catechu	
Onion	Alium cepa	
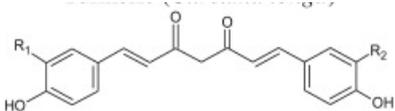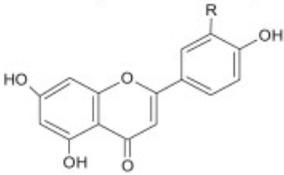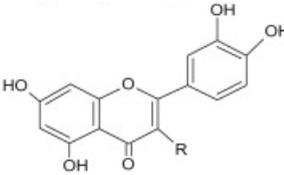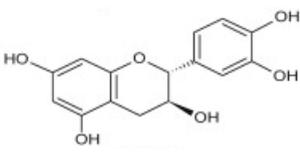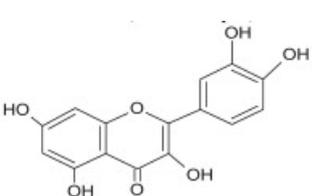
Flos sophorae	Sophora japonica	
Henna	Lawsonia inermis	
Teak	Tectona grandis	
Berberry	Berberis aristata	
Indigo	Indigofera tinctoria	
Jackfruit	Artocarpus heterophyllus	
Cochineal	Dacylopius Coccus	
Indian Rhubarb	Rheum emodi	
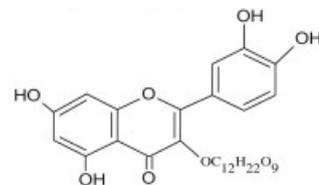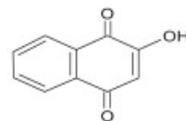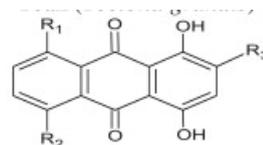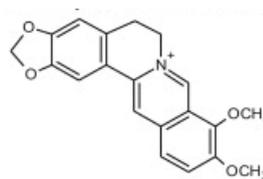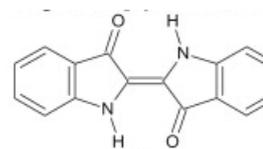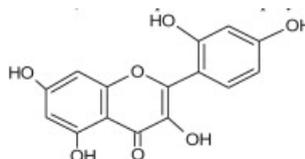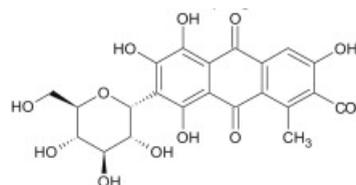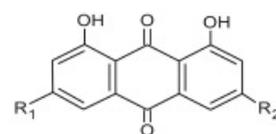
Table 2.2 Classification of dyes based on applications (Forgacs et al., 2004; Hernández-Montoya et al., 2013; Le Coz, 2005)

Dyes	Examples of dyes	Chemical structure's example	Applications of dyes
Acid dyes	Congo red Methyl (orange and red) Orange (I,II) Acid (blue, black, violet, yellow)	 Acid blue 25	Wool Silk Nylon (Polyamide) Polyurethane fibers
Direct dyes	Martius yellow Direct black Direct orange Direct blue Direct violet Direct red	 Direct black 38	Cotton Wool Flax silk Leather in (alkaline or netural bath)
Reactive dyes	Reactive red Reactive blue Reactive yellow Reactive black Remazol (blue, yellow, red, etc)	 Reactive black 5	Cellulosic fibres Wool Polyamide
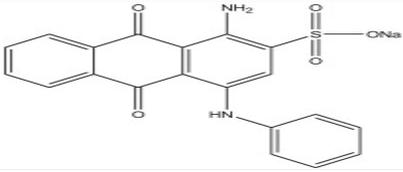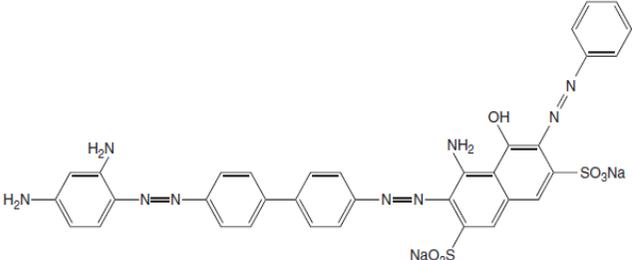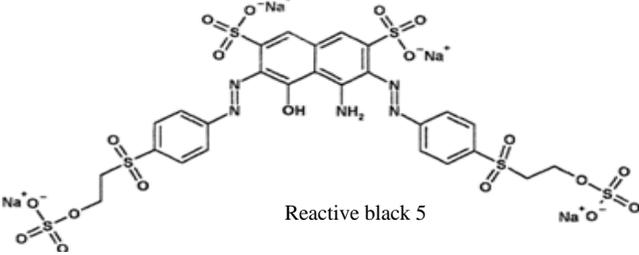
disperse dyes	Disperse blue Disperse red Disperse orange Disperse yellow Disperse brown	Disperse red 17	Polyamide fibers Polyesters Nylon polyacrylonitriles
Vat dyes	Indigo, Benzanthrone Vat blue Vat green	Vat green 6	Wool Flax Wool Rayon fibers
Basic dyes	Methylene blue Basic red Basic brown Basic blue Crystal violet Aniline yellow Brilliant green	Methylene blue	Polyester Wool Silk Mod-acrylic nylon
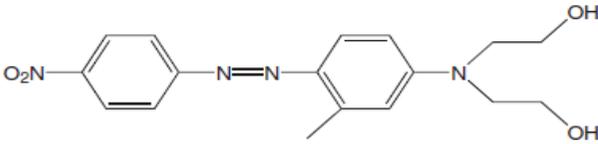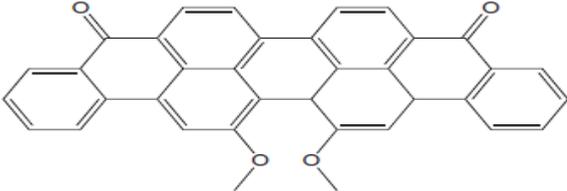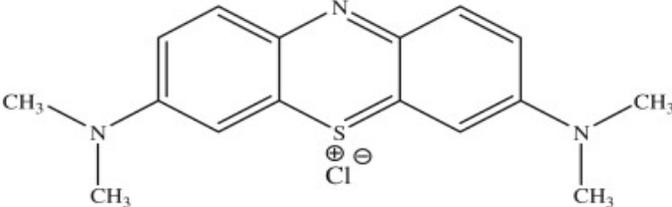
2.1.1 Cationic dyes and their toxicity effects

Cationic dyes are also called basic dyes due to the presence of positive ions in the molecule's structure. Basic dyes are water soluble and they are highly visible in water even at very low concentration. Basic dyes consist of monoazoic, diazoic and azine compounds (Le Coz, 2005). Malachite green, Aniline yellow, Butter yellow, Basic red, Basic black, Turquoise reactive, neutrichrome red and Methylene blue all are basic dyes which are used in textile and paper industries. They are used to dye wool, silk, nylon, mod-acrylic and polyester materials. Cationic functionality is found in various types of dyes such as cationic azo dyes, methane dyes, anthraquinone, di- and tri-arylcarbenium, phthalocyanine dyes, polycarbocyclic and solvent dyes (Salleh et al., 2011).

The azo dyes have good properties, strong colour and cheap thus they are used widely in textile industry. Therefore, basic dye bearing effluents are toxic and can cause allergic dermatitis, skin irritation, mutations and even cancer (Eren, 2009). Also, cationic dyes can cause increased in heart rate, shock, vomiting, cyanosis, jaundice, quadriplegia, heinz body formation and tissue necrosis in humans (Vadivelan and Kumar, 2005). Due to the health hazards associated with the basic dyes, they are used intensively in the dye adsorption studies by low cost adsorbents such as removal of Methylene Basic red 46 (Deniz and Karaman, 2011), Crystal violet (El-Sayed and Owes, 2011) and Malachite green (Srivastava and Rupainwar, 2011) .

2.1.2 Anionic dye and its toxicity effects

Anionic dyes have negative ions due to the excess presence of the OH^- ions in aqueous solution. Anionic dyes are water soluble and they include acid dyes, azo dyes, direct dyes and reactive dyes. Reactive dyes attach to their substrates by a chemical reaction (hydrolysis of the reactive groups in the water) that forms a covalent bond between the molecule of dye and that of the fiber (Demirbas, 2009). Anionic dyes removal is the most challenging task as they produced very bright colours in water and show acidic properties.

Reactive dyes contain reactive groups such as vinyl sulfone, chlorotriazine, trichloropyrimidine, and difluorochloropyrimidine that covalently bonded with the fiber during the dyeing process (Labanda et al., 2009). Moreover, azo dyes represent the largest class of reactive dyes used in the textile industry followed by anthraquinone and phthalocyanine classes (Wu et al., 2008). Azo dyes have the largest variety of dyes and under anaerobic conditions, the dye's linkage can be reduced to form aromatic amines which are colourless but can be toxic and carcinogenic (Yaneva and Georgieva, 2012). It was estimated that 130 of 3,200 azo dyes in use can form carcinogenic aromatic amines during degradation process (Yaneva and Georgieva, 2012).

The solubility of anionic dyes such as Congo red in wastewater is very high, since the dye generally contains sodium salt which is strongly soluble in water. The high solubility of the anionic dyes makes them difficult to biodegrade and photodegradation (Vimonses et al., 2009). Due to its stable and strong structure, Congo red (CR) can persist in the environment. Acid dye (CR) effluents contain organic sulphonic acids and this may cause harm to the environment and the human beings. Anionic dyes such as (CR) are highly toxic due to the presence of large number of metal complex and known to cause human carcinogen (Cheng et al., 2012). Various studies have been carried out to investigate the removal of anionic dyes such as Congo red (Chen and Zhao, 2009; Mane and Vijay Babu, 2013; Vimonses et al., 2009) , Acid black 26,Acid blue 7 (Mahmoodi et al., 2011), Red dye 141 (Leechart et al., 2009), Acid blue (Arami et al., 2006). Reactive Yellow 4 (El Boujaady et al., 2011) and Eriochrome Black T (de Luna et al., 2013) from aqueous solution by various types of adsorbents.

2.1.2.1 Congo red and its toxicity

Congo red was synthesized in 1883 by Paul Bottiger. It is an anionic diazo dye prepared by coupling tetrazotised benzidine with two molecules of napthionic acid. Congo red is an example of anionic diazo dyes discharged in the wastewater from textile, printing, dying, paper and rubber industries (Yaneva and Georgieva, 2012). It is used mainly in textile to colour cotton directly. (CR) is a very bright colour and highly visible in water even at very low concentration such as 1 part per million (ppm). (CR) is highly soluble in water, ethanol and acetone however, it is not soluble in xylene (Yaneva and Georgieva, 2012).

Also, CR is used as a pH indicator as the colour changes to dark blue at acidic pH and to red at alkaline and neutral solutions where the red colour is slightly different from the original red colour at neutral pH(Kaur et al., 2013). It has a chemical formula of $C_{32}H_{22}N_6Na_2O_6S_2$ and molecular weight of 696.66 g/mol. Furthermore, Congo red has other scientific and trade names such as sodium salt of 3,3'-([1,1'-biphenyl]-4,4'-diylbis-)(azo) (4-aminonaphthalene-1-sulfonic acid), disodiurn salt, Atlantic Congo red, Arul Congo red, Azocard red Congo, Benzo Congo red, Brasilarnina Congo 4B, Cerven Congo, Cerven Prima 28, C.I. 22120, C.I. Direct red 28, Congo red 4B, Congo red 4BX, Congo red CR, Congo red H, Congo red K, Congo red L, Congo red M, Congo red N, Congo red R, Congo red RS, Congo red TS, Congo red W, Congo red WS, Congo red sodium salt, Congo red, Colton red 4BC, Cotton red 5B, Cotton red L, Congorot, Diacotton Congo red, Direct Congo red , Erie Congo 4B and Haemomedical (Yaneva and Georgieva, 2012) (Vimonses et al., 2009)
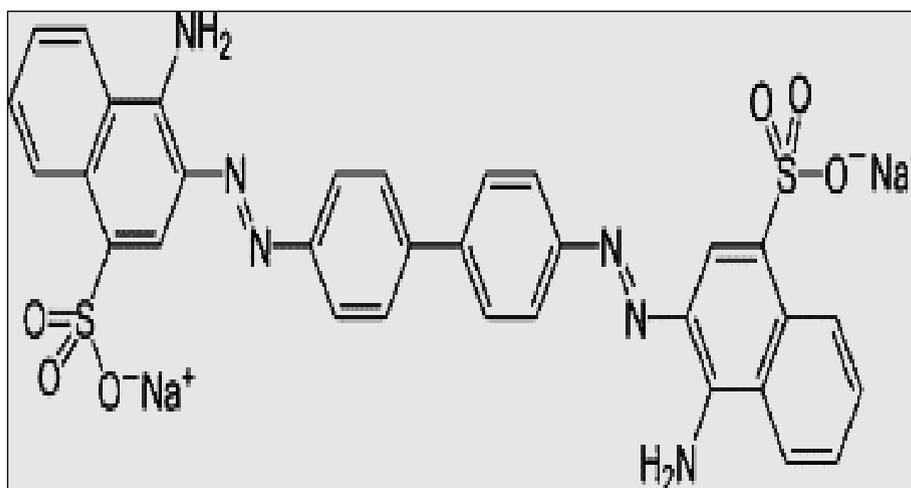
Figure 2.1 Congo red molecular structure (Vimonses et al., 2009)

During the biodegrading process, Congo red can be reduced to form carcinogenic aromatic amines which are toxic and may cause direct harmful effect to the environment and human being (Yaneva and Georgieva, 2012). According to the Material Safety Data (MSD) (Fisher Scientific, 2006), CR has caused adverse reproductive and fetal effects in laboratory animals where rats, mice, and hamsters developed liver and mammary tumors. Also, it is been reported that humans and dogs develop increased incidences of urinary bladder cancer.

Dye-bearing water treatment by adsorption using low cost ecofriendly alternative solid waste adsorbent is a demanding area as it has double benefits i.e. water treatment and waste management. A number of non-conventional, low-cost adsorbents such as organo-attapulgite (Chen and Zhao, 2009), pellets of Trametes versicolour (Binupriya et al., 2008), palm shell (Sreelatha et al., 2011), montmorillonite (Yermiyahu et al., 2003); bentonite (Lian et al., 2009); rice hull ash (Chou et al., 2001), leaf (Bhattacharyya and Sharma, 2005), rice husk (Han et al., 2008), Eucalyptus wood(Mane and Vijay Babu, 2013), papaya seed (Nasuha et al., 2011) and sugar cane bagasse (Zhang et al., 2011) has been successfully used for the removal of Congo red from aqueous solution.

2.2 Dye separation techniques

Wastewater effluents contain synthetic dyes which may cause a potential hazard to the environment. Due to the environmental and health concerns associated with the wastewater effluents, different separation techniques have been used in the removal of dyes from aqueous solutions. Physiochemical, chemical and biological methods have been used for the treatment of dye-bearing wastewater. All dye separation techniques have their own limitation in terms of design, operation efficiency and total cost. A list of different dye removal methods along with their advantages and disadvantages are presented in Table.2.3.

Table 2.3 The advantages and disadvantages of various dye removal techniques (Pang and Abdullah, 2013; Salleh et al., 2011)

Separation Technique	Advantages	Disadvantages
Physiochemical		
Adsorption	• High adsorption capacity for all dyes.	• High cost of adsorbents. Need to dispose of adsorbents. Low surface area for some adsorbents.
Ion exchange	• No loss of sorbents.	• Not effective for disperse dyes.
Membrane filtration	• Effective for all dyes with high quality effluent.	• Suitable for treating low volume and production of sludge.
Electrokinetic coagulation	• Economically feasible.	• Need further treatments by flocculation and filtration and production of sludge.
Chemical		
Fenton reagent	• Effective process and cheap reagent.	• Sludge production and disposal problems.
Ozonation	• No production of sludge.	• Half-life is very short (20 min) and high operational cost.
Photocatalyst	• Economically feasible and low operational cost.	• Degrade of some photocatalyst into toxic by-products.
Biological		
Aerobic degradation	• Efficient in the removal of azo dyes and low operational cost.	• Very slow process and provide suitable environment for growth of microorganisms.
Anaerobic degradation	• By-products can be used as energy sources	• Need further treatment under aerobic conditions and yield of methane and hydrogen sulfide.

2.2.1 Chemical Methods
2.2.1.1 Advanced Oxidation Technologies (AOTs)

Oxidation process is one of the traditional methods used for the removal of inorganics/organics from wastewater. The effectiveness of advanced oxidation technologies (AOTs) are based on the generation of oxidizing reagent (●OH) radicals as they attack the Chromophores leading to the production of organic peroxide radicals and finally convert to CO_2, H_2O and inorganic salts (Antoniadis et al., 2010). Chemical oxidation is very effective but the efficiency strongly influenced by the type of oxidant (Forgacs et al., 2004). ATOs include the use of oxidants such as chloride, ozone, Fenton and Fenton-like reagents and chlorine dioxide.

i.   Fenton's reagent

Fenton's reagent is also known as hydrogen peroxide and it is more effective if applied at acidic solution. Iron ions such as Fe^{+2} and Fe^{+3} are the most common reagents used in Fenton activation. Fenton's reagent is cheap and easy to handle compared to other reagents. The decomposition of Fenton-like reagent is presented in the following equations (Jiang et al., 2013)

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe^{III}(HO_2)^{2+} + H^+ \tag{2.1}$$

$$Fe^{III}(HO_2)^{2+} \rightarrow Fe^{2+} + HO_2 \tag{2.2}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^- \tag{2.3}$$

The iron (III) reacts with hydrogen peroxide to form iron (III) peroxo complex. The complex is decomposed to produce iron (II) then it reacts with hydrogen peroxide to yield the oxidant, hydroxyl radicals. The removal efficiency of this process depends on the production of the oxidant, hydroxyl radicals which exhibit higher removal percentage at higher dyes concentration. This process has its own limitations as these reagents are toxic and may cause more harm to the biological treatment system used for the post treatment than the original textile dyes (Arslan-Alaton et al., 2008). Also, the large volume of sludge formation and the hazards associated with its disposal limits the use of this process in industrial scale. Previous studies of Fenton and Fenton-like reagents are used to remove textile dyes such as reactive red, acid blue and direct blue (Forgacs et al., 2004), acid orange and reactive blue (Arslan-

Alaton et al., 2008) and Reactive Black 5 ,Reactive Orange 16 and Reactive Blue 2 (Su et al., 2011).

ii.   Ozonation

Ozonation is one of the AOT used in the removal of synthesis dyes from wastewater effluents. It is a very effective technology in treating wastewater and is considered to be a good method in the decolourization of textile effluents as ozone (O_3) attacks the nitrogen conjugated double bonds which are often associated with colours (Gao et al., 2012; Turhan et al., 2012). Ozonation reactions can be classified into direct reaction and indirect reaction based on the pH of the solution. The decomposition rate of ozone is affected by solution pH and initial dye concentration. At basic medium, ozone rapidly decomposes to yield the hydroxyl radical but in acidic conditions, ozone can directly react with organic substrates as an electrophile (Turhan et al., 2012). Ozonation process does not form a sludge because of complete decomposition of dyes thus reduce the toxicity of by-products (Sharma et al., 2013). However, the half-life of ozone is very short and it requires a high voltage to run a continuous ozonation process thus increases the capital cost and limits its uses in the industrial scale (Robinson et al., 2001).

2.2.1.2 Photocatalyst

Photocatalyst is a process used in the removal of organics contaminations such as dyes from wastewater. It is also used in the production of hydrogen by water spilling method. Band gap can be described as a region between the valence band and the conduction band of the semiconductor. Photon energy equal or higher than the band gap energy is required to excite the electrons from the valence band to the conduction band and the movement of the electrons leave holes with positively charged ions (H^+) in the valence band as shown in Fig.2.2 (Pai et al., 2012). The positively charged holes are powerful oxidants and can destroy adsorbed organic pollutants where the electrons at the conduction band react with the oxygen molecules to form strong oxidative radicals that also cause the decomposition of organic and inorganic contaminations in wastewater (Cao et al., 2011). The presence of photocatalyst enhances the rate of decomposition.
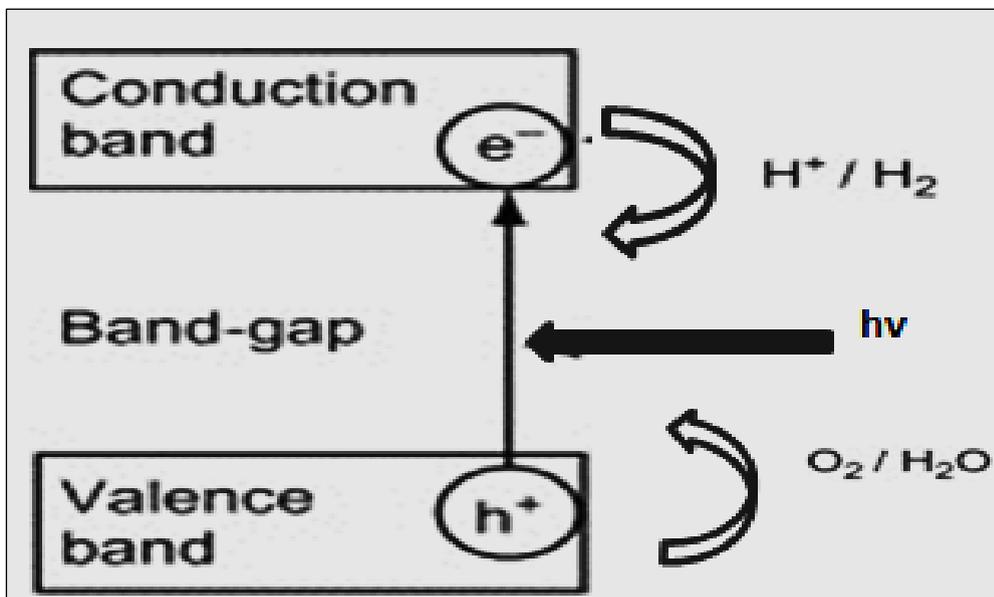
Figure 2.2 The basic principle of water splitting using Photocatalyst –
Adapted from (Pai et al., 2012)

Current studies are focused on the production of various photocatalyst for dye degradation such as cucurbit[6] uril- polyoxometallates (CB[6]–POMs) composite, α-Keggin type polysilicontungstate anions $KH[SiW_{12}O_{40}]$ $[Ni(H_2O)_6]CB[6] \cdot 7H_2O$ (Cao et al., 2011), Bi-based oxyhalide Bi_4TaO_8I (Fan et al., 2012), Ternary nanocomposite of grapheme TiO_2-Fe_3O_4 (GTF) (Lin et al., 2012), α-bismuth molybdite $\alpha-Bi_2Mo_3O_{12}$ (Martínez-de la Cruz and Obregón Alfaro, 2009) and Bismuth phosphate $BiPO_4$ (Liu et al., 2012).

Also, photocatalyst is used in the removal of dyes from wastewater such as Methyl Orange (Cao et al., 2011; Fan et al., 2012), Reactive red and direct green (Wawrzyniak and Morawski, 2006). Photocatalyst selection depends on dye's chemical properties as some dyes are resistant to photo-degradation process (Kabra et al., 2004). Photocatalyst has feasible applications in wastewater treatment as it can operate at ambient temperature in the range of 20°C-80°C and pressure of <300 kPa with complete mineralization thus reduce total operating cost (Chong et al., 2010). On the other hand, some photocatalyst are degraded along the process and generate toxic products.

2.2.2 Biological Methods
2.2.2.1 Aerobic Degradation

The microorganisms such as bacteria and fungi are used in the decolourization of dyes under aerobic conditions. Bacteria are able to culture and grow more quickly than fungi as they are able to metabolize chlorinated and other organic contaminants and use them as carbon or energy source (Balamurugan et al., 2011). Bacteria are classified as mono-oxygenase or di-oxygenase enzymes and they are used to catalyse the incorporation of oxygen from O_2 into the aromatic ring of organic compounds such as azo dyes and reactive dyes (dos Santos et al., 2007). Many researchers have investigated the use of bacteria for the decolourization of dyes such as removal of Blue Bezaktiv dye BB150 by *lyophilised bacterial consortium* (Khouni et al., 2012).

The use of fungi in the removal of dyes is more effective compared to bacteria and algae. Many results have been reported such as the removal of azo dyes by *Candida tropicalis* (Tan et al., 2013) and acid red B by *Pichia sp TCL* (Qu et al., 2012). Fungi have high capacity of biodegradation of dyes as they are able to deplete complex organic compounds by producing extracellular ligninolytic enzymes including laccase, manganese peroxidase and lignin peroxidise (Tan et al., 2013). White-rot fungi such as *Dichomitus, squalens, Daedalea flavida, Irpex flavus* and *Polyporus sanguineus* have been used widely in the decolourization and degradation of textile waste of many chromophoric groups of dyes (Chander and Arora, 2007). Bacteria and fungi strains commonly used in the biodegradation of textile dyes are presented in Table 2.4.

The use of bacteria and fungi for the complete decolourization and degradation of dyes from textile effluent have the advantages of low cost process compared to other methods and the ability to complete mineralization of dyes with nontoxic by-products (Dawkar et al., 2010). However, this process is not applicable for real textile wastewater treatment because it is a very slow process and provides a suitable environment for the growth of autochthonous microorganisms(Toor, 2010). Sometimes the effluent temperature does not favour for microorganism enhanced dye removal.

Table 2.4 Bacteria and Fungi strains commonly used in dye biodegradation

Culture	Dye	Dye removal (%)	References
P. chrysosporium fungi	Coracryl violet	100	(Chander and Arora, 2007)
P. chrysosporium fungi	Coracryl pink	100	(Chander and Arora, 2007)
D. squalens fungi	Coracryl pink	100	(Chander and Arora, 2007)
T.versicolor ATCC 20869	Remozol blue	98	(Toh et al., 2003)
P. chrysosporium ATCC 24725	Remozol red	97	(Toh et al., 2003)
P. chrysosporium ATCC 24725	Remozol blue	95	(Toh et al., 2003)
Aspergillus niger fungi	Direct violet	92	(Abd El-Rahim et al., 2009)
Bacteria consortium SKB-II	Congo red	90	(Tony et al., 2009)
C. polyzona MUCL 38443	Acid blue 62	90	(Junghanns et al., 2008)
Trametes species CNPR 4783	Remazol blue	89	(Toh et al., 2003)
T.Versicolor ATCC 20869	Remozol red	85	(Toh et al., 2003)
Bacteria consortium SKB-I	Blue BCC	74	(Tony et al., 2009)
P. sanguineus fungi	Coracryl black	67	(Chander and Arora, 2007)

Lyophilised bacterial consortium	Blue Bezaktiv 150	62	(Khouni et al., 2012)
Trametes species CNPR 4801	Remazol blue	58	(Toh et al., 2003)
D. flavida fungi	Coracryl pink	53	(Chander and Arora, 2007)

2.2.2.2 Anaerobic Degradation

Anaerobic degradation process occurs in the absence of oxygen. Anaerobic digestion process is able to decompose complex organic compounds so that they can be further treated either aerobically or by other dye removal methods (Balamurugan et al., 2011). The biodegradation process consists of decolourization stage where the microorganism breaks the dye azo linkage of nitrogen double bond followed by second stage involves the degradation of the aromatic amines (van der Zee and Villaverde, 2005). The decolourization stage occurs usually under anaerobic conditions. Researchers investigated the use of bacteria for dye reduction under anaerobic conditions such as removal of Methyl orange (MO) and Naphthol green B (NGB) by *Shewanella oneidensis MR-1* (Cao et al., 2013) and Reactive red by *Halomonas variabilis and Halomonas glaciei* (Balamurugan et al., 2011). The disadvantages of this process include the need for further treatment under aerobic conditions and production of toxic by-products. Thus a combination of anaerobic and aerobic process is recommended for the biodegradation of textile dye and an overview of the combined process is presented in Fig 2.3.
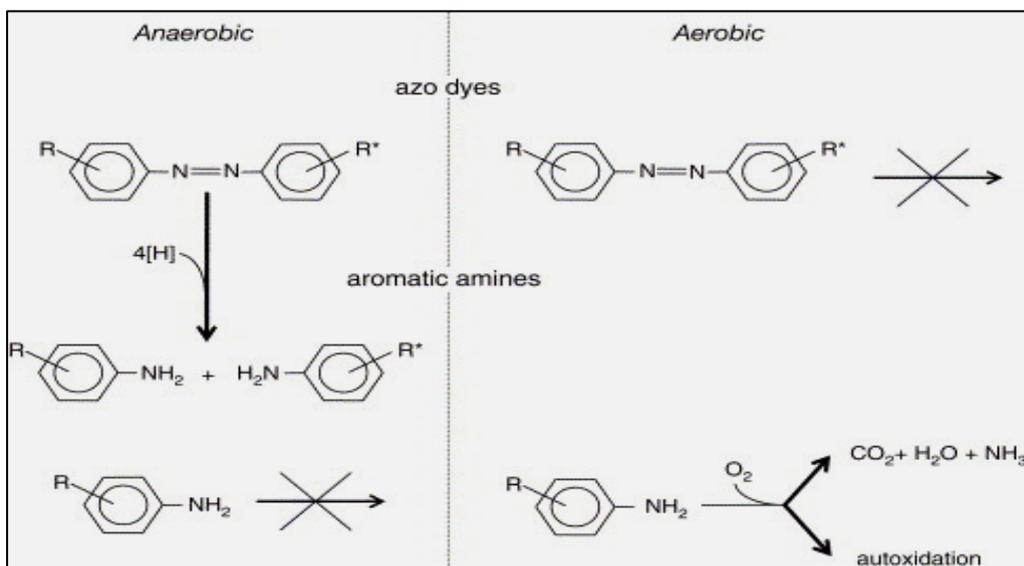
Figure 2.3 Overview of azo dye biodegradation under anaerobic and aerobic conditions (van der Zee and Villaverde, 2005)

2.2.3 Physicochemical methods
2.2.3.1 Ion Exchange

Ion exchangers are solid materials or liquid solutions which are able to absorb positively or negatively charged ions from aqueous electrolyte solutions and at the same time release other ions of equivalent amount into the aqueous solution (Haddad, 2005). Most synthesis resins are polymeric structures. The synthetic ion exchange materials can be classified into four main groups of solid membranes, solid sheets, organic solvent solution of liquid ion exchangers and solid particle (Haddad, 2005). Commercial anion exchange resins have the potential to possess excellent adsorption capacity and show high regeneration property for the removal and recovery of reactive dyes (Wu et al., 2008).

The applications of the ion exchange in the field of wastewater treatment, sugar and alcohol processing, pharmaceutical applications such as biological recovery and purification and hydrometallurgy industry (Rousseau, 1987) has been reported. Also, ion exchange is used to remove toxic dyes from wastewater such as removal of anionic dye Orange-G (Labanda et al., 2009) and cationic dye Methyl violet 2B (Wu et al., 2008). Ion exchange is a good method to separate toxic and soluble dyes from water effluents although the high capital cost associated with this process limited its use.

2.2.3.2 Membrane Filtration

Filtration is used to separate ion independent particles from solution. Some undesirable particles may pass into the filtrate solution depend on the pore size and thickness of the filter membrane. Filtration is used to remove dyes in the wastewater treatment. Microfiltration, ultrafiltration and nanofiltration are considered one of the economical and critical technologies in chemical and biochemical processing due to the availability of membranes with higher flux and lower process cost (Nandi et al., 2008). Nanofiltration membrane is a combination of reverse osmosis and ultrafiltration processes and it is used in the removal of textile dyes such as Methylene blue (Cheng et al., 2012) and cotton dye effluent (Avlonitis et al., 2008). The disadvantages of this process such as the high pressure needed, clogging of the membrane's pores and incapability to treat large volume of effluents limit its uses (Toor, 2010).

2.2.3.3 Electrokinetic Coagulation

Electrokinetic coagulation (EC) is a physio-chemical process used in the wastewater treatment. EC technique uses a direct current source between metal electrodes such as aluminium and iron immersed in water effluent to cause the dissolution of metal plates into wastewater (Aoudj et al., 2010). The metal ions form coagulated for particulates flocculating which cause metal hydroxides to precipitate and chemically adsorb dissolved contaminants (Chen, 2004). EC process provides a simple, reliable and low cost method for the removal of dyes such as direct red(81) from wastewater (Aoudj et al., 2010), reactive blue 140 (Phalakornkule et al., 2010) and disperse red (Merzouk et al., 2011). The main advantages of electro coagulation in compare to other conventional technique such as chemical coagulation are the compact of equipment used and no generation of secondary pollution (Phalakornkule et al., 2010). The disadvantages associated with this process are the need for further treatment by flocculation and filtration and high amount of sludge produced.

2.2.3.4 Adsorption

The process of adsorption involves the ions, atoms or molecules of the adsorbate to transfer and adhere to the surface of the adsorbent creating a thin film as shown in Fig 2.4. The adsorbate can be in gas, liquid or dissolved solute phases. There are two different types of adsorption: physical adsorption (physisorption) when the adsorbate adheres to the surface because of van der Waals interaction, and chemical adsorption (Chemisorption or Langmuir adsorption) if the adsorbate is chemically bound to the adsorbent's surface (Artioli, 2008). Adsorption reaction can be endothermic or exothermic. The adsorption process is basically controlled by both physical adsorption and chemical adsorption. The physical adsorption is controlled by physical forces such as Van der Waals forces, hydrophobicity, hydrogen bond, polarity, static interaction, dipole –dipole interaction, л- л interaction etc. In the physical adsorption, pollutants get accumulated on adsorbent surface by the above mentions interactions. The extend of adsorption depends on the nature of adsorbate such as molecular weight, molecular structure, molecular size, polarity and solution concentration. It is also depends on the surface properties of adsorbent such as particle size, surface area, surface charge etc. (Slejko, 1985).
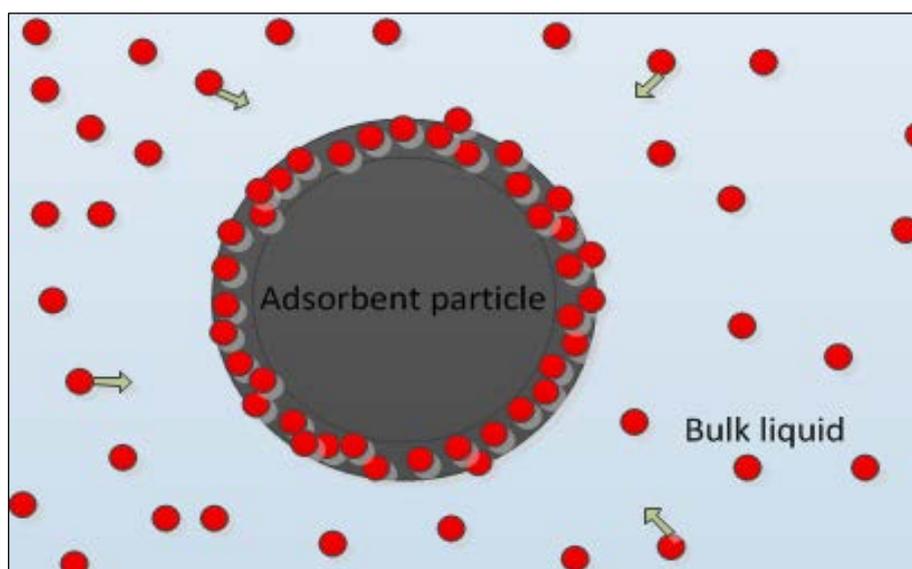
Figure 2.4 Adsorption process where the molecules of the dyes migrate
from the bulk solution to the surface of the adsorbent

Adsorption process is widely used in various industrial effluent treatments by commercial activated carbon. It is a very effective separation technique and now it is considered to be superior to other techniques for water treatment in terms of initial cost, simplicity of design, ease of operation and insensitive to toxic substances (EI-Latif et al., 2010; Sen et al., 2011). Commercial activated carbon (Purkait et al., 2007), mineral (Hernández-Montoya et al., 2013), Clay (Errais et al., 2012), agricultural solid wastes (Deniz and Karaman, 2011; Somasekhara Reddy et al., 2012) and agricultural solid waste based activated carbon (Auta and Hameed, 2013; Poinern et al., 2011) are used as adsorbents in dye removal from aqueous solution. Although commercial activated carbon (AC) is the most widely used adsorbent with great success, the use is restricted due to high cost and difficulties in regeneration. Therefore, recent trend of research is to develop alternative cost effective and nonconventional potential adsorbents in the removal of dye from its aqueous solution.

It is evident that natural materials, waste materials from industry and agriculture, inorganic clay and oxides and bentonite are interesting alternatives to replace commercial activated carbon. The efficiency of adsorption process depends on the physical and chemical properties of the adsorbents and adsorbate. Adsorbent's selectivity is based on the adsorption capacity, surface area, availability and total cost. Also, there are various factors such as solution pH, initial dye concentration, adsorbent dose, contact time and temperature which affect the rate of adsorption. It is reported that the adsorption capacity increased with increases in initial dye Concentration and contact time (Deniz and Karaman, 2011; Sen et al., 2011). Some alternative cost effective alternative adsorbents in the removal of dyes are presented below:

2.2.4 Raw and treated agricultural solid wastes in the removal of dyes

The application of adsorption is used widely in wastewater treatment. The high cost associated with use and regenerate of commercial activated carbon (CAC) leads the researchers to investigate and develop low-cost agricultural waste adsorbents. Agricultural wastes usually have high molecular weight due to the presence of lignin, cellulose and hemicelluloses components (Salleh et al., 2011). These solid wastes are renewable sources and they are available in large quantities with little or no value.

The utilization of these large amounts of solids wastes as adsorbents poses the double benefits such as effective wastewater treatment and waste management. Various cost effective adsorbents are reported in the removal of textile dyes from wastewater such as eucalyptus wood, Organo-attapulgite, pellets of trametes versicolour, pine cone, palm shell etc. (Mahmoodi et al., 2011). Table 2.5 presented the compilation results on various agricultural by-product adsorbent in the removal of dyes from aqueous solution.

Table 2.5 Compilation results on the removal of various dyes by various raw and treated agricultural by-product waste adsorbent

Adsorbents	Dyes	Adsorption capacity q_{max} (mg/g)	Reference
Eucalyptus wood	Congo red	66.7	(Mane and Vijay Babu, 2013)
Date Stones	Methylene blue	43.5	(Belala et al., 2011)
Palm-Trees	Methylene blue	39.5	(Belala et al., 2011)
Palm shell	Reactive red 141	14.0	(Sreelatha et al., 2011)
Palm shell	Reactive blue 21	24.7	(Sreelatha et al., 2011)
Acid treated papaya seed	Methylene blue	250	(Nasuha et al., 2011)
Papaya seed	Methylene blue	200	(Nasuha et al., 2011)
Papaya seed	Congo red	71	(Nasuha et al., 2011)
Acid treated papaya seed	Congo red	59	(Nasuha et al., 2011)

Peanut hull	Reactive black 5	55.6	(Tanyildizi, 2011)
Pine cone	Methylene blue	109.9	(Sen et al., 2011)
Pine tree leave	Methylene Blue	126.6	(Yagub et al., 2012)
Neem bark	Malachite green	0.36	(Srivastava and Rupainwar, 2011)
Mango bark	Malachite green	0.5	(Srivastava and Rupainwar, 2011)
Pine cone	Acid Black 26	62.9	(Mahmoodi et al., 2011)
Pine cone	Acid Green 25	43.3	(Mahmoodi et al., 2011)
Pine cone	Acid Blue 7	37.4	(Mahmoodi et al., 2011)
Pine tree leaves	Basic red 46	71.9	(Deniz and Karaman, 2011)
palm kernel fiber	Crystal violet	78.9	(El-Sayed and Owes, 2011)
palm kernel fiber	Methylene blue	95.4	(El-Sayed and Owes, 2011)
Organo-attapulgite	Congo red	189.4	(Chen and Zhao, 2009)
Garlic peel	Methylene blue	142.9	(Hameed and Ahmad, 2009)
Rice husk	Indigo Carmine	65.9	(Lakshmi et al., 2009)

Yellow Passion fruit	Methylene blue	44.7	(Pavan et al., 2008)
Soy meal hull	Direct red 81	120.5	(Arami et al., 2006)
Soy meal hull	Acid blue 92	114.9	(Arami et al., 2006)
Soy meal hull	Acid red 14	109.9	(Arami et al., 2006)
Rice husk	Methylene blue	40.6	(Vadivelan and Kumar, 2005)
Sugar cane bagasse	Congo red	38	(Zhang et al., 2011)

2.2.4.1 Pine cone as an agricultural by-product adsorbent

Raw and treated pine cone biomass was utilized as effective adsorbents in the removal of Congo red (CR) dye in this study. Pine tree cone (P. radiate) is a low-cost agricultural waste available throughout the world. Large quantities of pine cone are produced annually as agricultural by-product throughout the world. The ovulate cone is the well-known cone of the pinus and other conifers. Chemical decomposition of pine cone indicates the presence of significant amounts of glucose (derived from cellulose), lignin, ethanol/toluene extractives and small quantity of mannose, galactose, and xylose which are derived from hemicelluloses (Buyuksari et al., 2010; Gonultas, 2008). Lignin is used to strengthen and protect the cell wall from chemical, physical, and biological attacks thus pine cone may have low carboxyl group content with high lignin concentrations (Ofomaja et al., 2009). Researchers have focused on the use of raw and modified pine cone as an economical and effective adsorbent in dye removal such as Methylene blue (Sen et al., 2011), Acid Black 26, Acid Green 25 and Acid Blue 7 (Mahmoodi et al., 2011) removal from aqueous solution and inorganic removal such as copper ions (Ofomaja et al., 2009) and phosphate ion (Benyoucef and Amrani, 2011).

2.2.5   Biomass based activated carbon in dye removal

Activated carbon (AC) is an extremely adaptable material with a high pore volume and a large surface area. AC is mainly generated from non-renewable source such as coal. The effectiveness of this versatile adsorbent is due to its external surface area, pores structure, high adsorption capacity and high degree of surface reactivity. Micropores AC are responsible for the active sites for dyes or ions adsorption while mesopores AC act as transportation routes (Skodras et al., 2007).

Activated carbon is classified into granular and powder forms. Activated carbon has various effluent treatment applications such as in oil and gas, food, chemical industries, solvent recovery, air pollution control and in hydrometallurgy industry for the recovery of gold and silver (Sugumaran et al., 2012). In the recent years, growing research interest is focusing on the agricultural solid residual biomass based AC. Biomass may offer inexpensive and renewable additional source of AC. These waste materials have little or no economic value and often present a disposal problem (EI-Latif et al., 2010). Therefore, there is a need to valorise these low cost by-products. This conversion into AC will add economic value, help to reduce the cost of waste disposal and provide a potentially inexpensive alternative into existing commercial activated carbons. Biomass based activated carbon is synthesized by physical or chemical modification of the biomass solid waste at high temperature profile. Previous studies on the use of CAC and biomass based AC in the removal of dyes are presented in Table.2.6.

2.2.5.1 Biomass based activated carbon synthesis by chemical activation

 Reagents such as phosphoric acid, zinc chloride, potassium hydroxide and sodium hydroxide are used in the chemical activation of carbon under different conditions (Fathy et al., 2012; Tay et al., 2009). Alkali hydroxides and Zinc chloride are not preferred due to their corrosive natures and the harmful effects associated with the disposal thus potassium carbonate and phosphoric acid are used (Gurten et al., 2012). Potassium carbonate is used as a food addictive thus it is preferred as an activating agent due to environmental and economic concerns. AC production depends on the precursor properties, reagent used, impregnation ratio, activation time and temperature.

Chemical activation has more advantages than physical activation because it is carried out in single step i.e. carbonization and activation are united at relatively lower temperature operation and higher yield (Fathy et al., 2012; Tay et al., 2009). There are many reported results on the use of chemically activated biomass based AC (Auta and Hameed, 2013; Fathy et al., 2012; Foo and Hameed, 2011b; Gurten et al., 2012) and its effective adsorptive capacity towards dye removal.

2.2.5.2 Biomass based activated carbon by physical Activation

Physical activation method is used to improve the porosity of AC by exposing carbonaceous material to carbon dioxide gas, air mixture or steam under high temperature profile. An abundance of pores, particularly micropores, were generated after activation due to the oxidation of partial carbon atoms by carbon dioxide gas and steam (Liu et al., 2013). Physical activation involves carbonization of a carbonaceous material followed by activation of the resulting charcoal at high temperature in the presence of suitable oxidizing gases where oxidization agents such as steam has shown the best potential for producing activated carbons with high surface area and good pore ratio (Şahin and Saka, 2013). Biomass based activated carbon (AC) through physical activation and its adsorptive behaviour has been reported by various researchers (Ahmad and Kumar, 2010; de Luna et al., 2013; Poinern et al., 2011).

Table 2.6 Removal of dyes by Commercial activated carbon (CAC) and biomass based activated carbon (AC)

Material	Dye	Adsorption capacity q_{max}(mg/g)	Reference
Commercial activated carbon	Acid Red 97	52	(Gómez et al., 2007)
Commercial activated carbon	Acid Orange 61	169	(Gómez et al., 2007)
Commercial activated carbon	Acid Brown 425	222	(Gómez et al., 2007)
Commercial activated carbon	Congo red	300	(Purkait et al., 2007)
Commercial activated carbon	Remazol red B	145	(Uğurlu et al., 2008)
Bael shell based AC	Congo red	98	(Ahmad and Kumar, 2010)
Waste tea based AC	Acid blue 29	596	(Auta and Hameed, 2013)
Bamboo based AC	Methylene blue	454	(Hameed et al., 2007)
Cattail based AC	Neutral red	192	(Shi et al., 2010)
Cattail based AC	Malachite green	196	(Shi et al., 2010)
Pomelo skin based AC	Acid blue 15	444	(Foo and Hameed, 2011a)
Pomelo skin based AC	Methylene blue	501	(Foo and Hameed, 2011a)
Date stone based AC	Methylene blue	316	(Foo and Hameed, 2011b)

Olive stone based AC	Remazol red B	9	(Uğurlu et al., 2008)
Rice husk based AC	Methylene blue	442	(Foo and Hameed, 2011c)
Rambutan peel based AC	Malachite green	329	(Ahmad and Alrozi, 2011)
Rubber seed coat based AC	Malachite green	227	(Hameed and Daud, 2008)
Myrtus communis based AC	Congo red	19	(Ghaedi et al., 2012)
Pomegranate based AC	Congo red	10	(Ghaedi et al., 2012)

2.2.6 Clay Minerals

Clays are natural aluminosilicates with the presence of small amount of metal ions and organics compounds. Clays are available as the colloidal fraction in soils, sediments, rocks and water. The use of clays is considered to be a good adsorbent because of its large surface area, high cation exchange capacity, chemical and mechanical stability and layered structure (Aries and Sen, 2009). Also, they are abundantly available at lower cost in compare to other high cost adsorbents such as commercial activated carbon.

Natural clays are usually used for the removal of cationic dyes such as methylene blue due to their natural negative charged; however modifications to the surface of clay using surfactants can change the surface charge of clay from negative to positive (Errais et al., 2012). These modifications enhance the adsorption of anionic dyes. Researchers studied various type of clays in the removal of textile dyes and metal ions such as Reactive red 120 by raw clay (Errais et al., 2012), Brilliant green dye by red clay (Rehman et al., 2013), Congo red by sodium bentonite, kaolin and zeolite (Vimonses et al., 2009), zinc ions by kaolin (Aries and Sen, 2009) and Methylene blue by montmorillonite clay (Almeida et al., 2009). Clay minerals are classified into nine groups and they are presented in Fig 2.5.
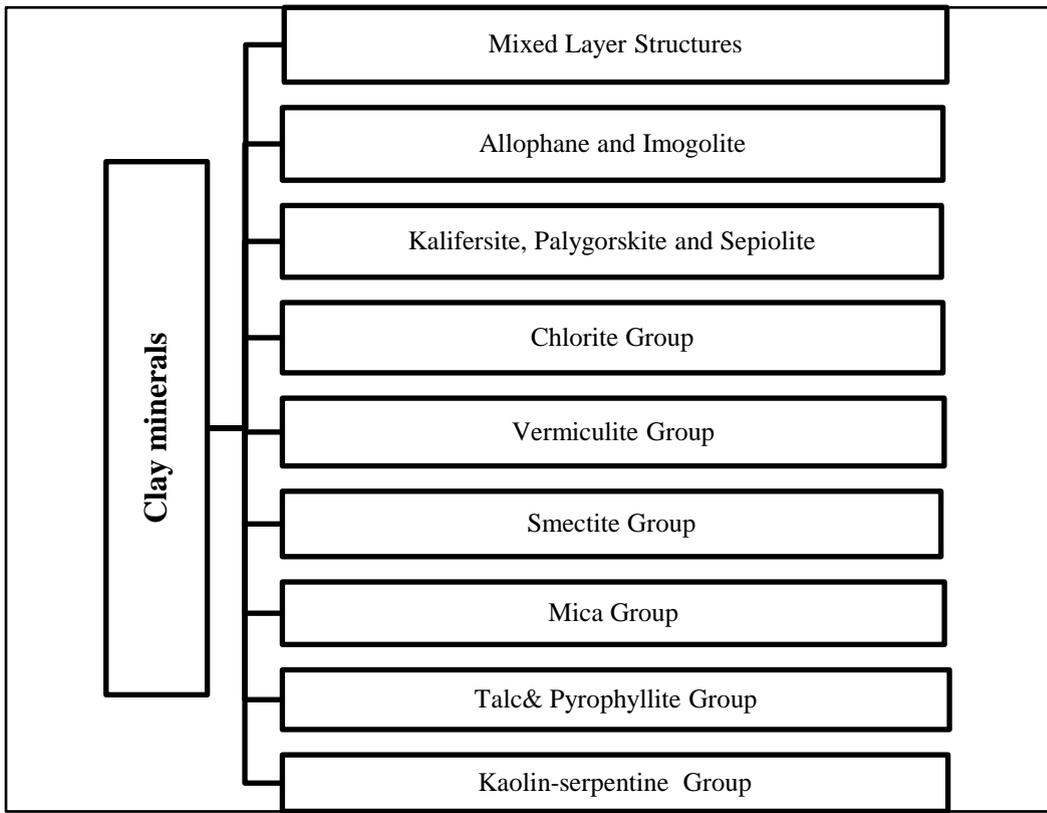
Figure 2.5 Classification of Clays (Brigatti et al., 2013)

2.3 Adsorption Theory

2.3.1 Adsorption kinetic

In order to investigate the mechanism of adsorption and the transient behaviour of dye adsorption process, adsorption kinetics were evaluated and analysed using Pseudo-first-order, Pseudo-second-order , Elovich and Intra particles diffusion models by various researchers.

2.3.1.1 Pseudo-first-order model

Pseudo -first-order is also called Langergren kinetic model (Lagergren, 1898) and it is used to analyse the kinetic behaviour of liquid–solid adsorptive system (Tseng et al., 2010). The general form and integral form of this model are given below (Chatterjee et al., 2009; Tseng et al., 2010).

$$\frac{dq_t}{dt} = k_f(q_e - q_t) \tag{2.4}$$

The linearized form of equation (2.4) is as follows:

$$\text{Log } (q_e - q_t) = \log q_e - \frac{k_f}{2.303} t \tag{2.5}$$

Where q_t (mg/ g) is the amount of dye adsorbed at time t, q_e (mg/g) is the adsorption capacity at equilibrium. The adsorption rate constant k_f (min^{-1}) and q_e (mg/g) were calculated from the slope and intercept of the linear plot of log (q_e –q_t) against (t).

2.3.1.2 Pseudo-second-order model

Pseudo-second-order model is developed in 1999 (Ho and McKay, 1999). The general form and integral form of Pseudo-second-order model is given below respectively (Chatterjee et al., 2009; Fathy et al., 2012)

$$\frac{dq_t}{dt} = k_s (q_e - q_t)^2 \tag{2.6}$$

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{k_s\, q_e^2} \qquad\qquad (2.7)$$

Equation (2.7) presented, the integral form of pseudo second order where the boundary conditions applied at t =0 to t = t and q= 0 to q= q_t. The pseudo second order rate constant k_s (g/mg.min) and q_e (mg/g) can be calculated from the slope and intercept of the linear plot t/q_t against (t).

2.3.1.3 Elovich model

Elovich equation was first developed and proposed in 1934 (Roginsky and Zeldovich, 1934). It is used to describe the chemical adsorption mechanism in nature for systems with heterogeneous adsorbing surfaces(Gómez et al., 2007)

$$q_t = \frac{1}{y} \ln t + \frac{1}{y} \ln(x.\,y) \qquad\qquad (2.8)$$

Where (x) and (y) are constants and present the initial sorption rate (mg/(g.min)) and the extent of surface coverage (g/mg) respectively. The constant's values were obtained from the slope and intercept of the linear equation of the plot q_t against ln t.

2.3.1.4 Intra particles diffusion model

Intra-particle diffusion model is used for identifying the adsorption mechanism for design purpose. The most adsorption processes, the uptake varies almost proportionately with t0.5 rather than with the contact time(EI-Latif et al., 2010)

$$q_t = k_{id}\, t^{0.5} + C \qquad\qquad (2.9)$$

$$t^{0.5} = 0.03\, r_0^{\,2}/D_p \qquad\qquad (2.10)$$

Where k_{id} (mg/g min$^{0.5}$) is the intra-particle diffusion rate constant and can be calculated from the slope of the linear equation of the plot q_t against $t^{0.5}$. D_P is the diffusion coefficient value in cm^2/s.

2.3.2 Adsorption isotherm
2.3.2.1 Freundlich isotherm

Freundlich model is developed in 1906 to explain how adsorption takes place on heterogeneous surfaces (Freundlich, 1906). The linearised format of Freundlich isotherm model is shown below:

$$\ln q_e = \frac{1}{n} \ln C_e {}_{+} \ln k_f \qquad\qquad (2.11)$$

Where qe (mg/g) is the amount of dye adsorbed at equilibrium time, C_e is equilibrium concentration of dye in solution (mg/L). The adsorption capacity of the system, K_f and the heterogeneity factor 1/n can be calculated from slope and intercept of the linear plot of ln q_e against ln Ce. The other Freundlich constant *n* is a measure of deviation from linearity of the adsorption and used to verify types of adsorption. It is suggested that if *n* is equal to unity, the adsorption is linear. Further, *n* below unity indicates that adsorption is a chemical process; whereas, *n* above unity is associated with a favourable adsorption and a physical process (Salleh et al., 2011; Sen et al., 2011; Vimonses et al., 2009).

2.3.2.2 Langmuir isotherm

Langmuir isotherm model was developed in 1916 (Langmuir, 1916) to explain how adsorption takes place on homogeneous surfaces. The linearized form of various Langmuir models are listed in Table 2.7

Table 2.7 Various types of Langmuir isotherm model

Type	Equation	Plot parameters	Equation
I	$\dfrac{C_e}{q_e} = \dfrac{1}{K_L\, q_e} + \dfrac{C_e}{q_m}$	$\dfrac{C_e}{q_e}$ versus C_e	2.12
II	$\dfrac{1}{q_e} = \dfrac{1}{k_L\, q_m\, C_e} + \dfrac{1}{q_m}$	$\dfrac{1}{q_e}$ versus $\dfrac{1}{C_e}$	2.13
III	$q_e = q_m - \left(\dfrac{1}{K_L} \dfrac{q_e}{C_e} \right)$	q_e versus $\dfrac{q_e}{C_e}$	2.14
IV	$\dfrac{q_e}{C_e} = K_L q_m - K_L q_e$	$\dfrac{q_e}{C_e}$ versus q_e	2.15

The maximum adsorption capacity q_m (mg/g) and Langmuir constant related to the energy of adsorption K_L (L/mg) are calculated from the slope and intercept of the linearized forms of the plot parameters as shown above in Table 2.7. The separation factor (R_L) is a dimensionless used to investigate the adsorption system feasibility at different initial dye concentration and it can be calculated from equation (2.16).

$$R_L = \frac{1}{1 + (K_L\, C_o)} \qquad\qquad (2.16)$$

The initial dye concentration is defined as C_o (mg/L). Favourable adsorption process takes place if R_L value is $0 < R_L < 1$ (Kaur et al., 2013).

2.3.2.3 Temkin isotherm

Temkin isotherm model is developed in 1940 (Temkin and Pyzhev, 1940) and used to describe the adsorbate and adsorbent indirect interactions as well as the sorption energy.

$$q_e = B_1 \ln K_T + B_1 \ln C_e \qquad\qquad (2.17)$$

Where R is universal gas constant (8.314 J/ (mol K)) and T (K) is absolute temperature. Temkin constant K_T (L/mg) and B_1 presented the equilibrium binding energy and the heat of adsorption respectively. These constants can be calculated from the slope and intercept of the linear equation of the plot where q_e versus $\ln C_e$.

2.4 Thermodynamic study

Thermodynamic studies used to investigate the temperature effect on adsorption capacity. Gibb's free energy change (ΔG^0), enthalpy change (ΔH^0) and change in entropy (ΔS^0) were calculated by using the following equations (Arias and Sen, 2009; Milonjić, 2007) respectively.

$$\text{Log}\left(\frac{q_e}{C_e}\right) = \frac{\Delta S^\circ}{2.303\,R} + \frac{-\Delta H^\circ}{2.303\,RT} \tag{2.18}$$

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ \tag{2.19}$$

Where q_e is the solid phase concentration at equilibrium (mg/L), Ce is equilibrium concentration in solution (mg/L), T is temperature in K and R is the gas constant (8.314 J/mol K). The enthalpy change (ΔH^0) and change in entropy (ΔS^0) values are calculated from the slope and intercept of the linear Van't Hoff plot of Log ($\frac{q_e}{C_e}$) versus 1/T. Gibb's free energy (ΔG^0) is calculated as per equation (2.19). The adsorption process is usually considered as a physical adsorption if the enthalpy change (ΔH^0) < 84 kJ .mol $^{-1}$ and as chemical adsorption process when the enthalpy change lies between 84 and 420 kJ .mo^{-1} (Yaneva and Georgieva, 2012). Also, the negative value of (ΔH^0) indicates an exothermic adsorption process where positive value of (ΔH^0) indicates an endothermic adsorption process.

2.5 Effect of various physico-chemical process parameters on adsorption

2.5.1   Effect of solution pH

The pH of a solution is a measure of molar concentration of hydrogen ions. Acidic solution occurs when the solution pH < 7 where a solution pH > 7 indicates a basic solution. The change in solution pH is an important parameter for solute adsorption because of change in surface characteristics of adsorbent and change in chemistry of dye. Thus, the adsorption capacity of dye depends on the pH of the solution. Low pH solution generally results in an increase in the percentage of anionic dye removal because of the electrostatic attraction between anionic dye and the positive surface charge of the adsorbent (Salleh et al., 2011). At higher solution pH, electrostatic repulsion is found between the negatively charged surface and dye molecules, thus decreasing the adsorption capacity and percentage removal of anionic dyes (Foo and Hameed, 2011a).

From previous studies, the optimum solution pH on the removal of anionic dyes such as Congo red by nut shells charcoal was at pH of 2 (Kaur et al., 2013), Acid blue 15 by Pomelo skin at pH of 2 (Foo and Hameed, 2011a) while Reactive blue by chitosan at pH of 4 (Sreelatha et al., 2011).

Furthermore, high solution pH solution results in an increase in the percentage of cationic dye removal because the positive charge on the solution interface will decrease and the adsorbent surface appears negatively charged (Salleh et al., 2011). From previous studies, the optimum solution pH on the removal of cationic dyes such as Methylene blue by pine tree leave was at pH of 9.2 (Yagub et al., 2012) and Basic red 46 by Pine tree leaves at pH of ~8 (Deniz and Karaman, 2011)

2.5.2 Effect of adsorbent dose

The effectiveness of various adsorbent doses on both anionic and cationic dyes removal is reported by many researchers to determine the most economical minimum dosage. According to (Salleh et al., 2011), the dye removal percentage is increasing with the increase of the adsorbent dosage due to the increase of sorption active sites at the adsorbent surface. It was reported that the amount of Methylene blue dye removal by pine cone was increased from 62.9% to 97.2% with the increase of adsorbent mass from 0.01 to 0.05 g (Sen et al., 2011). Also, that the amount of Indigo carmine dye removal by rice husk was increased from 36% to 96% with the increase of adsorbent dose from 2-20 g/L (Lakshmi et al., 2009). Furthermore, according to (Kumar et al., 2010), the amount of Congo red dye removal also increased from 56.3% to 99.3% for an increase in adsorbent dose from 5 to 30 g/L.

2.5.3 Effect of temperature

The temperature of the solution plays an important role on the adsorption capacity. The correspondence of dye molecule's movement to the increase in the solution temperature will determine the adsorption process (Senthilkumaar et al., 2006). If the adsorption capacity increases with the increase in temperature then the adsorption is an endothermic process. The dye removal percentage of various dyes such as Congo red by modified hectorite (Xia et al., 2011), Congo red by organo-attapulgite (Chen and Zhao, 2009) and Reactive red 195 by *Pinus sylvestris* were increased with the increase of solution temperature. However, the dye removal of Methylene blue by pine cone (Sen et al., 2011) and Methylene blue by montmorillonite clay (Almeida et al., 2009) were reported to decrease with the increase of solution temperature therefore the adsorption process is an exothermic process.

2.5.4   Effect of initial dye concentration and contact time

The effect of the initial dye concentration plays a significant role in the amount of dye adsorbed q_t (mg/g) and percentage of dye removal. Generally, increasing the initial dye concentration leads to decrease the percentage of dye removal which may be due to the saturation of adsorption sites on the adsorbent surface (Salleh et al., 2011). The amount of dye adsorption q_t (mg/g) increases with increasing contact time at all initial dye concentrations as reported by various researchers (Foo and Hameed, 2011a; Purkait et al., 2007; Sen et al., 2011). This is so because the initial dye concentration provides the driving force to overcome the resistance to the mass transfer of dye between the aqueous and the solid phase.

2.6 Design of single-stage batch adsorber from isotherm data

Adsorption isotherms can be used to predict the design of single batch adsorption system (Sen et al., 2011). Due to lack of extensive experimental data, empirical design procedures based on adsorption isotherm studies are the most common method to predict the adsorber size and performance. The design objective is to reduce initial dye concentration of C_0 to C_t (mg/L) for which total dye solution is V (L). The schematic diagram for a single-stage adsorption process is shown as Fig 2.6 as per methods described (Vadivelan and Kumar, 2005). The mass balance for the single-stage operation under equilibrium is presented as in equation (2.20).

$$V\,(C_0 - C_e) = m\,(q_e - q_0) = m.\,q_e \qquad\qquad (2.20)$$

Freundlich and Langmuir adsorption isotherm data are usually used to utilise and design a single-stage batch adsorption system. The amount of added adsorbent m (g) and the solute loading increasing from q_0 (mg/g) to q_e (mg/g) where $q_0 = 0$.
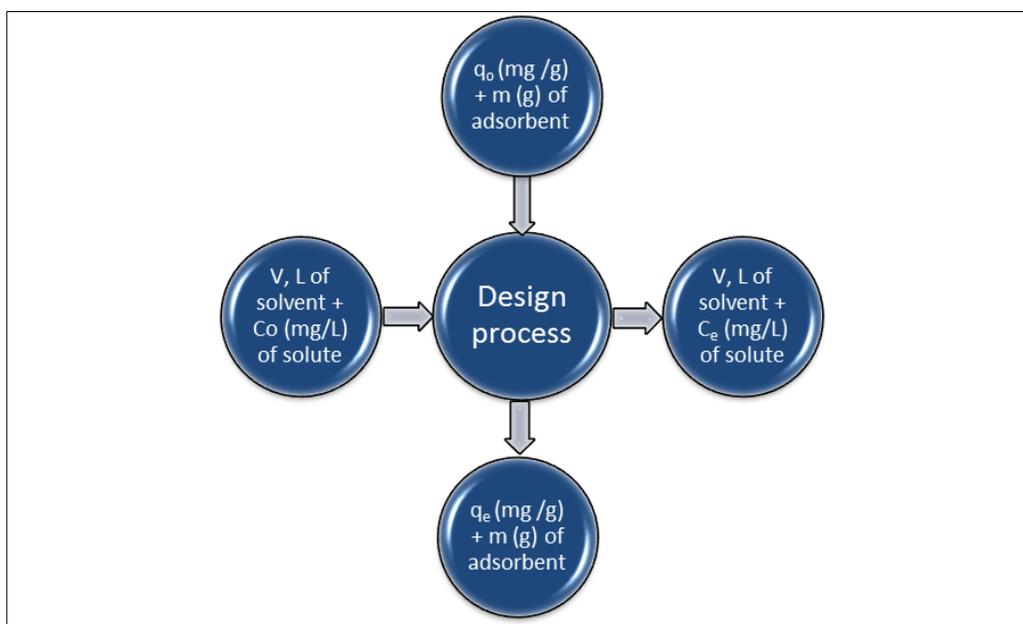
Figure 2.6 Schematic diagram of a single-stage batch adsorber

2.7 Desorption process

Desorption studies help to elucidate the mechanism and recovery of the adsorbate and adsorbent. Regeneration is the most significant aspect of the adsorption study as it helps to minimise the waste and recovery of the adsorbent for further use (Jain et al., 2010). Desorption rate is proportional to the driving force where desorption kinetics study is important for the contaminant transport modelling purpose (Salleh et al., 2011). Previous desorption studies are carried out to determine the feasibility of the dye removal process of dyes such as removal of Naphthol Yellow S from activated carbon (Jain et al., 2010), Methylene blue from pine cone powder (Sen et al., 2011) and Congo red from jujuba seed (Somasekhara Reddy et al., 2012).

2.8 Summary and Recommendation

Wastewater effluents contain synthetic dyes which may cause a potential hazard to the environment. These dyes are purged from multiple sources such as textile, cosmetic, paper, leather, rubber and printing industries(Chatterjee et al., 2009). There are various types of dyes such as acid dyes, reactive dyes, basic dyes, azo dyes, direct dyes, vat dyes and disperse dyes (Demirbas, 2009). The total dye consumption in textile industry worldwide is more than 10,000 tonnes per year and approximately 100 tonnes per year of dyes are discharged into water streams (Gupta et al., 2013). Therefore, many researchers have been studied the effectiveness of dyes removal from aqueous solution by various adsorbents since last two decades. Different separation techniques have been used for the treatment of dye-bearing wastewater such as physiochemical, chemical and biological techniques. All dye separation techniques have their own limitation in terms of design, operation efficiency and total cost. However, adsorption process is a very effective separation technique and it is considered to be superior to other techniques for water treatment in terms of initial cost, simplicity of design, ease of operation and insensitive to toxic substances (EI-Latif et al., 2010; Sen et al., 2011). Commercial activated carbon is used widely as an adsorbent in the removal of these dyes with great success. Commercial activated carbon is made mainly from non-renewable source such as coal or from coconut shell. However, commercial activated carbon treatment processes have clear disadvantages including the high cost and difficulties with regeneration. Therefore, researchers are focusing on the production of cheap and renewable adsorbents such as the use of agricultural solid waste and biomass based activated carbon. Basically, the development of the adsorption process requires further investigation in the direction of low cost adsorbents for the dye removal from its aqueous phase. This chapter provides extensive literature information about dyes, its classification and toxicity together with various treatment methods and dye adsorption characteristics of several non-conventional cost effective adsorbents. An extensive test of various adsorbents such as natural raw materials, wastes from industry agricultural by-products and biomass based activated carbon in the removal of dyes have been compiled here. Further adsorptive mechanism and kinetic studies under various process conditions are required to find out the effectiveness of adsorbents;

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particularly biomass based novel adsorbent in the removal of dye which is undertaken in this study.

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3. CHAPTER THREE- MATERIALS, CHARACTERISATION AND EXPERIMENTAL METHODS

3.1 Adsorbents

3.1.1 Collection of raw pine cone and its preparation

Pine tree cones (*P. radiate*) were obtained from the campus of Curtin University Perth Western Australia and it was collected between February and April of 2011. The cones were washed several times with distilled water to remove dust, dirt and soluble impurities. The cones were placed in the oven to dry at temperature of 80˚C for 24 hours. The dried pinecone biomass was ground in a domestic blender to a fine powder as shown in Fig. 3.1 and passed through British Standard Sieves (BSS) of 150 µm and 106 µm. The powdered biomass was stored in an airtight plastic container and used for analysis, adsorption experiments and further treatments and modifications.

Figure 3.1 Preparation of raw pine cone powder

3.1.2 Acid modified pine cone powder

Acid modified pine cone powder adsorbent was prepared by mixing 25 g of raw pine cone powder (150 µm) with 250 ml of 0.1 M hydrochloric acid (HCL) solution. The whole reaction mixture was placed in a glass bottle and stirred in a magnetic stirrer at speed of 120 rpm as shown in Fig. 3.2 for a period of 20 hours at room temperature. The final mixture was filtered and repeatedly washed with distilled water to remove excess presence of hydrochloric acid ions. The washed powder was oven dried overnight at temperature of 50°C and then stored in an airtight plastic container for future use.
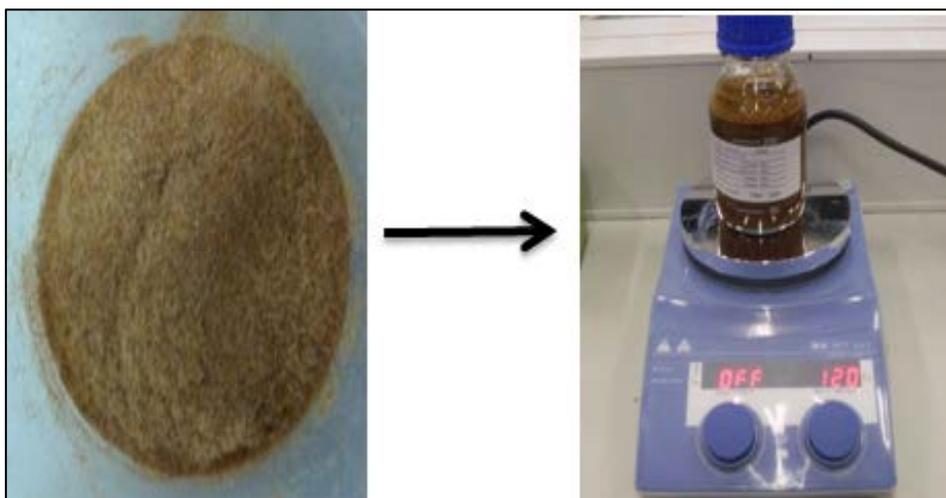
Figure 3.2 Preparation of acid modified pine cone powder

3.1.3 Preparation of pine cone biomass based activated carbon

Pine cone biomass based activated carbon is prepared by mixing various concentration of phosphoric acid (H_3PO_4) such as 0.5M, 1M, 3M and 14.7M with raw pine cone powder at an impregnation ratio of 1:2 respectively for 3 hrs under different temperature profiles. The mixture is placed in a horizontal tube furnace with constant flow of nitrogen gas to avoid oxidation. Full synthesized pine cone biomass based activated carbon procedure is explained in chapter 5.

3.2 Chemicals

3.2.1 Congo red chemical

The anionic dye, Congo red (CR) was selected as the model adsorbate in this study. It has a formula of $C_{32}H_{22}N_6Na_2O_6S_2$ and molecular weight of 696.66 g/mol. The analytical grade was obtained from Sigma Aldrich with 99.9% purity. A stock solution of 1000 mg/L was prepared by dissolving 1000 mg powder of CR in 1000 ml of ultra-pure water. Various dye concentrations such as 20, 30, 40, 50 and 60 mg/L were prepared by diluting the stock solution with ultra-pure water to give the appropriate concentration of the working solutions. Chemical risk assessment is carried out to identify and control any risk associated with the use of Congo red (CR) dye in this study. The required data are obtained from Chem Alert and Safety Data Sheet (SDS).The pH of the solutions was adjusted by addition of 0.5 M phosphoric acid, 0.1 M hydrochloric acid or 0.1 M sodium hydroxide solutions and measured by Adwa pH meter. Congo red solution changes colour to purple/ dark blue at low pH and to red at alkaline and neutral solutions as shown in Fig.3.3.

Figure 3.3 effect of pH solution on Congo red dye colour

The SP-8001 UV/VIS (V-670) spectrophotometer was used to measure the concentration of Congo red dye in solution. The concentration of residual dye was measured at $Λ_{max}$. The maximum adsorption for the dye solution was measured at $Λ_{max} = 500$ nm Fig 3.4 using UV/VIS spectrometer Fig 3.5. The calibration curve was plotted between the absorbance and concentration of the dye solution to obtain the linear calibration equation as shown in Fig 3.6. The concentration of the unknown solution was measured by using this calibration plot shown in Figure 3.4.
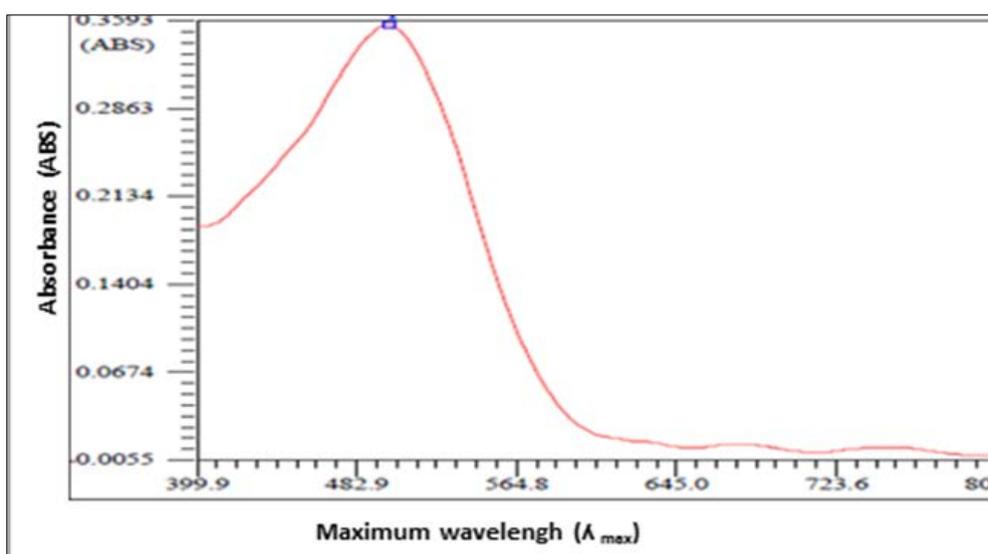
Figure 3.4 Maximum peak of Congo red is measured using Spectrophotometer

Figure 3.5 SP-8001 UV/VIS (V-670) Spectrophotometer
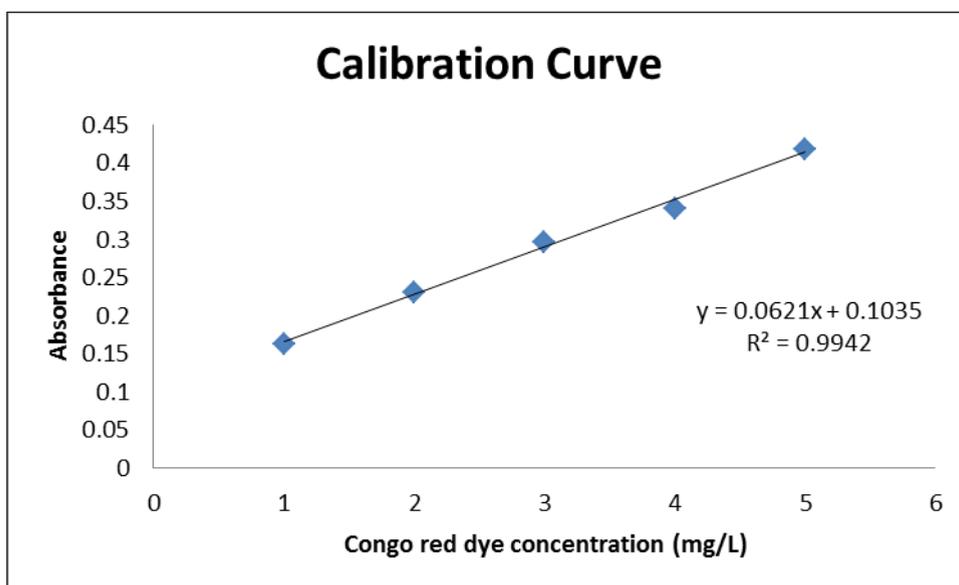
Figure 3.6 the Calibration curve of initial Congo red dye concentrations

3.2.2 Hydrochloric acid

Hydrochloric acid (HCL) is a highly corrosive solution used in this study to adjust the pH of the working solution. Also, it is used to chemically modify the raw pine cone powder. A stock solution of hydrochloric acid 37.5% is obtained from Sigma Aldrich. In order to prepare 0.1M hydrochloric acid solution, 8.2 ml of 37.5% concentrated HCL is added to 991.8 ml ultra-pure water to make 1000 ml of the required solution. The required data are obtained from Chem Alert and Safety Data Sheet (SDS).

3.2.3 Phosphoric acid

Phosphoric acid (H_3PO_4) is used as an activation agent in the synthesis of pine cone based activated carbon. Also, it is used to adjust the solution pH of Congo red dye. A stock solution of 85%   phosphoric acid (14.7 M) is obtained from Asia pacific specialty chemicals limited. Further dilutions are required to prepare 1 L of 0.5M, 1M and 3M of phosphoric acid solution as shown in Table. 3.1. Chemical risk assessment is carried out to identify and control any risk associated with the use of phosphoric acid in this study. The required data are obtained from Chem Alert and Safety Data Sheet (SDS).

Table 3.1 Different phosphoric acid concentration prepared from a stock solution

H_3PO_4 (M)	Amount required to form 1L phosphoric acid from stock solution (ml)
0.5	34.0
1	68.0
3	204.1
14.7	No further dilution required

3.2.4   Sodium hydroxide

Sodium hydroxide (NaOH) is a colourless solution. It is highly corrosive solution with a solution pH of 13 even at low concentration such as 0.1 M. In this study sodium hydroxide solution is obtained from Orica (Australia) and used to adjust the pH of Congo red dye solution. Chemical risk assessment is carried out to identify and control any risk associated with the use of sodium hydroxide in this study. The required data are obtained from Chem Alert and Safety Data Sheet (SDS).

3.3 Experimental and characterization of selected adsorbents

3.3.1   Biomass based activated carbon synthesis by using Horizontal Tube Furnace

The horizontal tube furnace is used in this research study to synthesis pine cone biomass based activated carbon from Australian raw pine cone. The pine cone mixture is placed inside the glass tube and exposed to high temperature profile under nitrogen flow to avoid oxidation as shown in Fig 3.7.

Figure 3.7 Horizontal Tube furnace used in the preparation of
biomass based activated carbon

3.3.2 Functional surface groups of adsorbents by using FTIR

Fourier-transform infrared (FTIR) with a Universal ATR Sampling Accessory with MIR detector and SPECTRUM Version 6.3.4 software from Perkin Elmer Fig. 3.8 is used to investigate the functional groups presented in raw pine cone, acid modified pine cone and pine cone biomass based active carbon.

Figure 3.8 FTIR Spectrums 100

3.3.3 Adsorbent surface morphology by using Scanning Electron Microscope (SEM)

Scanning Electron Microscope (SEM) is used to scan specimen with a focused electron beam that is scanned across a rectangular area of the specimen. The beam of electrons is used to produce signals that can be detected and collected to produce SEM images. These images analyze the morphological structure and the surface characteristic of the adsorbents. The SEM was carried out using Zeiss Evo 40XVP model. Prior to the analyses, samples were coated with ultra-thin layer of platinum under vacuum to eliminate accumulation of static electric charge on the adsorbent's surface.

3.3.4   Malvern particle sizer and zeta potential

Malvern master sizer (Hydro 2000S) instrument is used to measure the particle size distribution, specific surface area, surface weighted mean and volume weighted mean of the adsorbent solid particles through the use of laser diffraction technique (Fig.3.9). Zeta potential is used to measure the variation of adsorbent surface charges at various solution pH. Adsorbent dose of 15mg is added to 30 ml ultra pure water at various solution pHs and agitated constantly for 2 hours. The solution is left to settle the particles down then 2 ml of the solution is added into a disposable plastic cell and placed into the zetasizer chamber to measure the zeta potential and zero zeta potential charges of the adsorbents at various pH .

Figure 3.9 Malvern particle sizer and zeta sizer instruments

3.3.5 Determination of bulk density and activated carbon yield

Bulk density is a measure of a powder mass (g) per unit volume (ml). It is used to measure the bulk density of the adsorbents by placing the adsorbent powder into a known volume of 2 ml volumetric cylinder and weight it. Bulk density is an important parameter for consideration in the designing of adsorption towers for use in pilot plant structure as well as large commercial application. Bulk density is inversely proportional to particle size. The samples were added in 2 ml volumetric cylinder and the mass of the used samples were recorded. Activated carbon yield is used to measure the mass of precursor needed to yield a specific weight of activated carbon.

$$\text{Bulk Density} = \frac{\text{mass of dry sample(g)}}{\text{total volume used (ml)}} \qquad (3.1)$$

Also, the activated carbon yield was calculated based on the following equation.

$$\text{Yield (\%)} = \frac{wc}{wo} \text{ x } 100 \qquad (3.2)$$

Where w_c is the dry weight (g) of the final activated carbon and w_o is the dry weight (g) of precursor.

3.3.6 CHNS Analysis

CHNS analysis was performed by PerkinElmer (CHNS-O analyser 2400) as shown in Fig.3.10 and it is used to the simultaneous determination of the percentage amount of carbon, hydrogen, nitrogen and sulphur contents in the organic and inorganic substances. The adsorbent of less than two milligrams in weight is placed into an aluminium capsule and dropped into a quartz tube at 1020°C with constant carrier gas flow. During the combustion process, the sample is exposed to strong oxidizing environment to produce N_2, CO_2, H_2O and SO_2 which can be detected by Thermal Conductivity detector.

Figure 3.10 CHNS-O analyser 2400 by PerkinElmer

3.3.7 BET

BET and Langmuir surface areas were used to explain the physical adsorption of N_2 gas molecules on the monolayer solid surface of the adsorbents. From Fig. 3.11, the micromeritics (TriStar II 3020) is used to measure the surface area and pore volume of the adsorbents. Te sample is degassed at 60°C for 15 hours to eliminate any trace of volatile elements. The sample is left in the degassing chamber at the room temperature for 20 mins before placed into the Tristar nitrogen adsorption chamber at temperature of -196 °C.

Figure 3.11 Micromeritics (TriStar II 3020) and degassing chambers

3.4 Batch adsorption experiments

The adsorption of CR dye on raw pine cone, acid modified pine cone and biomass based activated carbon was carried out in a batch system. Batch adsorption experiments were conducted by varying the operational parameters such as the initial solution pH, adsorbent dose, initial dye concentration and temperature at predetermined time interval under the aspect of adsorption kinetics, adsorption isotherm and thermodynamic study. A known amount of the adsorbent was placed with 50 ml of aqueous Congo red solutions of known concentration in a series of 250 ml plastic bottles. The mixture was shaken in a constant temperature using Thermo line scientific Orbital Shaker Incubator (Fig 3.12) at speed of 120 rpm and temperature of 30°C temperature. At predetermined time, the bottles were withdrawn from the shaker and the residual dye concentration in the reaction mixture was separated from the adsorbents by centrifuging Fig 3.13.

The absorbance of the supernatant was measured at the wavelength that corresponds to the maximum absorbance of the sample and the dye concentration was calculated from the linear equation of the calibration curve. The calibration curve was plotted between the absorbance and concentration of the dye solution to obtain the linear calibration equation. The concentration of the unknown solution was measured from the calibration plot. The amount of dye adsorbed onto the adsorbent at time t, qt (mg/g) and % Adsorption were calculated from equations (3.3) and (3.4) respectively:

$$q_t = \frac{(C_o - C_t)V}{m} \tag{3.3}$$

$$\% \text{ Adsorption} = \frac{(C_o - C_t)}{C_o} \times 100 \tag{3.4}$$

Where C_o is the initial dye concentration (mg/L), C_t is the concentration of dye at any time t, V is the volume of solution in (L) and m is the mass of the adsorbents in (g). All experimental measurements are within ± 10 % accuracy.

Figure 3.12 Thermo line scientific Orbital Shaker Incubator
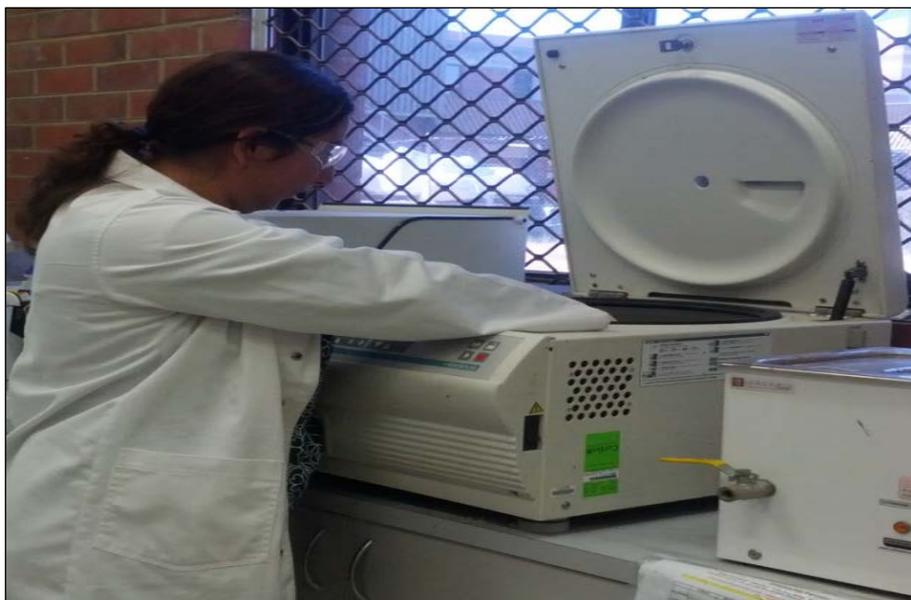
Figure 3.13 Centrifugal analyser of CR dye solution

3.4.1 Effect of initial adsorbent dose on dye adsorption experiment

The effectiveness of different doses of raw pine cone, acid modified pine cone and biomass based activated carbon on CR dye adsorption was studied at the batch scale. Adsorbent doses of 10 mg to 30 mg were used in this study. A known amount of the adsorbent was added to 50 ml of blue acidic CR solution with initial dye concentration of 20 (mg/L). At predetermined time, the bottles were withdrawn from the shaker and the residual dye concentration in the reaction mixture was separated from the adsorbents by centrifuging. The final dye concentration of the supernatant was measured using the UV Spectrophotometer. Equations (3.3) and (3.4) were used to calculate the adsorption capacity q_t (mg/g) and percentage of adsorption respectively.

3.4.2 Effect of initial dye concentration and contact time

The effect of initial dye concentration and contact time on the adsorption of CR dye was investigated at different initial dye concentration onto raw pine cone, acid modified pine cone and biomass based activated carbon. Initial dye concentrations of 20 mg/L to 60 mg/L are used in this study. A known concentration of blue acidic CR dye of 50 ml was added to 10 mg of biomass based AC and 20 mg in case of raw and acid modified pine cone adsorbents. At predetermined time, the bottles were withdrawn from the shaker and the residual dye concentration in the reaction mixture was separated from the adsorbents by centrifuging. The final dye concentration of the supernatant was measured using the UV Spectrophotometer. Equations (3.3) and (3.4) were used to calculate the adsorption capacity q_t (mg/g) and percentage of adsorption respectively.

3.4.3 Effect of solution temperature on dye adsorption experiment

The amount of CR dye adsorbed on the various types of adsorbents was investigated at different temperatures of 30°C, 40°C and 60°C. The mixture of 50 ml blue acidic CR solution with Initial dye concentration of 20 mg/L was added to 10 mg of biomass based AC and 20 mg in case of raw and acid modified pine cone adsorbents and agitated. At predetermined time, the bottles were withdrawn from the shaker and the residual dye concentration in the reaction mixture was separated from the adsorbents by centrifuging. The final dye concentration of the supernatant was measured using the UV Spectrophotometer. Equations (3.3) and (3.4) are used to calculate the adsorption capacity q_t (mg/g) and percentage of adsorption respectively.

3.4.4 Effect of initial solution pH on dye adsorption experiment

The effect of solution pH on CR dye adsorption capacity and dye removal percentage was studied. The pH of the solution is adjusted by adding either 0.1M hydrochloric acid (HCL) or 0.5 M phosphoric acid to lower the pH or 0.1 M sodium hydroxide to increase the pH. The solution pH was studied in the range of 2.2 to 10.9. The mixture of 50 ml CR solution with Initial dye concentration of 20 mg/L was added to 10 mg of biomass based AC and 20 mg in case of raw and acid modified pine cone adsorbents and agitated at temperature of 30°C. At predetermined time, the bottles were withdrawn from the shaker and the residual dye concentration in the reaction mixture is separated from the adsorbents by centrifuging. The final dye concentration of the supernatant is measured using the UV Spectrophotometer. Equations (3.3) and (3.4) were used to calculate the adsorption capacity qt (mg/g) and percentage of adsorption respectively.

3.4.5 Isotherm experiment

Equilibrium adsorption process was carried out by contacting 50 ml of various initial dye concentrations of 10, 20, 30, 40, 50 and 60 (mg/L) with a fixed amount of adsorbent, solution pH and temperature in a 250 ml conical flasks till the equilibrium time (t) of 2 hours. After equilibrium, the bottles were withdrawn from the shaker and the residual dye concentration in the reaction mixture was separated from the adsorbents by centrifuging. The final dye concentration of the supernatant is measured using the UV Spectrophotometer. Equations (3.3) and (3.4) were used to calculate the adsorption capacity qt (mg/g) and percentage of adsorption respectively.
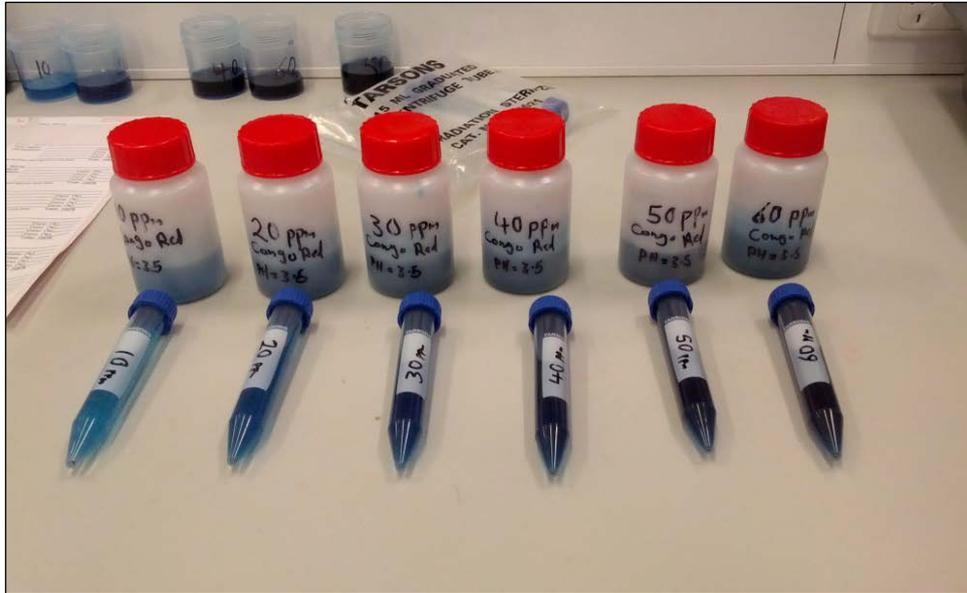
Figure 3.14 Isotherm experiment of various Congo red dye concentrations
and biomass based activated carbon

3.5 Desorption study

Desorption process was carried out by merging the dried dye-saturated adsorbent with water
at different pH values (2.2 -10.95) and agitated using Orbital Shaker Incubator with similar
conditions as obtained in the adsorption study. Mixture was withdrawn from the shaker and
the residual dye concentration in the reaction mixture is separated from the adsorbent by
centrifuging. The final dye concentration of the supernatant is measured using the UV
Spectrophotometer.

3.6 Summary

In this chapter, detailed description on materials, characterisation and experimental methods has been presented. The collection and characterisation of raw pine cone biomass, chemically activated pine cone biomass and biomass pine cone based activated carbon has been described. Raw pine cone and acid modified pine cone powders are prepared and stored in air tight bottles for future use as adsorbents in the removal of Congo red dye from its aqueous solution. Pine cone is used to synthesis biomass based activated carbon and full procedure is explained in this chapter. The physical and chemical characterization of raw pine cone, acid modified pine cone and pine cone biomass based activated carbon adsorbents are carried out using various instruments. The utilizations of these instruments such as Malvern particle sizer, SEM, CHNS-O analyse etc. are explained briefly. Also, kinetic and isotherm adsorption experimental procedure was outlined.

4. CHAPTER FOUR- Congo red dye adsorption characteristics of raw and acid treated pine cone powder: Equilibrium, thermodynamic, kinetics, mechanism and process design*

Abstract

Pine cone a natural, low-cost agricultural solid waste available in Australia has been studied for its potential application as an adsorbent in its raw and acid modified forms. Physical and chemical characterizations of raw and acid treated pine cone were investigated using Fourier transform infrared (FTIR), Malvern particle sizer and scanning electron microscopy (SEM). Hydrochloric acid is used in the modification process of raw pine cone powder which leads to increases in the specific surface area and decreases mean particle sizes of acid-treated pine cone when compared to raw pine cone biomass. Batch adsorption experiments were performed to remove anionic dye Congo red from aqueous solution. It was found that the adsorption capacity q_t (mg/g) of Congo red dye by both raw pine cone biomass and acid-treated biomass increased with initial dye concentration, contact time, temperature but decreased with increasing initial solution pH and adsorbent dose. Overall, kinetic studies showed that the dye adsorption process followed pseudo-second-order kinetics compared to pseudo-first-order and intra-particle diffusion models. The different kinetic parameters including rate constant, half-adsorption time, and diffusion coefficient were determined at different physico-chemical conditions. Equilibrium data were best represented by Freundlich isotherm model among Langmuir and Freundlich adsorption isotherm models. It was observed that the adsorption was pH dependent and the maximum adsorption of 32.79 mg/g occurred at pH of 3.55 for an initial dye concentration of 20 ppm by raw pine cone, whereas for acid-treated pine cone the maximum adsorption of 44.47 mg/g for the same experimental conditions. Freundlich constant 'n' also indicated favourable adsorption. Thermodynamic parameters such as ΔG^0, ΔH^0, and ΔS^0 were calculated. A single-stage batch absorber design for the Congo red adsorption onto raw pine cone biomass also presented based on the Freundlich isotherm model equation.

4.1 Introduction

Wastewater effluents from many industries such as textile, rubber, paper, leather, plastics, cosmetic, printing etc, contain several kinds of synthetic dyestuffs (Chatterjee et al., 2009). Over 10,000 dyes are commercially available and 5-10% of dyestuffs are lost in the industrial effluents (Sen et al., 2011; Yao et al., 2009; Rafatullah et al., 2009). This dye-bearing wastewater exhibit high colour, chemical and biochemical oxygen demands (Yao et al., 2009). Congo red an anionic dye has been known to cause an allergic reaction and to be metabolised to benzidine, a human carcinogen (Chatterjee et al., 2009; Chen and Zhao, 2009). A number of non-conventional, low-cost adsorbents such as organo-attapulgite (Chen and Zhao, 2009), pellets of Trametes versicolor (Binupriya et al., 2008), palm shell (Sreelatha et al., 2011), montmorillonite (Yermiyahu et al., 2003); bentonite (Lian et al., 2009); rice hull ash (Chou et al., 2001), leaf (Bhattacharyya and Sharma, 2005) and rice husk (Han et al., 2008) has been used for the removal of Congo red from aqueous solution. Pine cones (*P. radiate*) are produced annually as agricultural solid waste throughout the world in large quantities. Mature pine cones are composed of epidermal and sclerenchyma cells which contain cellulose, hemicelluloses, lignin, rosin and tannins in their cell walls (Ucun et al., 2003). There are only few studies various pine cone such as *Pinus sylvestris* have been used to remove chromium ions (Ucun et al., 2003), *Pinus pinaster* to remove phenol (Vazquez et al., 2006) and *P. Radiate* to remove Methylene blue dye (Sen et al., 2011).

However, no work has been reported on the use of raw cone biomass of Pinus radiate and acid-treated cone biomass as an effective adsorbent for the removal of anionic dye Congo red from aqueous solution. Therefore, the present study is aimed to study the potential of Congo red dye removal from its aqueous solution using a low cost and an abundantly available adsorbent such as raw pine and treated pine cone biomass of P. radiate. This present research work will explore the mechanism of adsorption and adsorption kinetics of Congo red dye and will determine the various physicochemical controlling factors on the rate of adsorption and also on the capacity of adsorbent. Further this paper also discusses various thermodynamic parameters such as Gibbs free energy change (ΔG^0), heat of adsorption (ΔH^0) and entropy change (ΔS^0) respectively. Finally, a single stage batch adsorber has been designed for the removal of Congo red by P. radiate based on the equilibrium data obtained.

4.2 Materials and Methods

4.2.1 Adsorbent

Pine tree cones (*P. radiate*) were obtained from the campus of Curtin University Perth Western Australia between February and March 2011. The cones were washed with deionised water to remove dirt and soluble impurities. The cones were placed in the oven to dry at temperature of $80°C$ for 24 h. The dried pine cone biomass was crushed in a mortar to a fine powder and passed through British Standard Sieves (BSS) of 150 µm. The raw pine cone powder was stored in an airtight plastic container for analysis as well as for adsorption experiments.

Acid treated pine cone powder was prepared by adding 10 g of raw pine cone powder with 100 ml of 0.1 M HCL solution in a glass bottle. The mixture was stirred in a magnetic stirrer of 120 rpm for a period of 20 h at room temperature. The treated powder was filtered and washed with distilled water until a constant solution pH obtained. The washed powder was then oven dried overnight at $50°C$ and used for analysis as well as for adsorption experiments.

4.2.2 Chemicals

All chemicals used were of analytical grade. The anionic dye, Congo red (CR) was selected as the adsorbate in this study. Congo red dye obtained from Sigma Aldrich with 99.99% purity. A stock solution of 1000 mg/L was prepared by dissolving 1000 mg powder of Congo red in 1000 ml of ultra-pure water. Further details are presented in section 3.3.4.

Hydrochloric acid (HCL) is a highly corrosive solution used in this study to adjust the pH of the working solution. Also, it is used to chemically modify the raw pine cone powder. A stock solution of hydrochloric acid concentration of 37.5% was used to prepare 0.1M hydrochloric acid as shown in section 3.3.5. Furthermore, sodium hydroxide (NaOH) is a colourless solution. In this study sodium hydroxide solution of 0.1 M is obtained from Orica (Australia) and used to adjust the pH of Congo red dye solution. Chemical risk assessment is carried out to identify and control any risk associated with the use of sodium hydroxide in this study. The required data are obtained from Chem Alert and Safety Data Sheet (SDS).

4.2.3 Adsorption experiments

The adsorption of Congo red dye on raw pine cone and acid modified pine cone was carried out in a batch system. Batch adsorption experiments are conducted by varying the operational parameters such as the initial solution pH, adsorbent dose, initial dye concentration and temperature at predetermined time interval under the aspect of adsorption kinetics, adsorption isotherm and thermodynamic study. A known amount of the adsorbent was mixed with 50 ml Congo red solutions of known concentration in a series of 250 ml plastic bottles. The mixture is shaken in a constant temperature using Thermo line scientific Orbital Shaker Incubator at speed of 120 rpm and temperature of 30°C temperature. At predetermined time, the bottles were withdrawn from the shaker and the residual dye concentration in the reaction mixture was separated from the adsorbents by centrifuging. The amount of dye adsorbed onto the adsorbent at time t, qt (mg/g) and % Adsorption were calculated from equations (3.3) and (3.4) respectively.

Furthermore, equilibrium isotherm adsorption process was carried out by contacting 50 ml of various initial dye concentrations of 10, 20, 30, 40, 50 and 60 (mg/L) with 20 mg raw pine cone, solution pH of 3.55 and 60°C temperature in 250 ml conical flasks till equilibrium time reached. At predetermined time, the bottles were withdrawn from the shaker and the residual dye concentration in the reaction mixture is separated from the adsorbents by centrifuging. The amount of dye adsorbed onto the adsorbent at equilibrium, q_e (mg/g) was calculated from equation (3.3). Detailed methods have been described in chapter three.

4.3 Results and discussion

4.3.1 Characterizations of raw and acid-treated pine cone

Pine cones contain cellulose, hemicelluloses, lignin, rosin, and tannins in their cell walls which contains polar functional groups such as alcohols, aldehydes, ketones, carboxylic phenolic and other groups (Sen et al., 2011; Ofomaja et al., 2009). These functional groups create active sites on pine cone surface which are responsible for binding of anionic dye. FTIR spectrum of raw pine cone and acid treated pine cone powder is shown in Fig 4.1. Various bands observed at 3331.97 and 2928.33 cm^{-1} represent -OH and aliphatic C-H group (Ofomaja et al. 2009; Mahmoodi et al., 2011). The peak at 1602.37 cm^{-1} corresponds to C≡O and vibration of C≡C. The peak at 1443.31 cm^{-1} corresponds to N-alkyl ted aromatic amines and peaks at 1263.56 cm^{-1} indicates C-N stretching with amine or C-O vibration of carboxylic acid (Argun et al., 2008). Similar type of FTIR spectra of pine cone has been reported by few other investigators (Mahmoodi et al., 2011, Ofomaja et al., 2009; Argun et al., 2008). The spectra's of the acid-treated pine cone sample showed similar characteristics as the raw pine cone except for slight changes. The FTIR spectra's all show similar peaks but with slight difference in the intensity in the band at 3331.97 cm^{-1}, the peak at 2928.33 cm^{-1} and 1602.37 cm^{-1}, indicating unbounded-OH, aliphatic C-H group and C≡O stretch (Ofomaja and Naidoo, 2011).
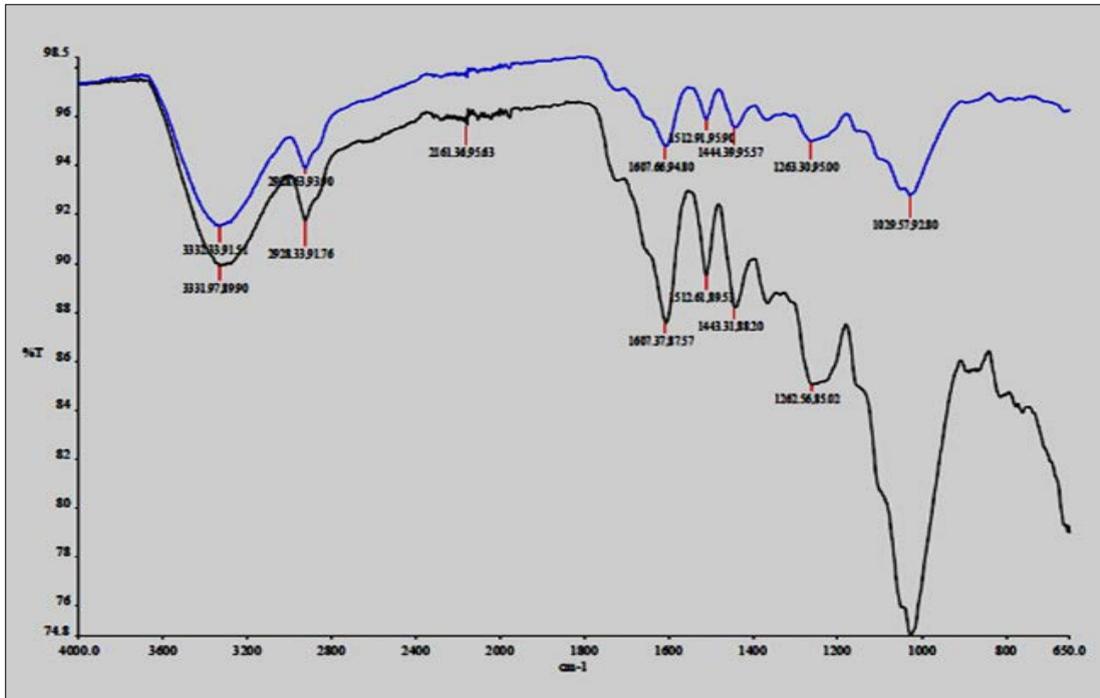
Figure 4.1 FTIR spectrum of raw and acid modified pine cone powder

Scanning Electron Micrograph (SEM) of raw and acid treated pine cone biomass before and after adsorption is shown in Fig 4.2 and Fig 4.3 respectively. The availability of pores and internal surface is displayed in the SEM pictures of the raw and acid treated pine cone biomass before adsorption while SEM pictures of raw and acid treated pine cone after adsorption showed the coverage of the surface and the pores by the adsorbed Congo red dye. The specific surface area of raw and acid modified pine cone biomass was $0.0993 m^2/g$ and $0.122 m^2/g$ respectively. Also, from the particle size distribution plots (Fig 4.4), the mean particle size for the raw pine cone biomass used was calculated as 60.44 µm whereas for acid modified pine cone it was 49.03 µm.
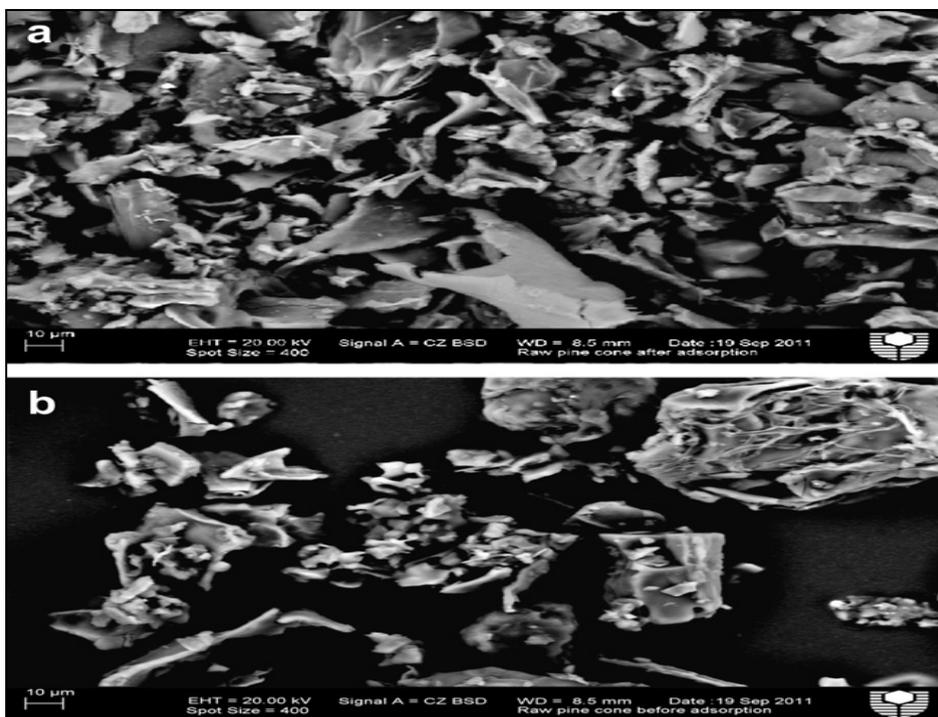
Figure 4.2 SEM of raw pine cone after adsorption of Congo red (a) and before adsorption (b)
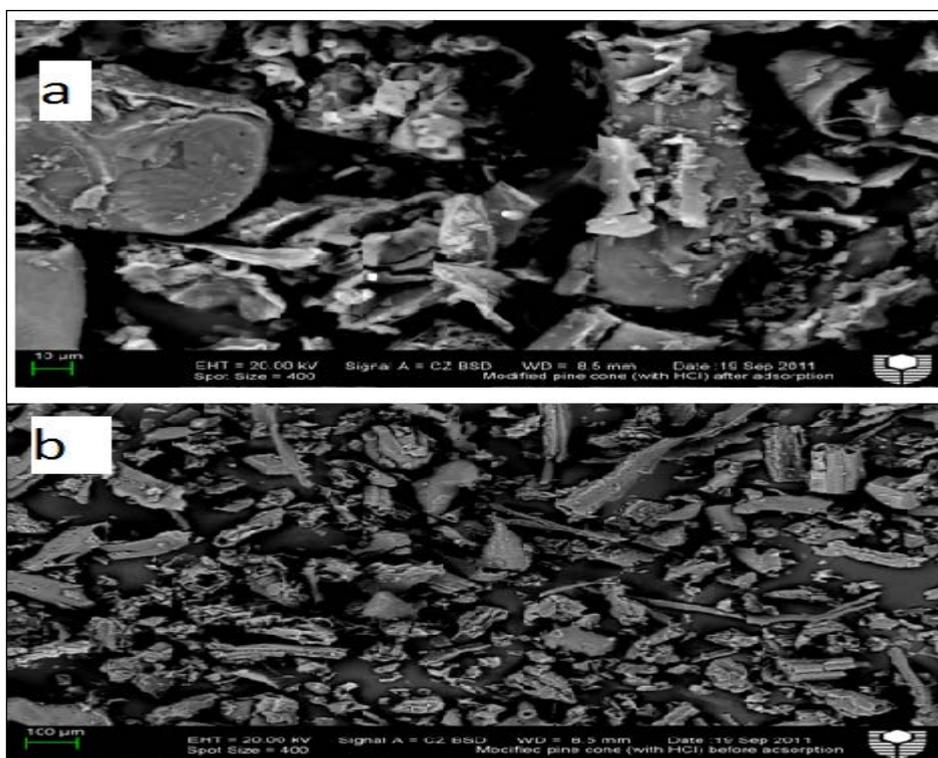
Figure 4.3 SEM of acid treated pine cone after adsorption of Congo red (a) and before adsorption (b)
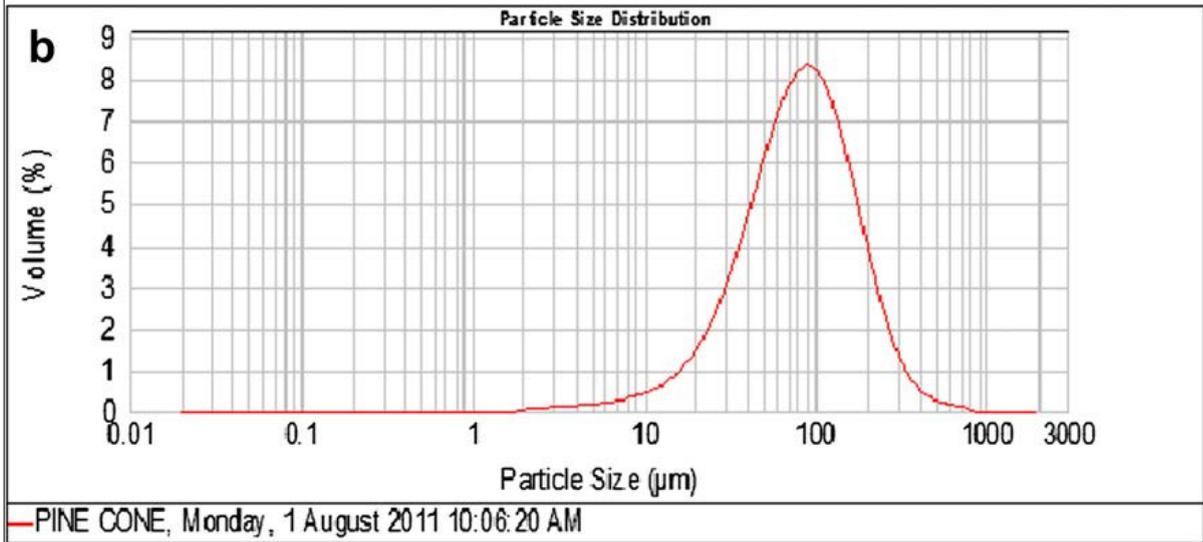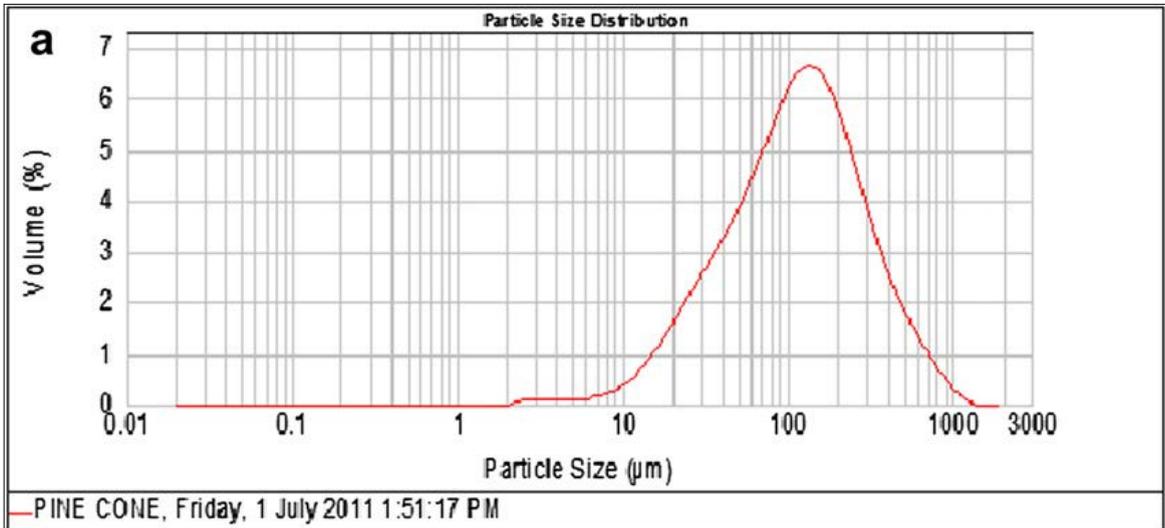
Figure 4.4 Particle size distribution of raw pine cone (a), Particle size distribution of acid-treated pine cone (b)

4.3.2 Effect of initial solution pH

The colour of Congo red dye changes to dark blue at acidic pH and to red at alkaline solution pH but the red colour is slightly different from the original red colour at neutral pH. The results of blank dye solution studies indicate that change of the initial solution pH (pH 3.55-10.95) of dye solution has negligible effect on the ⅄ max of Congo red dye. Similar observation was also reported by Kaur et al., (2013). The effect of initial solution pH on the adsorption capacity was studied in the range of 3.55-10.95 for raw pine cone powder as presented in Fig 4.5. The effect of solution pH on the adsorption of Congo red from aqueous solution using acid-modified pine cone powder was studied in the pH range of 3.61 to 7.45 as shown in Fig 4.6. It was found that the amount of dye adsorbed increased from 2.88 mg/g (5.75% removal efficiency) to 31.9 mg/g (63.87% removal efficiency) due to change in pH from 10.95 to 3.55 for a fixed initial dye concentration of 20 ppm at equilibrium. Similarly from Fig 4.6, it was found that the amount of dye adsorbed increased from 8.34 mg/g (16.25% removal efficiency) to 39.48 mg/g (79.25% removal efficiency) with the change in solution pH 7.51 to 3.61. It is found that the amount of adsorbed mass of Congo red dye, q_t (mg/g) consistently decreased with increasing solution pH but increases with time. However the acid-treated pine cone had higher dye adsorption capacity (Fig 4.6) than the raw pine cone (Fig 4.5). This is because of increase of the internal surface area of acid modified biomass than the raw pine cone biomass powder will lead to increased adsorption capacity of Congo red. The maximum adsorption of dye occurs at acidic pH for both raw and acid treated pine cone biomass. This can be explained as pine cone biomass contains several functional groups such as amino, hydroxyl and carbonyl groups which are affected by the pH of the solution. The point of zero charge, pH_{PZC} of pine cone particles in aqueous solution is 4.4 and negative zeta potential increased with increasing alkaline solution pH (Nuhoglu and Oguz, 2003; Blazque et al., 2011). Surface modification reduced pH_{PZC} and therefore point of zero charge, pH_{PZC} of activated pine cone is 3.06 which were reported by Nomcelovic et al. (2011). In other words, at acidic solution pH, positive ions are excessively presented at the surface of the adsorbent thus creating an electrostatic attraction between the adsorbent and the negatively charged anionic dye. The negative charge on cone biomass increased with increasing pH which was also reported by Ucun et al. (2003). The adsorption capacity of Congo red on raw and acid modified pine cone biomass tends to decrease at higher solution

pH, which can be explained by the increasing electrostatic repulsion between the anionic dye adsorbate species and negatively charged (OH⁻) adsorbent surfaces. A similar behaviour was observed for Congo red dye adsorption on agricultural solid waste based activated carbon (Namasivayam and Kavitha, 2002), on organo-attapulgite (Chen and Zhao, 2009), on various agricultural solid waste (Salleh et al., 2011) and on chitosan (Chatterjee et al., 2009). Full calculation on the adsorption capacity q_t (mg/g) and dye removal percentage is presented in appendix 4.1.
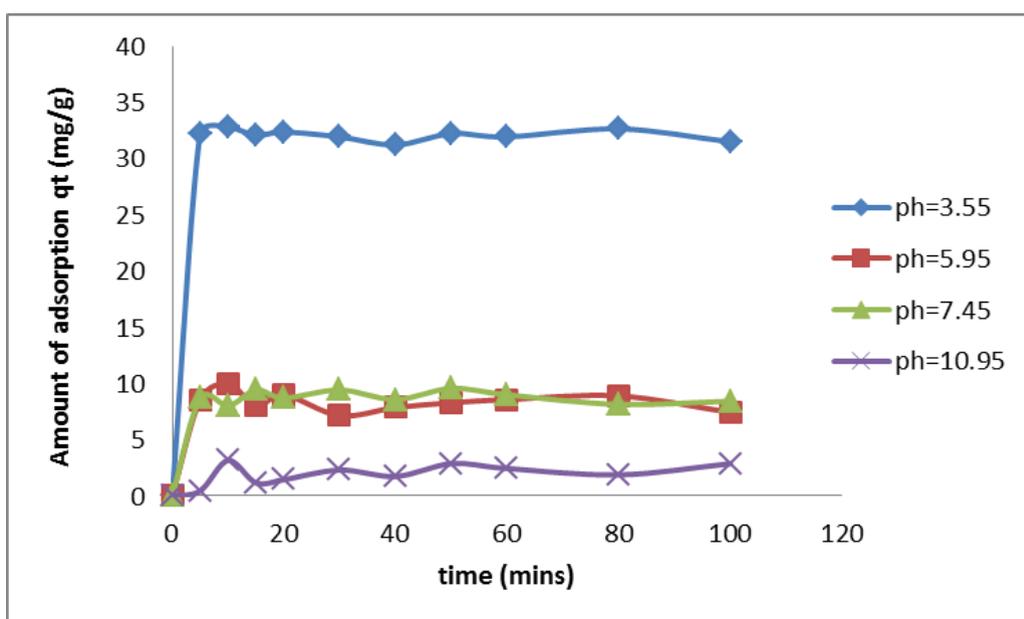
Figure 4.5 Effect of initial solution pH on the adsorption of CR dye onto raw pine cone powder: Mass of Adsorbent 20 mg; Volume of CR Solution 50 ml; Initial CR Concentration 20 ppm; Temperature 30°C; Shaker Speed 120 rpm.
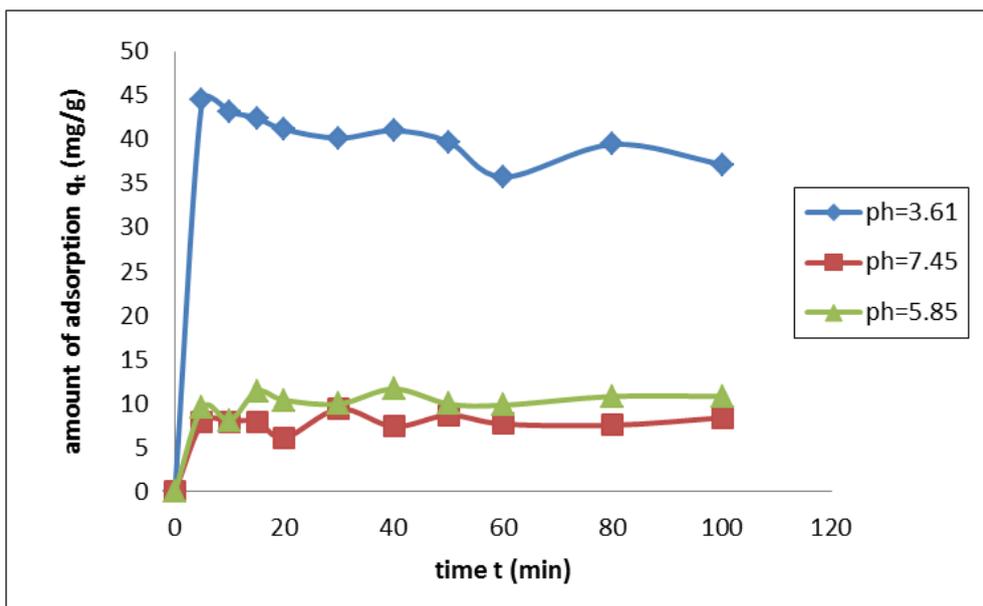
Figure 4.6 Effect of initial solution pH on the adsorption of CR dye onto acid modified pine cone powder: Mass of Adsorbent 20 mg; Volume of CR Solution 50 ml; Initial CR Concentration 20 ppm; Temperature 30°C; Shaker Speed 120 rpm

4.3.3 Effect of adsorbent dose on Congo red adsorption

Study of the effect of adsorbent dosage gives an idea of the effectiveness of an adsorbent and the ability of a dye to be adsorbed with an economical minimum dosage (Salleh et al., 2011). It was found from Fig. 4.7 and Fig 4.8 that the increase in raw pine cone dosage from 0.01 g to 0.03 g resulted in decrease of amount of adsorbed dye from 13.44 mg/g to 6.28 mg/g but increased in the percentage dye removal from 13.45% to 18.96%. These adsorbent dose experiments were carried out at slightly alkaline solution pH of 7.65 and therefore low removal efficiencies were observed. The dye removal percentage of 30mg raw and acid modified pine cone powder was shown in Fig 4.9. From Fig 4.9, higher dye removal of 73% was observed for acid treated pine cone compared to 18.96% raw pine cone powder. The increase in percentage of dye removal with increasing adsorbent dosages is due to increase of sorption active sites at the adsorbent surface with increasing the dose (Ghaedi et al., 2011a).

Similar adsorbent dose behaviour for Congo red adsorption onto various adsorbents was reviewed by Salleh et al. (2011). At higher pine cone to Congo red concentration ratios, there is a very fast superficial sorption onto the pine cone surface that gives a lower dye concentration in the solution compared to the lower biomass to CR concentration ratio. This is because a fixed mass of pine cone can only adsorb a fixed amount of dye. Therefore, the more the adsorbent dosages, the larger the volume of effluent that a fixed mass of pine cone biomass can purify. Thus leads to decrease in amount of dye adsorbed, qe (mg/g) with increasing adsorbent mass is due to the split in the flux or the concentration gradient between solute concentration in the solution and the solute concentration in the surface of the adsorbent (Vadivelan and Kumar, 2005; Kumar et al., 2010). Full calculation on the adsorption capacity q_t (mg/g) and dye removal percentage is presented in appendix 4.2.
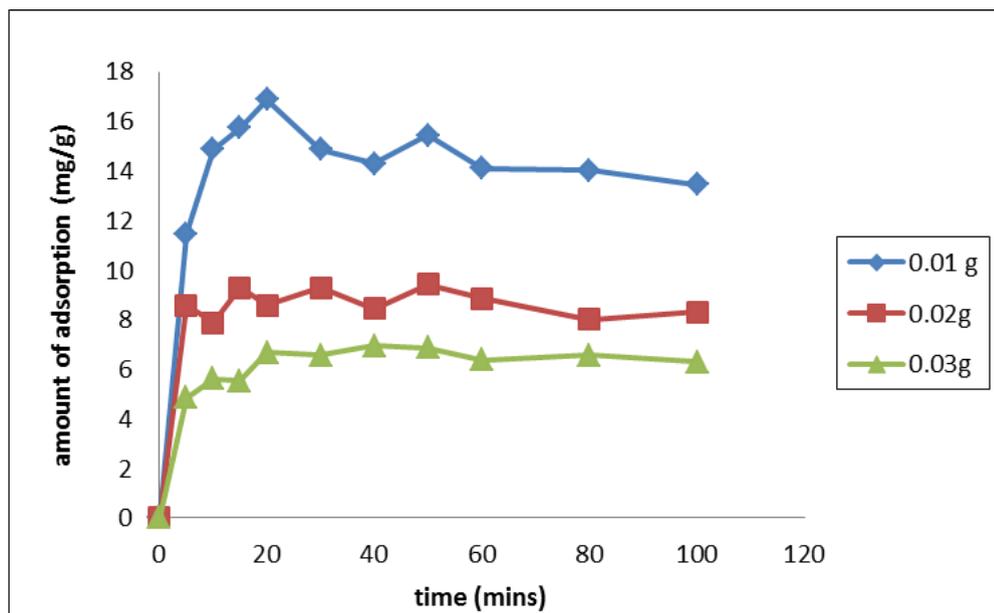
Figure 4.7 Effect of adsorbent dosages on the amount of CR adsorption by raw pine cone biomass. Volume of CR Solution50ml; Initial CR Concentration 20 ppm; pH 7.45; Temperature 30 $^{\circ}$C; Shaker Speed 120 rpm
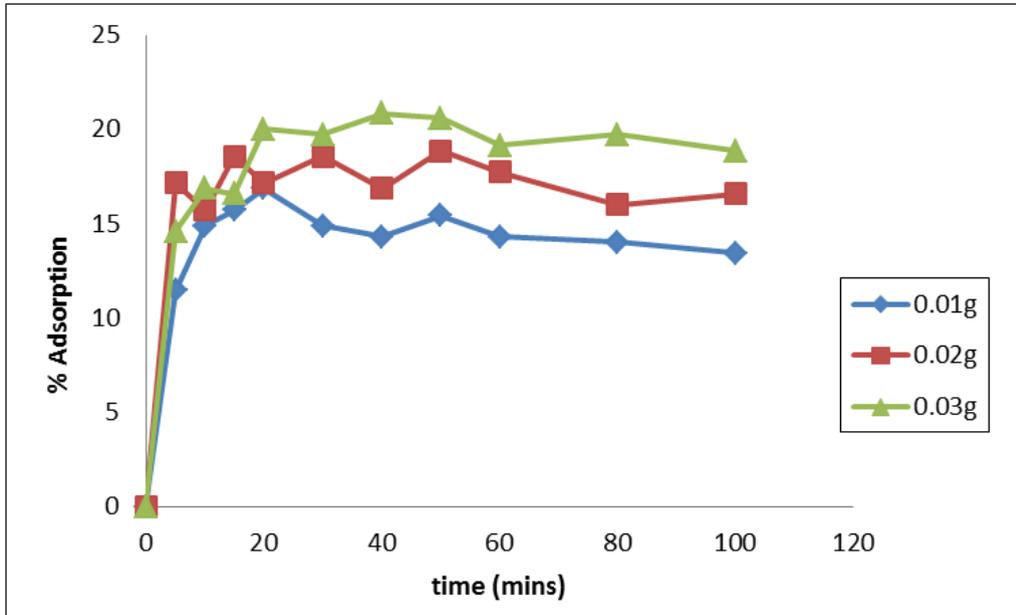
Figure 4.8 Effect of adsorbent dosages on % adsorption by raw pine cone biomass. Volume of CR Solution50ml; Initial CR Concentration 20 ppm; pH 7.45; Temperature 30 °C; Shaker Speed 120 rpm
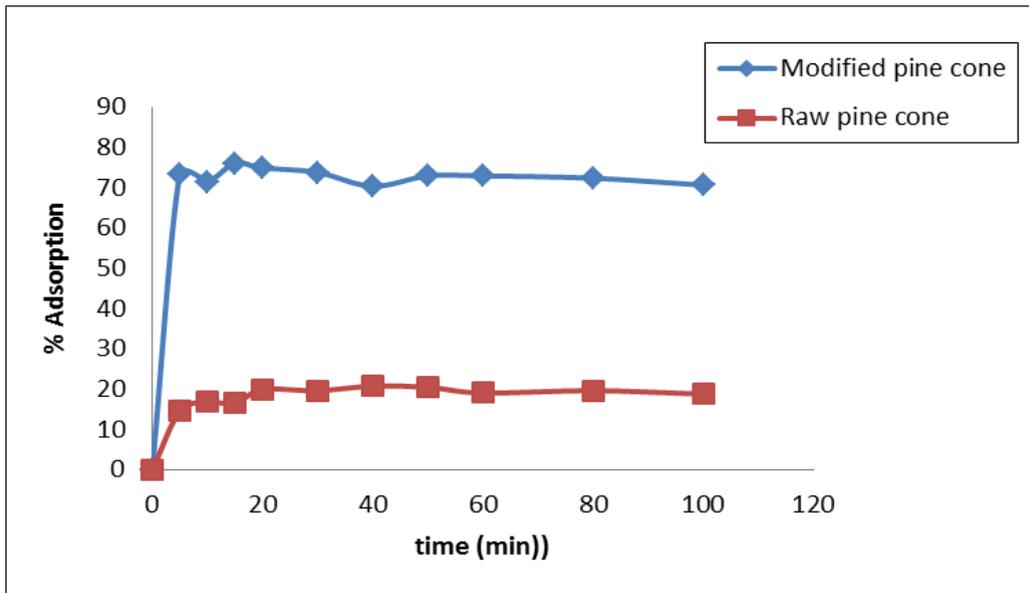
Figure 4.9 Effect of adsorbent dose of 0.03 g on % adsorption by raw and acid treated pine cone biomass. Volume of CR Solution50ml; Initial CR Concentration 20 ppm; pH 7.45; Temperature 30 °C; Shaker Speed 120 rpm

4.3.4   Effect of initial dye concentration and contact time

The effect of contact time on the adsorption of Congo red dye was investigated at different initial dye concentration onto raw pine cone adsorbent and results were presented in Fig 4.10. It was found that the amount of dye adsorption increased from 8.4 mg/g to 25.4 mg/g with increasing initial concentration of CR dye from 20 ppm to 50 ppm (Fig 4.10). It was also found that the adsorption capacity q_t mg adsorbate per g of adsorbent increases with increasing contact time at all initial dye concentrations and equilibrium is attained within 100 min. These results can be explained as increase in the initial dye concentration provides the driving force to overcome the resistance to the mass transfer of dye between the aqueous and the solid phase. For constant dosage of adsorbent, at higher initial dye concentration, the available adsorption active sites of the adsorbent become saturated hence reduce the dye removal percentage of CR (Shahryari et al., 2010). The increase in initial concentration also enhances the interaction between adsorbent and dye Therefore, an increase in initial dye concentration leads to increase in the adsorption capacity q_t (mg/g). Also, from Fig 4.10, the removal of dye by adsorption on pine cone is very fast at the initial period of contact then become stable. Kinetic experiments clearly indicated that adsorption of Congo red on raw pine cone followed three-step processes, a rapid initial adsorption followed by a period of slower uptake of CR and finally no significant uptake. The first step is attributed to the instantaneous utilisation of the most readily available active sites on the adsorbent surface (bulk diffusion). Second step, exhibiting additional adsorption is attributed to the diffusion of the adsorbate from the surface film into the macro-pores of the adsorbent (pore diffusion or intra-particle diffusion) stimulating further movement of CR molecules from the liquid phase onto adsorbent pine cone surface. The last stage is an equilibrium stage (Mohammad et al., 2010). The rapid kinetics has significant practical importance, as it facilitates smaller reactor volumes, ensuring high efficiency and economy (Arias and Sen, 2009; Sen and Sarzali, 2008). Full calculation on the adsorption capacity qt (mg/g) and dye removal percentage is presented in appendix 4.3.
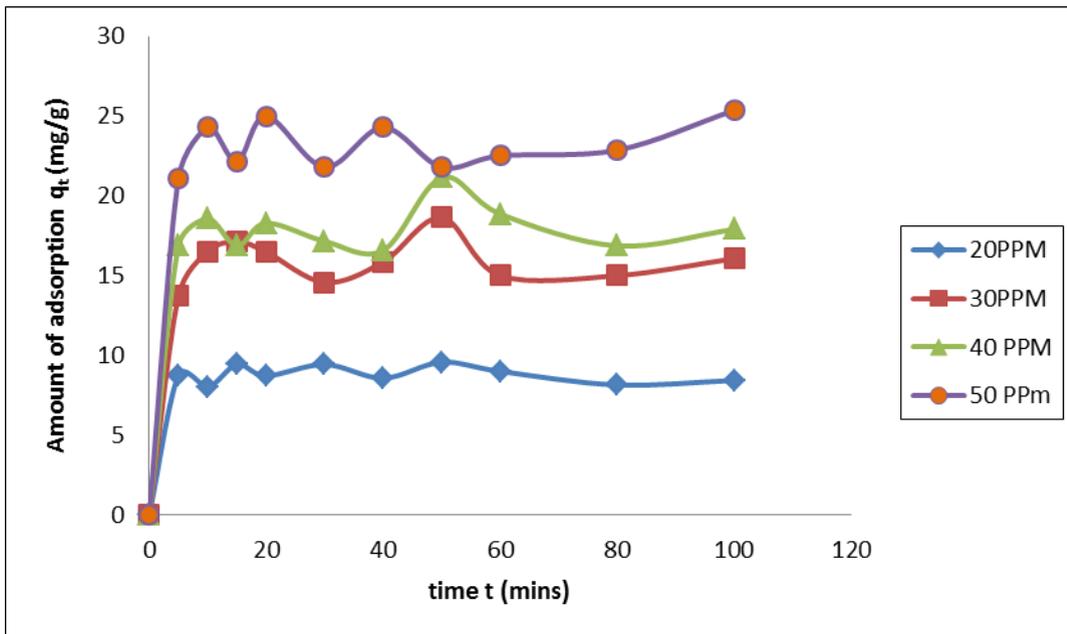
Figure 4.10 Effect of contact time and initial CR concentration on the adsorption capacity of CR onto raw pine cone powder: Mass of Adsorbent 20 mg; Volume of CR Solution 50 ml; pH 7.45 Temperature 30 °C; Shaker Speed 120 rpm

4.3.5 Effect of temperature on dye adsorption kinetics and thermodynamic studies

Several textile dye effluents are produced at relatively high temperatures; therefore, temperature is an important parameter for the real application of Congo red dye adsorption by pine cone. Temperature is an indicator for the adsorption nature whether it is an exothermic or endothermic process (Ghaedi et al., 2011a). It was found that the amount of Congo red adsorption on raw pine cone increased with increasing temperature of the solution, which indicates that the process was endothermic as shown in Fig 4.11. This result can be explained as increasing the temperature of the solution will lead to increase the mobility of the dye molecules and an increase in the number of active sites for the adsorption (Salleh et al. 2011, Mahmoodi et al., 2011; Ghaedi et al., 2011a). An increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface.

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Further, increasing temperature may produce a swelling effect within the internal structure of the pine cone enabling large dye molecule to penetrate further. Similar type of results for the Congo red adsorption at various temperatures on organo-attapulgite (Chen and Zhao, 2009), on agricultural solid waste (Salleh et al., 2011) and on hectoritel (Xia et al., 2011) has also been reported. Also, the thermodynamics properties such as Gibb's free energy (ΔG^0), change in entropy (ΔS^0) and enthalpy change (ΔH^0) have been determined by the application of equations (2.18) and (2.19) and also with the help of Van't Hoff plot. All three thermodynamic parameters are presented in Table 4.1. The positive values of ΔH^0 confirm the endothermic nature of adsorption. The endothermic CR adsorption on other adsorbent system has also been reported (Namasivayam and Kavitha, 2002; Benyoucef and Amrani, 2011; Mahmoodi et al., 2011). The positive value of ΔS^0 suggests increased randomness at the solid solution interface occurs in the internal structure of the adsorption of Congo red dye onto pine cone. Furthermore, the negative ΔG^0 values were observed at all various temperatures, indicating spontaneous nature of the adsorption process. Similar trend has also been observed for Congo red dye adsorption onto activated carbon prepared from coir pith (Namasivayam and Kavitha, 2002). Full calculation on the adsorption capacity qt (mg/g) and dye removal percentage is presented in appendix 4.4.

Table 4.1 Thermodynamic parameters for adsorption of CR at different temperatures

Temperature, T (K)	ΔG^o (kJ mol^{-1})	ΔH^o (kJ mol^{-1})	ΔS^o (kJ mol^{-1})
303.15	-15.601	13.865	97.254
313.15	-16.574	13.865	97.254
333.15	-18.519	13.865	97.254
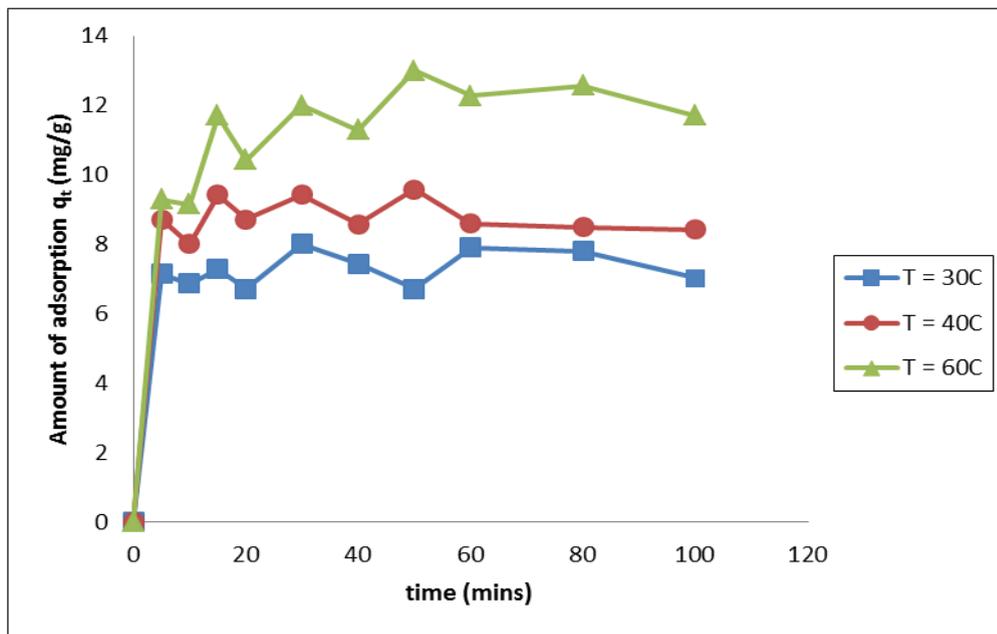
Figure 4.11 Effect of Temperature on the adsorption of CR onto raw pine cone, powder: Mass of Adsorbent= 20 mg; Volume of CR Solution = 50 ml; Initial CR Concentration = 20 ppm; pH = 6.95; Shaker Speed = 120 rpm

4.3.6   Adsorption kinetic modelling

4.3.6.1 Pseudo-first-order and pseudo-second-order kinetic models

The prediction of batch adsorption kinetics is important for the design of industrial adsorption system. The nature of the adsorption process will depend on the physical and chemical characteristics of   the adsorbent system and system conditions. In this study, the applicability of the pseudo-first-order and pseudo-second-order models was tested for the adsorption of Congo red (CR) into raw pine cone and acid modified pine cone biomass particles as per equations (2.5) and (2.7) respectively. Both these models have been fitted with experimental data at various physico-chemical process parameters. Lagergren pseudo-first-order model gives very poor linear regression coefficient (R^2) of less than in 0.31 at various physico-

chemical conditions as shown in Table 4.2. Also, pseudo- first-order kinetic model predicted a significantly lower value of the calculated equilibrium adsorption capacity (q_e) than the experimental value as shown in Table 4.2 which suggests the inapplicability of this model for the design of industrial column . Furthermore, the kinetic experimental data were analysed using the pseudo-second-order kinetic model. Fig 4.12 shows pseudo-second-order kinetic model fitted with experimental data of various physico-chemical parameters. The plot t/q_t versus t gives a straight line with higher linear correlation coefficients which suggests the applicability of this model. However, all kinetic parameters including the values of q_e, k_2, h and R^2 were calculated from the slope and intercept of the plots respectively, as shown in Table 4.3. From Table 4.2 and 4.3, it can be concluded that the linear correlation coefficient for pseudo-first-order is less than the pseudo-second-order correlation coefficient. Also, the values of linear correlation coefficient for pseudo-second-order were very high and the theoretical adsorption capacity q_e (mg/g) values were closer to the experimental q_e (mg/g) values under different physico-chemical conditions. Moreover, it was found that the adsorption capacity increases with increase in initial dye concentration but decreases within initial solution pH and amount of adsorbent respectively. In view of these results, it can be concluded that the pseudo-second-order kinetic model delivered a better correlation for the adsorption of Congo red onto raw and acid-treated pine cone. Also from Table 4.3, the rate constant k_2 decrease with the increases of initial dye concentration. This is due to the fact that at higher concentrations, the competition for the surface active sites will be high and consequently lower sorption rates are obtained. The overall rate constant, k_2 increased as the adsorbent dosage increased and also initial adsorption rate, h varied with the variation in the adsorbent dosage. Similar type kinetic model parameters were obtained by various researchers for a few other observations systems reported in the literature (Ofomaja and Naidoo, 2011; Ofomaja et al., 2009; Sen et al., 2011; Abd EI-Latif et al., 2010). The half-adsorption time of the surfactant, $t^{1/2}$ i.e. the time required for the pine cone to uptake half of the amount adsorbed at equilibrium, is often considered as a measure of the rate of adsorption and for the second-order process is given as per equation (2.9). The calculated values of $t^{1/2}$ for the Congo red adsorption by raw pine cone were 83.63 s (1.39 min), 55.88 s (0.931 min), 65.68 s (1.09 min) and 74.36 s (1.23 min) for an initial concentration range of 20, 30, 40 and 50 ppm respectively.

Table 4.2 Pseudo-first-order kinetic parameters for Congo Red Dye adsorption on raw pine cone and acid modified pine cone

System Parameters	q_e (mg/g), Experimental	K_1 (g/mg-min)	q_e (mg/g), Calculated	R^2
Initial dye Concentration (mg/L)				
20	9.57	0.0007	1.05	0.0009
30	18.63	0.0028	1.69	0.0284
40	21.14	0.0044	1.98	0.0923
50	25.36	0.0053	1.64	0.0581
Solution pH				
3.55	32.65	0.0014	1.05	0.0012
5.95	10.28	0.0012	1.34	0.0018
7.45	9.57	0.0021	1.03	0.0031
10.95	2.88	0.0097	1.24	0.3092
Temperature				
30°C	7.01	0.001	1.39	0.000
40°C	8.43	0.012	1.12	0.185
60°C	12.56	0.044	1.24	0.059
Acid modified pine cone - solution pH				
3.61	44.47	0.0067	1.68	0.045
5.85	9.43	0.0097	1.48	0.2007
7.45	11.71	0.0122	1.47	0.1757
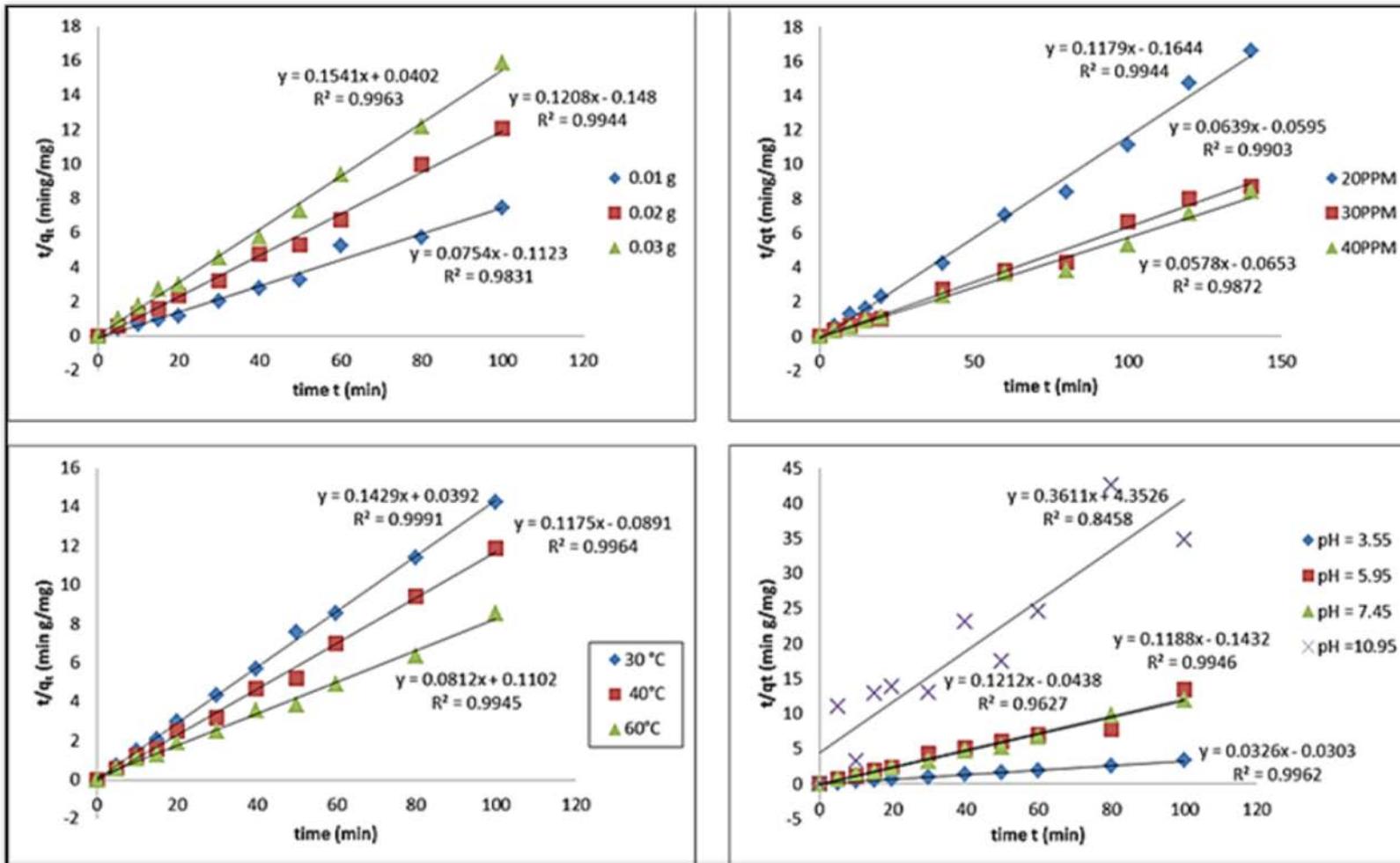
Figure 4.12 Pseudo-second-order kinetic model for Congo red dye adsorption by raw pine cone at various physico-chemical parameters
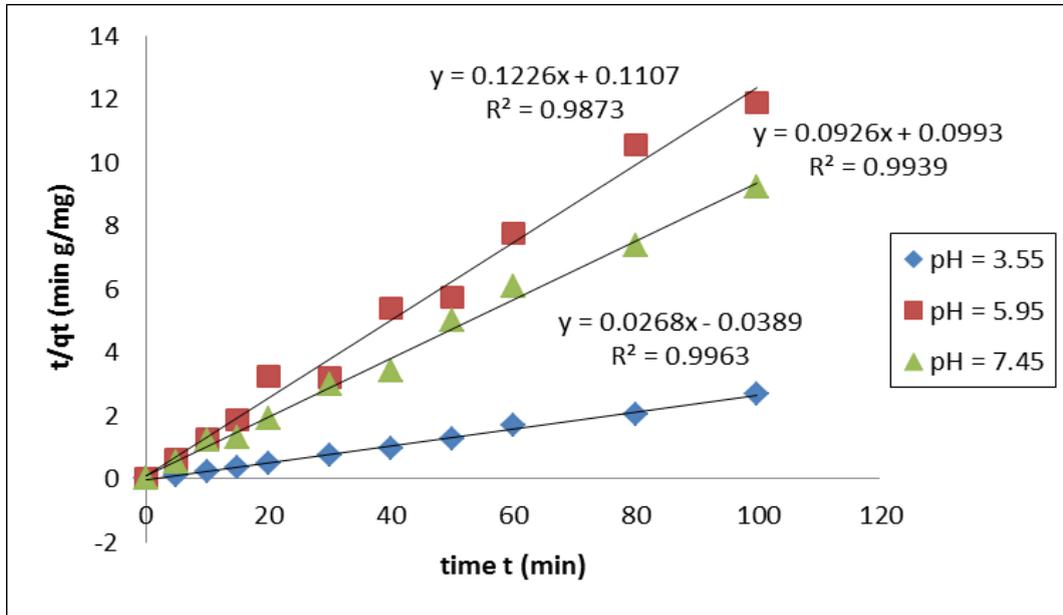
Figure 4.13 Pseudo-second-order kinetic model for Congo red dye adsorption by acid modified pine cone at varied solution pH

Table 4.3 Pseudo-second-order kinetic parameters for Congo red dye adsorption on raw pine cone and acid modified pine cone

System Parameters	q_e (mg/g), Experimental	K_2 (g/mg-min)	q_e (mg/g), Calculated	h (mg/g-min)	R^2
Adsorbent Dose (mg)					
10	15.44	0.0506	13.26	8.90	0.9831
20	9.43	0.0986	8.28	6.76	0.9944
30	6.86	0.5907	6.49	24.88	0.9963
Initial dye Concentration (mg/L)					
20	9.57265	0.0846	8.48	6.08	0.9944
30	18.63248	0.0686	15.65	16.81	0.9903
40	21.1396	0.0528	17.30	15.80	0.9872
50	25.36	0.0338	23.87	19.23	0.9924
Solution pH					
3.55	32.64957	0.0351	30.67	33.00	0.9963
5.95	10.28	0.1026	8.25	6.98	0.9873
7.45	9.002849	0.3222	8.42	22.83	0.9939
10.95	2.877493	0.0300	2.77	0.23	0.8458
Temperature					
30^0C	7.009	0.5215	6.99	25.51	0.9991
40^0C	8.433	0.1550	8.51	11.22	0.9964
60^0C	12.56	0.0897	10.06	9.07	0.9945
Acid modified pine cone - Solution pH					
3.61	39.49	0.0185	37.31	25.71	0.9963
5.85	8.43	0.1358	8.16	9.03	0.9873
7.45	10.85	0.0864	10.80	10.07	0.9939

4.3.6.2 Intra-particle diffusion and adsorption mechanism

For the process design and control of adsorption systems, it is essential to understand the underlying mechanism that results in the dynamic behaviour of the adsorption system. The adsorption capacity of Congo red dye on raw pine cone biomass was found to be fast at the initial period of contact time and then become slow and almost stable with increase in contact time. For a solid/liquid adsorption process, the solute transfer is usually determined by boundary layer diffusion and/or intra-particle diffusion. The adsorption process of liquid/solid phase is consisting consist of four steps where the dye molecules immigrate from the bulk solution to the surface of the adsorbent and diffuse through the boundary layer to the surface of the adsorbent followed by adsorption at sites and intra-particle diffusion into the interior of the adsorbent (Vimonses et al., 2009; Vadivelan and Kumar, 2005; Oladoja et al., 2008; Nandi et al., 2009). The overall rate of adsorption will be controlled by the slowest step, which would be either film diffusion or pore diffusion. However, the controlling step might be distributed between intra-particle and external transport mechanisms. The external diffusion will be involved in the adsorption process. The adsorption of Congo red dye onto raw pine cone particles may be controlled due to film diffusion at earlier stages and as the adsorbent particles are loaded with dye ions, the adsorption process may be controlled due to intra-particle diffusion. The most recommended technique for identifying the mechanism involved in the adsorption process is by fitting the experimental data with the intra-particle diffusion model(Fig 4.14) as per equations (2.9) and (2.10). This figure shows that the adsorption plots are not linear over the entire time and can be divided into 2-3 linear regions which confirm the multi stages of adsorption. Intra-particle diffusion calculation and plots for various process parameters are given in the appendix 4.5.
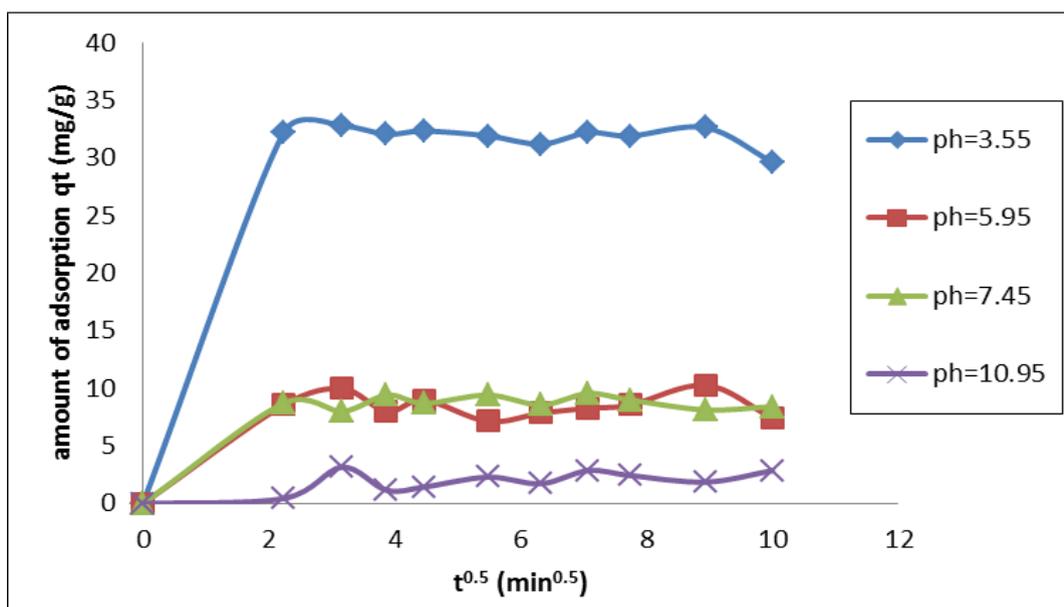
Figure 4.14 Intra particle diffusion model on different solution pH

4.3.7 Adsorption equilibrium isotherm

The adsorption isotherm is important for the description of how the adsorbate will interact with the adsorbent and give an idea of the adsorption capacity of the adsorbent (Salleh et al., 2011). The adsorbent surface phase may be considered as a monolayer or multilayer. The Freundlich isotherm model is valid for multilayer adsorption and is derived by assuming a heterogeneous surface with interaction between adsorbed molecules with a nonuniform distribution of heat of sorption over the surface (Ghaedi et al., 2011a; Vimonses et al., 2009). The favourable adsorption of the adsorption model can be determined from Freundlich constants of equation (2.11). K_F is indicative of the adsorption capacity of the adsorbent i.e. the greater K_F value, the greater adsorption capacity (Vimonses et al., 2009). The other Freundlich constant *n* is a measure of deviation from linearity of the adsorption and used to verify types of adsorption. It is suggested that if n is equal to unity, the adsorption is linear. Further, n below unity indicates that adsorption is a chemical process; whereas, n above unity is associated with a favourable adsorption and a physical process (Vimonses et al., 2009;

Mohammad et al., 2010; Sen et al., 2011; Salleh et al., 2011). Figure 4.15 gives results on Freundlich isotherm fittings for pine cone with linear correlation coefficient (R^2) of 0.96. Freundlich constants i.e. adsorption capacity, K_f and rate of adsorption, n, are calculated from this plot which are 18.33 mg/g and 1.17 respectively. The value of 'n' is larger than 1 which indicates the favourable nature of adsorption and a physical process.

Unlike the Freundlich isotherm, the Langmuir isotherm is valid for the adsorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites (Ghaedi et al., 2011b). Figure 4.16 gives results on Langmuir-1 isotherm fittings for raw pine cone biomass adsorbent with poor and lower regression coefficient (R^2) than Freundlich model. Poor linear regression coefficient (R^2) indicates the inapplicability of Langmuir isotherm. The Freundlich isotherm model gave a better fit than Langmuir. Similar results have been reported for the adsorption of phosphate ions by pine cone (Benyoucef and Amrani, 2011). Full calculations are presented in appendix 4.6.
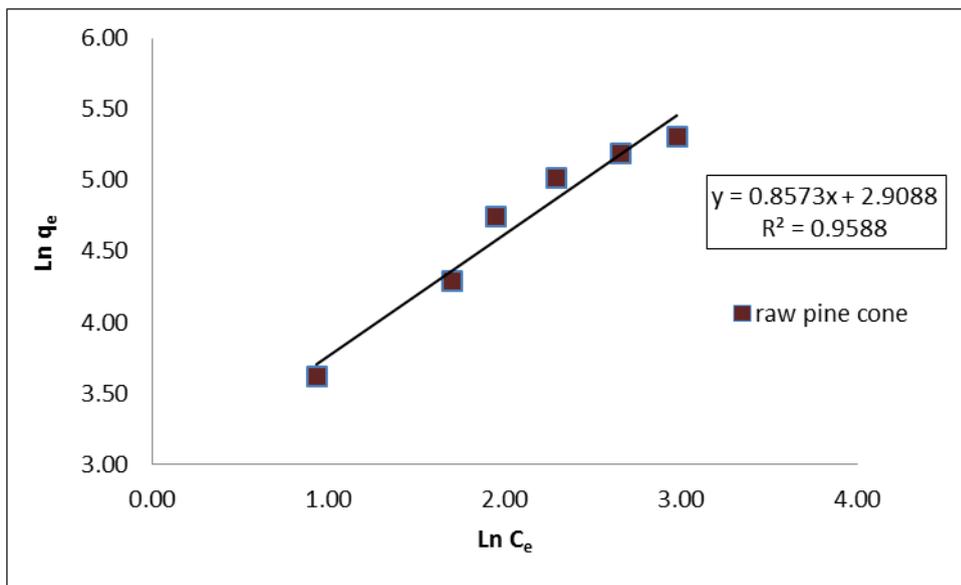
Figure 4.15 : Freundlich Plot: Amount of Adsorbent (Pine Cone) added = 10 mg; Initial CR Concentration = 10, 20, 30, 40, 50, 60 ppm; pH = 3.55 Temperature = 60°C; Shaker Speed = 120 rpm
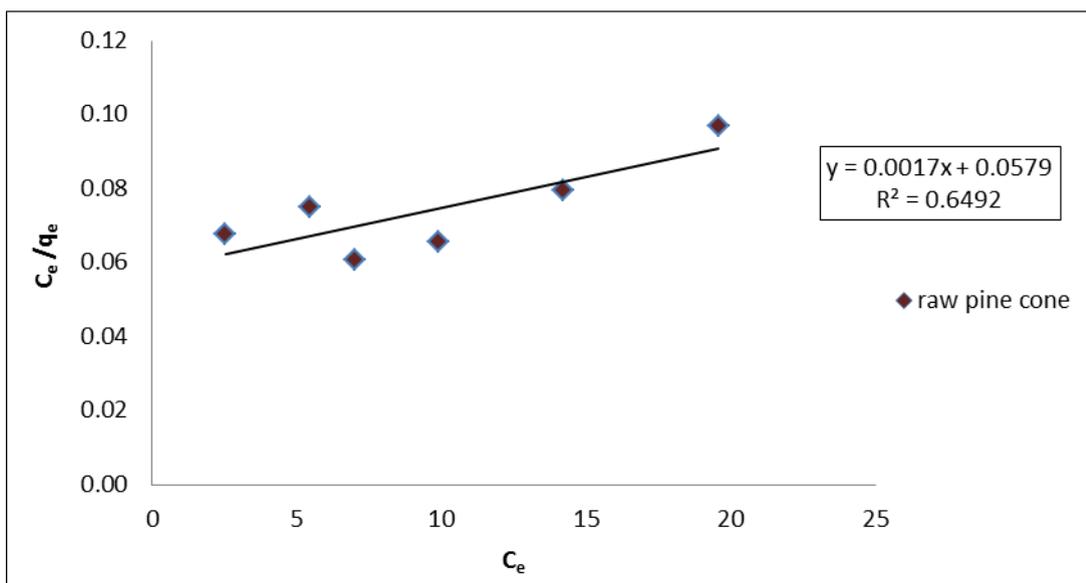
Figure 4.16 Langmuir-I Plot: Amount of Adsorbent (Pine Cone) added = 10 mg; Initial CR Concentration = 10, 20, 30, 40, 50, 60 ppm; pH = 3.55 Temperature = 60°C; Shaker Speed = 120 rpm

4.4 Desorption studies

Desorption studies help to elucidate the mechanism and recovery of the adsorbate and adsorbent. In the desorption studies, the loaded raw adsorbent that was used for the adsorption of dye solution was separated from solution by centrifugation and then dried. The dried adsorbent was agitated with 250 ml of distilled water at various solution pH of 4.2 -9.2 for the predetermined equilibrium time of the adsorption process. The desorbed dye was determined. It was found that percent desorption increased with increase in pH of the aqueous medium for which plot is not shown here. Desorption tests showed that maximum dye releasing of 78.12% was achieved in aqueous solution of alkaline solution. This is just opposite to the pH effect indicating that ion exchange is probably the major mode of adsorption process. Similar types of desorption of Congo red by tamarind fruit shell results was reported by Reddy, (2006).

4.5 Design of single-stage batch adsorber from isotherm data

It was found that Freundlich isotherm model was fitted with the equilibrium data. Adsorption isotherm can be used to predict the design of single batch adsorption system (Sen et al., 2011). Due to lack of extensive experimental data, empirical design procedures based on adsorption isotherm studies are the most common method to predict the adsorber size and performance as shown in Fig 2.6. The design objective was to reduce initial Congo red dye concentration of C_0 to C_t (mg/L) for which total dye solution is V (L) (Sen et al., 2011). The amount of added adsorbent m (g) and the solute loading increasing from q_0 (mg/g) to q_e (mg/g) where q_0 =0. The mass balance for the Congo red in the single-stage operation under equilibrium is presented as in equation 2.20. Freundlich adsorption isotherm data has been utilised to design a single-stage batch adsorption system as per method developed by Kumar et al. (2010). Rearranging equations (2.11) and (2.20) can be written as below

$$\frac{m}{V} = \frac{C_0 - C_e}{K_f \, Ce^{\frac{1}{n}}} \qquad\qquad (4.1)$$

Figure 4.17 shows a series of plots derived from Equation (4.1) between the predicted amount of pine cone particles required to remove Congo red dye of initial concentrations of 20 ppm for 50%, 60%, 70% and 80% dye removal at different solution volumes (1-10 L) for a single-stage batch adsorption system, for which the design procedure is outlined.
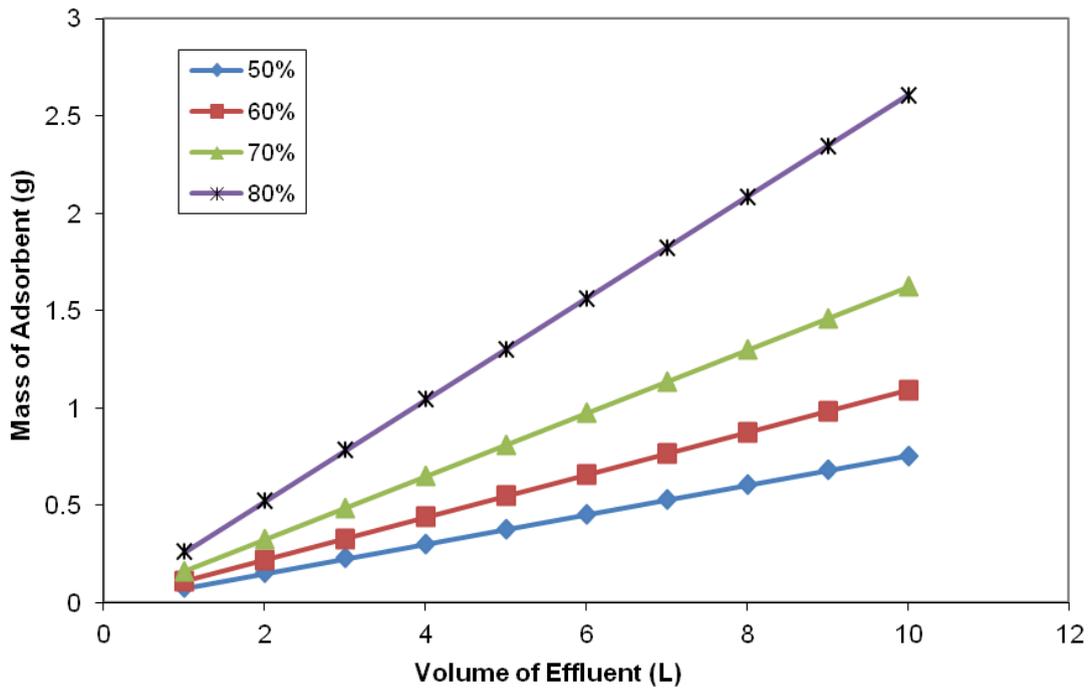
Figure 4.17 Adsorbent mass (m) against volume of solution treated (L).

4.6 Conclusion

The present study shows that the raw pine cone and acid treated pine cone, an agricultural by-product waste both can be used as an effective alternative low cost adsorbent for the removal of anionic dye, Congo red from aqueous solutions. The amount of Congo red dye uptake on raw and treated pine cone biomass was found to increases with an increase in initial dye concentration, contact time, temperature but was found to decrease with increase in solution pH and amount of adsorbent. It was observed that the adsorption was pH dependent and the maximum adsorption of 32.79 mg/g occurred at pH of 3.55 for an initial dye concentration of 20 ppm by raw pinecone, whereas for acid treated pine cone the maximum adsorption of 44.47 mg/g for the same experimental conditions. Kinetic experiments clearly indicated that adsorption of Congo red on both pine cone biomass is three step processes: a rapid adsorption of dye onto the external surface followed by intraparticle diffusion into the interior of adsorbent which has also been confirmed by intraparticle diffusion model. Overall, the kinetic studies showed that the Congo red dye adsorption process followed pseudo-second-order kinetics models and the adsorption was controlled by chemisorptions process. Freundlich isotherm model gave better fittings with experimental data than Langmuir model where the maximum adsorption capacity of raw pine cone biomass was found to be 18.33 mg/g. Freundlich constant, n, give an indication of favorable adsorption which was physical adsorption. The thermodynamic analysis indicates that system was endothermic and physical processes in nature.

4.7 References

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5. CHAPTER FIVE – Synthesis and characterization of novel pine cone biomass based activated carbon and its application in the removal of Congo red dye from aqueous solution by adsorption*

Abstract

This study was undertaken to synthesize a novel biomass based chemically activated carbon from Australian pine cone and to investigate its effectiveness in the removal of anionic dye Congo red from aqueous solution. The effect of activation parameters such as the concentration of phosphoric acid and temperature were identified as the most efficient parameters for activation in the Congo red removal. The synthesize activated carbon was characterized by Fourier transform infrared (FTIR) and different physical properties such as bulk density, CHNS analysis, carbon yield, particle size, zeta potential and BET surface area were also determined. Batch adsorption study showed that the amount of adsorption depends on various physico- chemical process parameters such as solution pH, dye concentration, temperature and adsorbent dose. It was observed that Langmuir maximum adsorption capacity (q_m) was 500 mg/g at a pH of 3.5. Furthermore, pseudo-first-order, pseudo-second-order, Elovich and Intra-particle diffusion models were fitted to examine the adsorption kinetic and mechanism of adsorption. Equilibrium data were fitted with Langmuir, Freundlich and Tempkin adsorption isotherm models. Thermodynamic parameters such as ΔG^0, ΔH^0, and ΔS^0 were also calculated. Finally, a single-stage batch adsorber design for the Congo red adsorption onto activated carbon particles was presented based on the Freundlich isotherm model equation. These results indicated pine cone biomass is good and cheap precursor for the production of an effective activated carbon adsorbent.

5.1 Introduction

The removal of dyes and organics in an economic way remains a very vital problem although a number of systems have been developed with adsorption techniques (Singh and Arora, 2011). Activated Carbon is proven to be an effective adsorbent for the removal of variety of organic and inorganic pollutants dissolved in aqueous media or from gaseous environment (Yin et al., 2007). It produced from coal or biomass is a porous material (Tay et al., 2009). The effectiveness of this versatile adsorbent is due to its external surface area, micro porous structure, high adsorption capacity and high degree of surface reactivity. There are variety of applications of activated Carbon (AC) such as in oil and gas industry, food and chemical industry, solvent recovery, air pollution control, waste water treatment and in hydrometallurgy for the recovery of gold and silver (Sugumaran et al., 2012). However, commercial activated carbon (CAC) treatment processes have clear disadvantages including the high cost and difficulties with regeneration. In the recent years, growing research interest is focusing upon agricultural residual biomass based AC. Biomass may offer inexpensive and renewable additional source of activated carbon which may help to reduce the cost of waste disposal and provide a potentially inexpensive alternative into existing commercial activated carbons. Commercially activated carbon material can be produced by two methods; physical activation with steam, air and/or carbon dioxide and chemical activation with reagents such as phosphoric acid, zinc chloride, potassium hydroxide and sodium hydroxide(Fathy et al., 2012; Tay et al., 2009). Chemical Activation has more advantages than physical activation because it is carried out in single step i.e. carbonization and activation are united and relatively lower temperature operation and higher yield (Fathy et al., 2012; Tay et al., 2009).

There are many reported biomass based activated carbon production such as from Myrtus communis & pomegranate(Ghaedi et al., 2012), date palm pits (Reddy et al., 2012), macadamia nut shells(Poinern et al., 2011) and Cattail(Shi et al., 2010). Large quantities of pine cone are produced annually as agricultural by-product throughout the world. The ovulate cone is the well-known cone of the pinus and other conifers. Although there are many recent studies reported for the synthesis of activated carbon from various agricultural by-product biomasses, to the best of our knowledge, no work has been reported on the activated carbon synthesis from pine cone (*Pinus. Radiate*) biomass. Therefore, one of the objectives of this work was to investigate the possibility of synthesising low cost novel activated carbon from locally available *Pinus. Radiate* biomass by chemical activation with phosphoric acid and its effective adsorptive removal of anionic Congo red (CR) dye from aqueous solution. The adsorption capacities of activated carbon depend upon the sources of raw materials used and method of activation. The preparation and treatment conditions that influence the properties of prepared activated carbon are specific surface area, pore structure, bulk density and surface charge, etc. Therefore, another objective of this work was to investigate the characterizations of carbon prepared during different treatment conditions. This present research work will also explore the mechanism and adsorption kinetics of Congo Red (CR) by pine cone derived Activated Carbon (AC) and will determine the various physico-chemical controlling factors on the rate of adsorption and on the capacity of adsorbent. The adsorption kinetic experiments are examined under various physico-chemical conditions such as initial pH solution, initial adsorbent dose, dye concentration and temperature. Also, the equilibrium isothermal models and thermodynamics properties were investigated.

5.2 Materials and Methods

5.2.1   Raw material collection and preparation of activated carbon

Pine tree cones (*P. radiate*) were obtained from the campus of Curtin University Perth Western Australia and it was collected between March and April of 2012. The cones were washed several times with distilled water to remove dust, dirt and soluble impurities. The cones were oven dried at temperature between 75 - 80˚C for 24 hours. The dried pinecone biomass was ground in a domestic blender to a fine powder and passed through British Standard Sieves (BSS) of 106 µm. Pine cone powder was mixed with phosphoric acid (H_3PO_4) at an impregnation ratio of 1:2 respectively and kept at room temperature for 3 hrs. The mixture was placed in a horizontal tube furnace with constant flow of nitrogen gas to avoid oxidation. The temperature inside the tube furnace was increased at the rate of 10˚C/min until it reached the set point then kept at the set point temperature for a period of 2 hrs. Pine cone biomass based activated carbon was prepared under various initial phosphoric acid concentrations and temperature profiles. Phosphoric acid with varied concentration of 0.5M, 1M, 3M and 14.7M were mixed with pine cone powder and the mixture was placed in the tube furnace. The temperature inside the tube furnace was increased at the rate of 10˚C/min until it was reached the set point of 350˚C for a period of 2 hrs. In the next stage, phosphoric acid with a concentration of 1M was mixed with pine cone powder at an impregnation ratio of 1:2 where the temperature inside the tube furnace increased at the rate of 10˚C/min until it reached the desired temperature. Various temperature profiles such as 120˚C, 180˚C, 250˚C and 350˚C are used in this study. The Activated Carbon (AC) samples were cooled down at room temperature followed by washing with distilled water until the solution reached at a pH ≥4.5 and the conductivity of the solution was measured to identify the possibility of any ions released in water. The final activated carbon samples were placed in the oven over night at a temperature of 50˚C to dry. An overview of the synthesized process is presented in Fig 5.1.

Figure 5.1 An overview of pine cone based activated carbon synthesis process

5.2.2 Chemicals

All chemicals used were of analytical grade. The anionic dye, Congo red (CR) was selected as the adsorbate in the present study. It is a sodium salt of 3,3'-([1,1'-biphenyl]- 4,4'-diyl) bis (4-aminonaphthalene-1-sulfonic acid) with a formula: $C_{32}H_{22}N_6Na_2O_6S_2$ and molecular weight of 696.66 g/mol.. The pH of the solutions was adjusted by addition of either 0.5M phosphoric acid or 0.1 M sodium hydroxide solutions and measured by Adwa pH meter. Also, Phosphoric acid of various concentrations was used as a chemical agent in the preparation of activated carbon. The experimental CR solution were prepared as per section 3.2.

5.2.3 Batch adsorption kinetic and isotherm experiments

Batch adsorption experiments were conducted by varying the operational parameters such as the initial solution pH, adsorbent dose, initial dye concentration and temperature at predetermined time interval under the aspect of adsorption kinetics, adsorption isotherm and thermodynamic study. A known amount of the adsorbent was placed with 50 ml of aqueous Congo red solutions of known concentration in a series of 250 ml plastic bottles. The mixture is shaken in a constant temperature using Thermo line scientific Orbital Shaker Incubator at speed of 120 rpm and temperature of 30 °C temperature. At predetermined time, the bottles were withdrawn from the shaker and the residual dye concentration in the reaction mixture was separated from the adsorbents by centrifuging. The amount of dye adsorbed onto the adsorbent at time t, q_t (mg/g) and % Adsorption were calculated from equations (3.3) and (3.4) respectively. Also, the equilibrium isotherm adsorption experiment was conducted by contacting 50 ml of various initial dye concentrations of 20, 30, 40, 50 and 60 ppm with 15 mg activated carbon powder in 250 ml conical flask for a period of 2. Full experimental procedures were described in section 3.4.

5.3 Results and Discussion

5.3.1 Effect of phosphoric acid concentration and temperature profile on various synthesized pine cone based activated carbon and its adsorption efficiency

The synthesized activated carbons under different acid concentrations and temperature profiles were used as adsorbents in the removal of dye Congo red from its aqueous solution under various solution pH. The effect of solution pH on the adsorption process was studied in the medium pH range of 2.6 to 8.2 as shown in Fig 5.2. It was found that the amount of dye adsorbed at time t, q_t (mg/g) decreased dramatically for all biomass activated carbon samples due to the increase in solution pH from 2.6 to 8.2 for a fixed initial dye concentration of 20 mg/L. Also, Fig 5.2 showed that the acidic pH was favourable for adsorption of CR dye. While the general mechanism of the chemical activation are not so well understood as for physical activation, the activation agents were reported to act as an acidic/alkaline catalyst to promote bond cleavage, hydrolysis, dehydration, accompanied by cross linkage between acid/alkaline and biopolymers (Sugumaran et al., 2012). At acidic pH medium there is a strong electrostatic attraction between the positively charged surface of the activated carbons and anionic dye. Higher pH range leads to increase the number of negatively charged sites on adsorbent and hence decreases the amount of adsorption due to electrostatic repulsion between the negatively charged surface of the activated carbons and anionic dye.

It was further observed that increasing in adsorbent dosage from 0.01 g to 0.03 g results in decrease of amount of dye adsorbed at time t, q_t (mg/g) as shown in Fig.5.3. The decrease in amount of dye adsorbed q_t (mg/g) with increasing adsorbent mass is due to the split in the flux or the concentration gradient between solute concentration in the solution and the solute concentration in the surface of the adsorbent (Kumar et al., 2010; Vadivelan and Kumar, 2005). Finally, it was found that synthesized biomass activated carbon of 1M/ 250°C and 14.7M/350°C exhibit the highest amount of dye adsorbed q_t (mg/g) with a minimum adsorbent dose. Full calculation on the adsorption capacity q_t (mg/g) and dye removal percentage is presented in appendix 5.1.
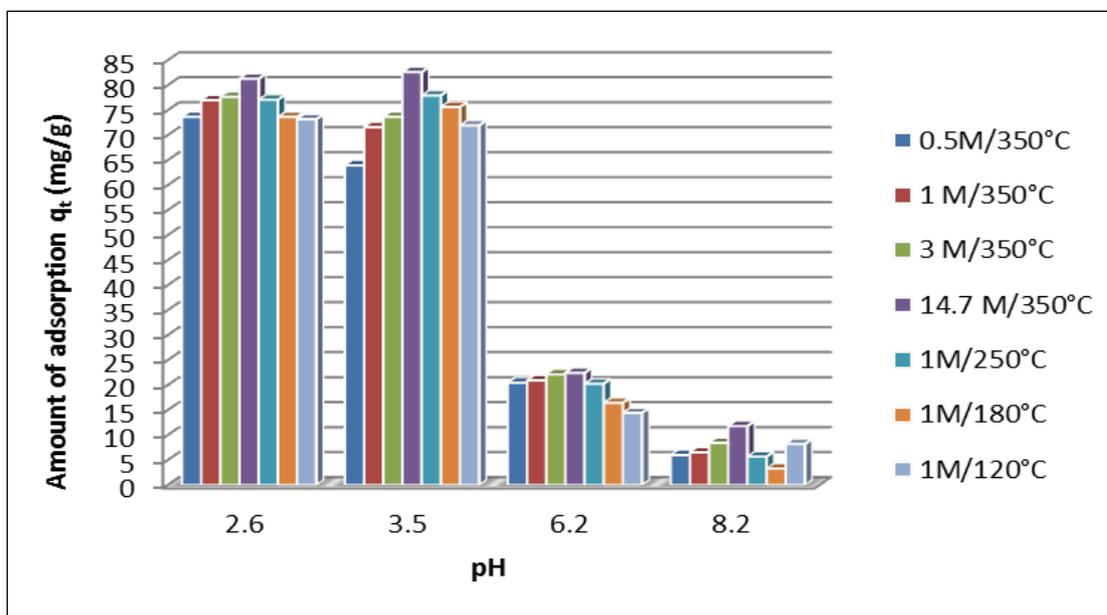
Figure 5.2 Effect of pH on biomass based activated carbon samples prepared under various acid concentration and temperature profiles in the removal of CR dye: Dose 10 mg, Volume of CR Solution 50 ml, Initial CR Concentration 20 ppm, Temp 30 °C , Shaker Speed 120 rpm and t =30 mins.
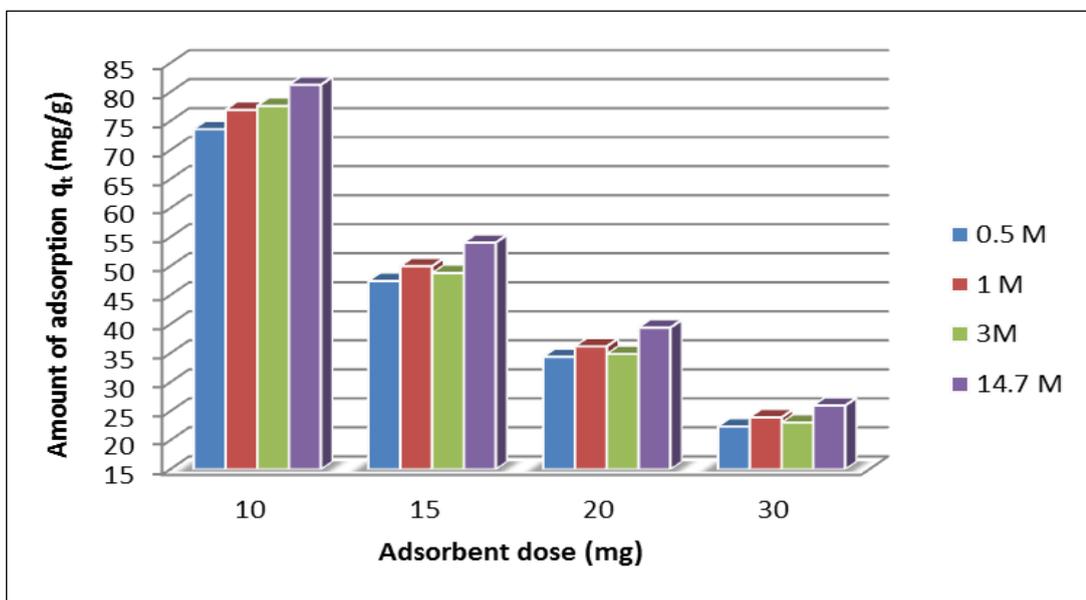
Figure 5.3 Effect of adsorbent dose on activated carbon samples prepared under different phosphoric acid concentration in the removal of CR dye: pH 2.6, Volume of CR Solution 50 ml, Initial CR Concentration 20 ppm, Temp 30 °C , Shaker Speed 120 rpm and T= 30mins.

5.3.2 Physical and chemical characterizations of synthesized pine cone biomass based activated carbon

5.3.2.1 C-H-N-S Analysis and Bulk Density

The adsorption efficiency of activated carbon is greatly affected by its physical and chemical properties such as particle size, total surface area, bulk density, CHNS analysis, FTIR and SEM various physico-chemical process parameters. Table 5.1 presents CHNS analysis and bulk density results of pine cone biomass based activated carbon at various carbonization temperature and acid concentration. Results obtained in this study were close to the reported results on C, H, N, S element analysis with other biomass based activated carbon (Tay et al., 2009). It was found from Table 5.1, activated carbon at $250^{\circ}C$ and at phosphoric acid concentration of 1 M had high C/H ratio with lowest sulphur content compared to raw pine cone and other AC samples.

Bulk density is an important parameter for consideration in the designing of adsorption towers for use in pilot plant structure as well as large commercial application. It affects the overall performance of the adsorption process. Also, it is inversely related to the particle size .The American Water Work Association has set a lower limit on bulk density at 0.25 g/cm^3 for practical use of activated carbon. The bulk density of synthesized activated carbon samples was shown in Table 5.1. It was found that synthesized activated carbon (1M/250°C) was 0.36 g/cm^3. Bulk density is inversely proportional to particle size. Similar bulk density of various biomass based activated carbon were reported by Sugumaran et al., 2012. Furthermore, the activated carbon yield of biomass AC of 1M phosphoric acid and temperature of 250°C was 49% which is quite high and very much comparative with other biomass based activated carbon and CAC (Sugumaran et al., 2012)

Table 5.1 CHNS analysis and bulk density of pine cone biomass based activated carbon

Samples	% (C)	% (H)	% (N)	% (S)	Bulk density (g/cm³)
AC-1 M / 350°C	69.75	3.71	1.98	2.2	0.310
AC-1 M / 250°C	62.28	3.69	1.85	2.1	0.360
AC-1 M / 180°C	53.91	4.03	1.60	2.45	0.282
AC-1 M / 120°C	53.59	5.77	1.18	3.18	0.256
AC-0.5 M/ 350°C	67.89	4.12	1.94	2.22	0.265
AC-3 M / 350°C	66.2	4.44	1.08	2.37	0.271
AC-14.7M/350°C	68.68	4.41	1.08	2.45	0.255

5.3.2.2 Characteristics of N$_2$ adsorption and particle size distribution

BET and Langmuir surface areas were used to explain the physical adsorption of N$_2$ gas molecules on the monolayer solid surface of raw pine cone of 106 µm and activated carbon. In this work, Micromeritics (TriStar II 3020) was used to measure the surface area of raw pine cone and activated carbon by degassing the sample to eliminate any trace of volatile elements at room at 60°C for 15 hours. BET surface area of raw pine cone and activated carbon were calculated as 1.79m^2/g and 66.4m^2/g respectively whereas Langmuir surface area of biomass based activated carbon was calculated as 88.2m^2/g . Also, the total pore volume and average pore size of AC were calculated as 0.03cm^3/g and 17.94 Å. Also, Malvern master sizer (Hydro 2000S) instrument was used to measure the particle size distribution and specific surface area of raw pine cone powder and various synthesized activated carbon. Fig 5.4, presented the particle size distribution of synthesized activated carbon (1M Phosphoric acid and temperature profile of 250°C). The surface weighted mean particle size for raw pine cone and 1M/250°C biomass activated carbon were calculated as 71.02 µm and 65.74 µm. Particle size distribution of various synthesized activated carbon samples are presented in appendix 5.2.
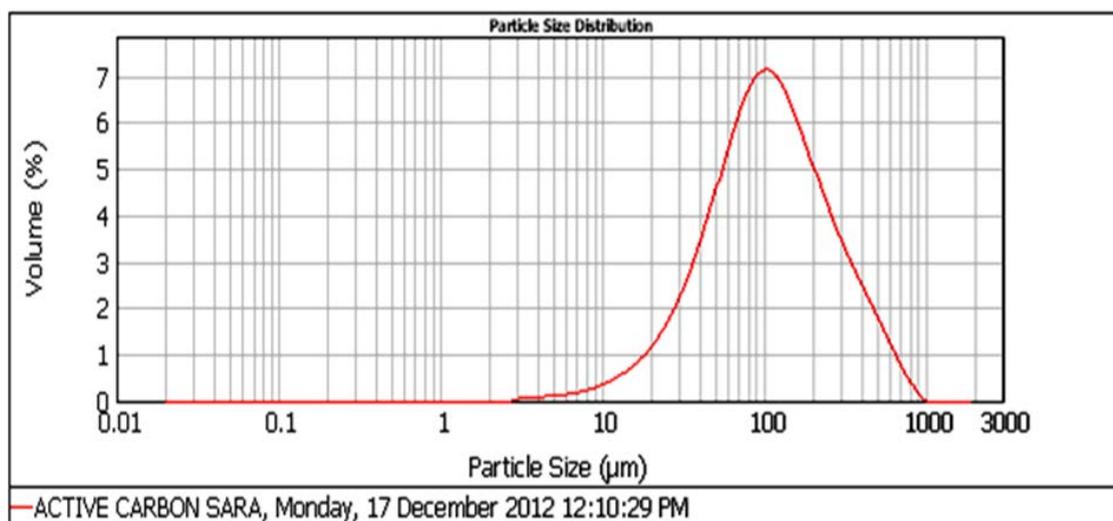
Figure 5.4 Particle size distribution of synthesized activated carbon (1 M Phosphoric acid and temperature profile of 250 $^\circ$C

5.3.2.3 FTIR analysis

Fourier-transform infrared (FTIR) spectrometer (Perkin Elmer-Spectrum100) was used to investigate the functional groups presented in the synthesized activated carbon sample as shown in Fig 5.5. The absorption band at 3200–3600 cm^{-1} was presented with a peak band at about 3158 cm^{-1}and this is due to O-H and N-H stretching groups. Another peak around 1594 cm^{-1} was found and can be describe as C=C weak stretch aromatic ring. Alkane small C–H absorption band was found at 1433 cm^{-1}. Another peak of 1175 cm^{-1} was detected as P =O and P–O–C. These function groups were found due to the present of H_3PO_4 acid as an activation agent in the preparation of activated carbon.
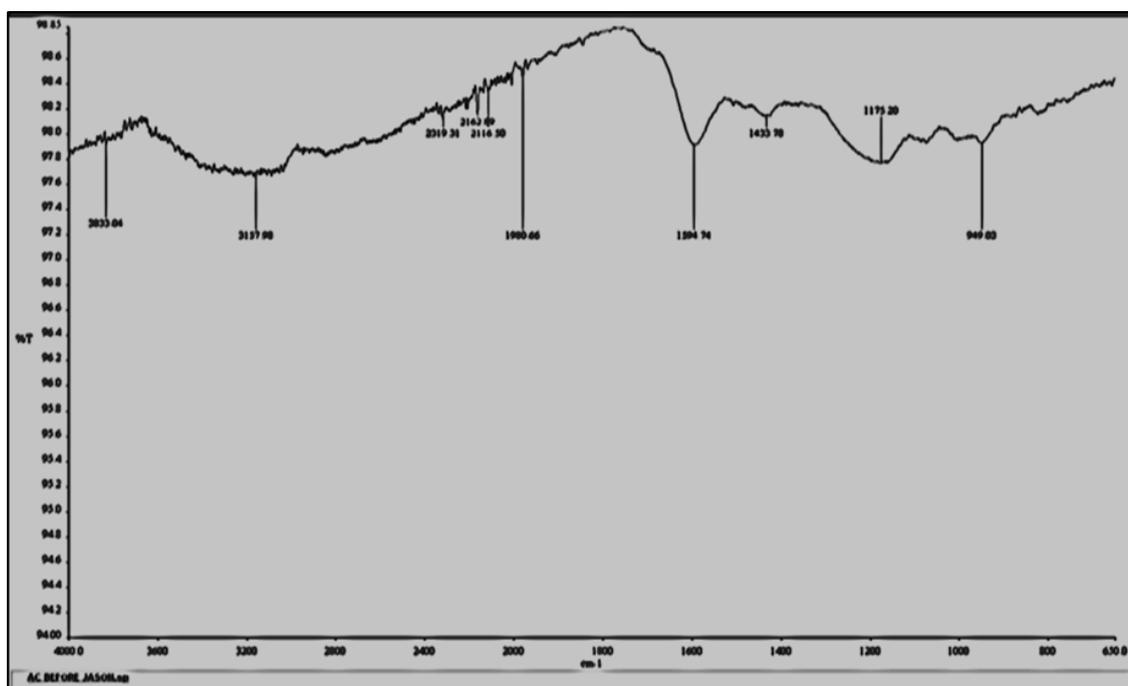
Figure 5.5 FTIR spectrum of synthesized biomass based activated carbon (1M/250°C)

5.3.2.4 SEM characterization

Scanning Electron Microscope (SEM) was used to scan and analyse the morphological structure and the surface characteristic of the synthesized activated carbon (1M/250°C) before and after adsorption of dye Congo red. The SEM was carried out using Zeiss Evo 40XVP model. The availability of pores and internal surface is clearly displayed in the SEM picture before adsorption and the coverage of the surface and the pores by the adsorbed Congo red as shown in Fig 5.6. Generally, the porous structure that appears in Fig 5.6 gets blurred in Fig 5.7 because of adsorption.
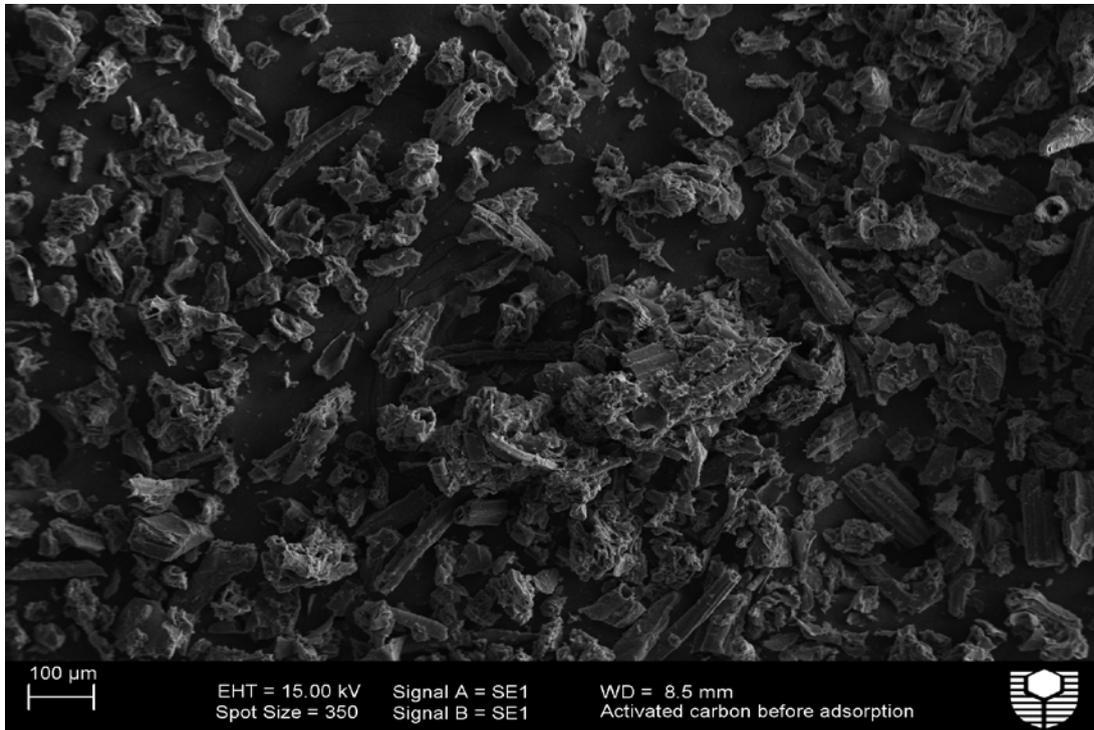
Figure 5.6 SEM analysis of synthesized activated carbon (1M/250°C) before adsorption
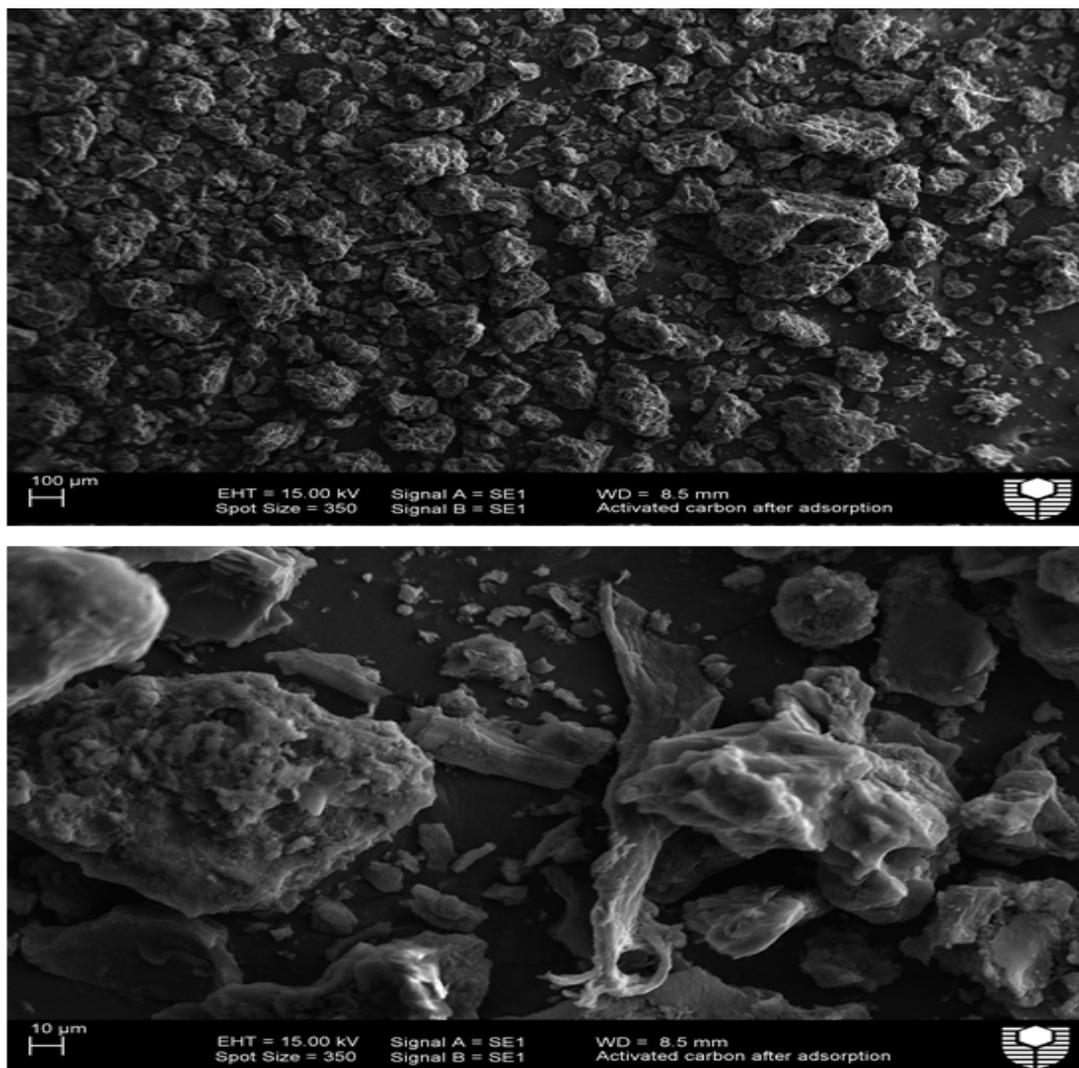
Figure 5.7 SEM analysis of synthesized activated carbon (1M/250°C) after adsorption

5.3.3 Adsorption kinetic experiments

5.3.3.1 Effect of initial solution pH on Congo red dye adsorption

The effect of CR dye solution is an important parameter for solute adsorption because of change in surface of adsorbent and change in chemistry of the adsorbate. The colour of CR dye changes to dark blue at acidic pH and to red at alkaline solution pH but the red colour is slightly different from the original red colour at neutral pH. Similar observation was also reported by Kaur et al., (2013). The effect of solution pH on the adsorption of Congo red dye from its aqueous solution by synthesized activated carbon (1M/250°C) was studied in the range of 2.6 to 8.2 as shown in Fig 5.8. It was found that the amount of dye removal efficiency decreased from 77.1% to 7.6% due to increase in solution pH from 2.6 to 8.2 for a fixed initial dye concentration of 20 mg/L. Also, the amount of adsorbed mass of CR dye, q_t (mg/g) consistently decreased with increasing solution pH as shown in Fig 5.8. The point of zero charge, pH_{PZC} of the synthesized activated carbon particles in aqueous solution was 2.2. From Fig 5.9, negative zeta potential increased with increasing alkaline solution therefore at acidic pH of 2.6, high adsorption takes place because of strong electrostatic attraction between the positively charged surface of the adsorbent and anionic dye. With the increase in solution pH, the number of negatively charged sites increases and the number of positively charged sites decreases and hence does not favour for anionic dye adsorption due to electrostatic repulsion. A similar behaviour is observed for Congo red dye adsorption on commercial activated carbon (Purkait et al., 2007) (Kaur et al., 2013). Full calculations on the adsorption capacity q_t (mg/g), dye removal percentage and zeta potential are presented in appendix 5.3.
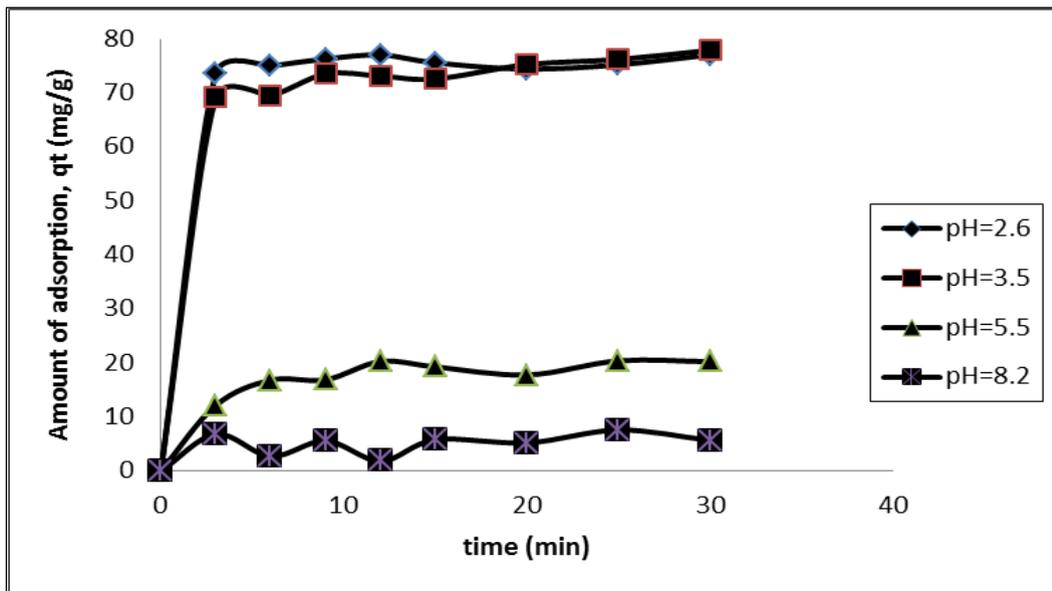
Figure 5.8 Effect of initial solution pH on the adsorption of CR dye onto AC powder:
Mass of Adsorbent 10 mg, Volume of CR Solution 50 ml, Initial CR Concentration
20 ppm, Temp 30 °C and Shaker Speed 120 rpm and T=3mins time interval.
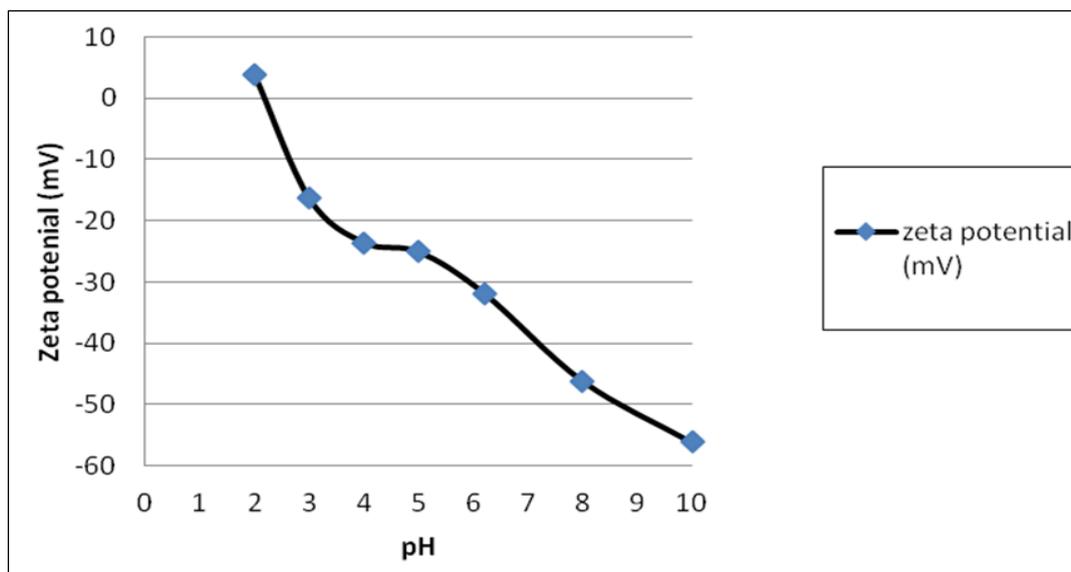
Figure 5.9 Variation of surface charges of synthesized activated carbon
(AC) particles at different solution pH.

5.3.3.2 Effect of adsorbent dosage on Congo red dye adsorption

The batch experiment was carried out to examine the effectiveness of different doses of biomass activated carbon (1M/250°C) adsorbent on CR dye and determine the most economical minimum dosage. It was observed that the increase in adsorbent dosage from 0.01 g to 0.03 g results in decrease of amount of dye adsorbed (q_t) from 77.1 (mg/g) to 26.9 (mg/g) as shown in Fig 5.10 while the percentage dye removal is increasing slightly from 77.1 % to 80.6 % as shown in Fig 5.11. This experiment was carried out at acidic solution pH of 2.6 thus higher removal efficiency was observed. The decrease in amount of dye adsorbed q_e (mg/g) with increasing adsorbent mass is due to the split in the flux or the concentration gradient between solute concentration in the solution and the solute concentration in the surface of the adsorbent(Kumar et al., 2010; Vadivelan and Kumar, 2005). Increasing the adsorbent mass leads to an increase in the dye removal percentage and this is due to increase the active sites on the adsorbent surface. Full calculations on the adsorption capacity q_t (mg/g) and dye removal percentage are presented in appendix 5.4.
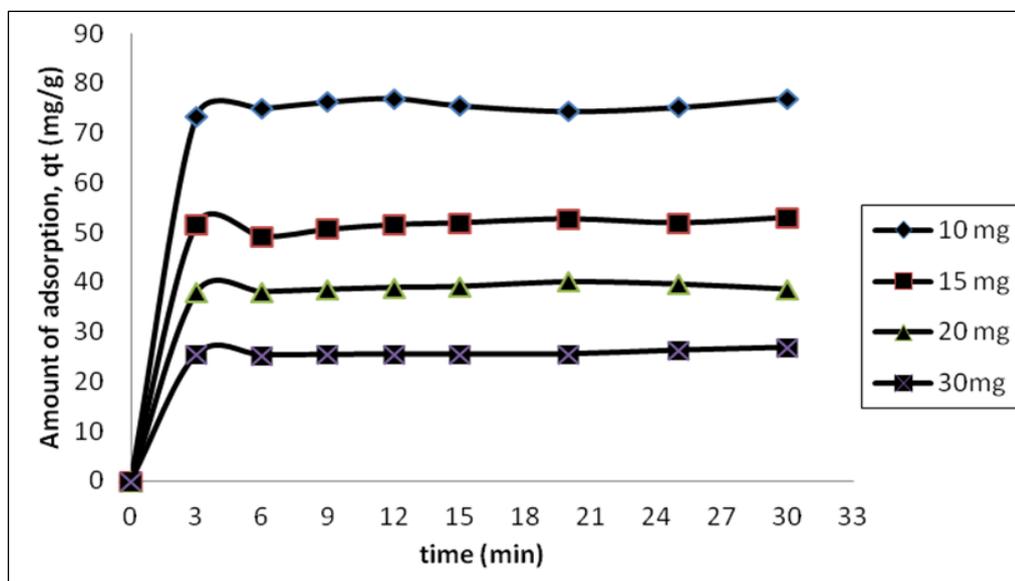
Figure 5.10 Effect of adsorbent dosage of CR dye adsorption: pH solution =2.60, Volume of CR Solution 50 ml, Initial CR Concentration 20 ppm, Temp 30 °C and Shaker Speed 120 rpm and T=3mins time interval .
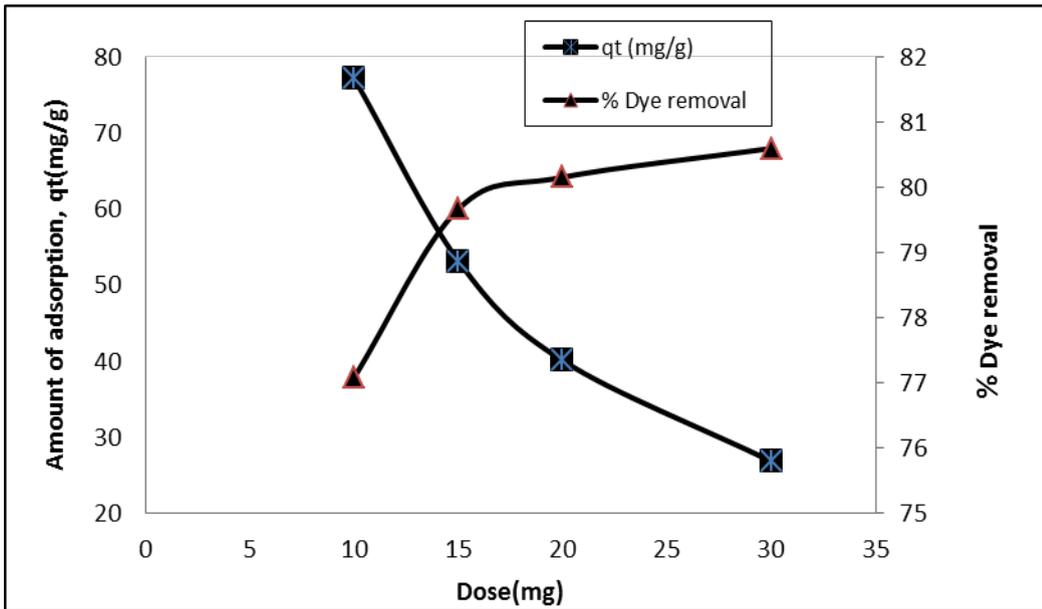
Figure 5.11 Effect of adsorbent dosage of CR dye adsorption: pH solution = 2.60, Volume of CR Solution 50 ml, Initial CR Concentration 20 ppm, Temp 30 °C , Shaker Speed 120 rpm and T= 30mins.

5.3.3.3 Effect of initial dye concentration and contact time

The initial dye concentration parameter has a significant effect on the amount of dye adsorbed q_t (mg/g) and percentage dye removal from its aqueous solution. The effect of contact time on the adsorption of CR dye was investigated during kinetic study under different physico-chemical process parameters. It was found that the amount of dye adsorbed q_t (mg/g) increased from 77.1to 215.7 (mg/g) with increasing initial concentration of CR dye from 20 to 60 (mg/L) while the dye removal percentage is decreasing from 77.1% to 71.9% for same initial dye concentration range as shown in Fig.5.12. This increase in amount of adsorption is because in batch adsorption, the initial dye concentration produces the driving forces to overcome the resistance to the mass transfer of dye between aqueous and solid phase. The increase in initial dye concentration also enhances the interaction between the adsorbent and dye. From kinetics adsorption models, it was also found that the amount of adsorption q_t (mg/g) increases with increasing contact time (Fig5.13) and equilibrium is attained within 30 mins. Overall, it was a two-step process: rapid adsorption from the bulk of solution to the adsorbent. Full calculations on the adsorption capacity q_t (mg/g) and dye removal percentage are presented in appendix 5.5.
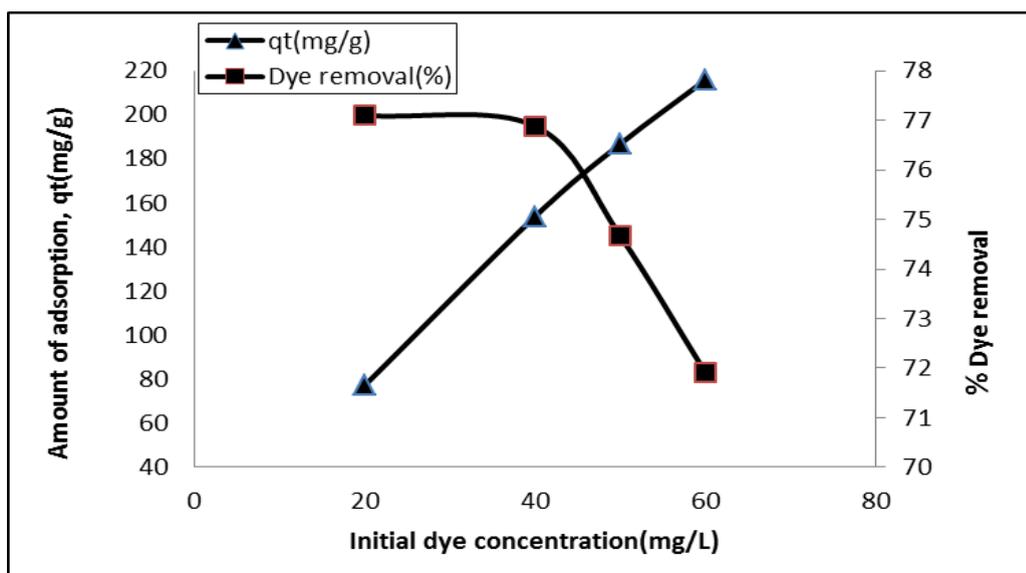
Figure 5.12 Effect of initial dye concentration of CR dye adsorption: pH solution =2.60, Volume of CR Solution 50 ml, Initial dose=10mg, Temp 30 °C , Shaker Speed 120 rpm and time= 30 mins.
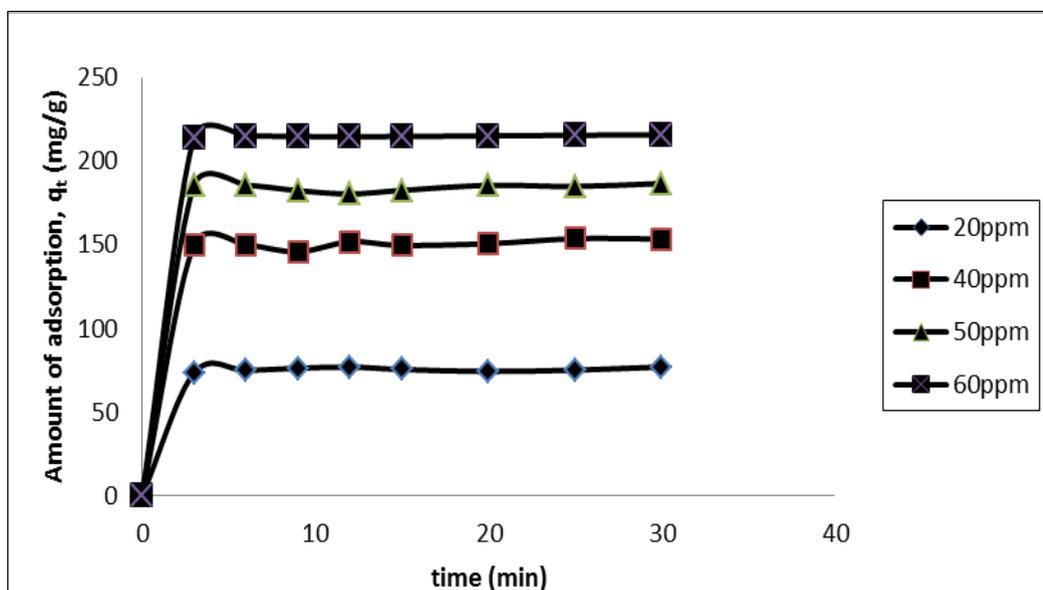
Figure 5.13 Effect of initial dye concentration on CR adsorption: pH solution =
2.60, Volume of CR Solution 50 ml, Initial CR Concentration 20 ppm, Temp 30
°C , Shaker Speed 120 rpm and T= 3 mins time interval.

### 5.3.3.4 Effect of solution temperature and thermodynamics studies

A batch experiment was carried out at different temperatures of 30°C, 40°C and 60°C as
shown in Fig 5.14. That amount of Congo red adsorption on biomass activated carbon slightly
increased from 77.1 mg/g to 81.6 mg/g with increasing temperature of the solution
respectively. This trend indicates that the process is endothermic. Increasing the temperature
leads to an increase in the number of active sites for the adsorbent(Salleh et al., 2011). The
thermodynamics parameters were calculated from equation 2.18 and 2.19 such as Gibb's free
energy (ΔG^0), entropy (ΔS^0) and enthalpy (ΔH^0) changes. The positive values of ΔH^0 and ΔS^0
indicate the endothermic nature and randomness at the solid solution interface occurs in the
internal structure of the adsorption respectively. The negative value of Gibbs free energy
(ΔG^0) suggests a favourable adsorption process at these temperatures. A summary of the
thermodynamics studies is presented in Table 5.2. Full calculations on the adsorption capacity
q_t (mg/g) and thermodynamics properties are presented in appendix 5.6.
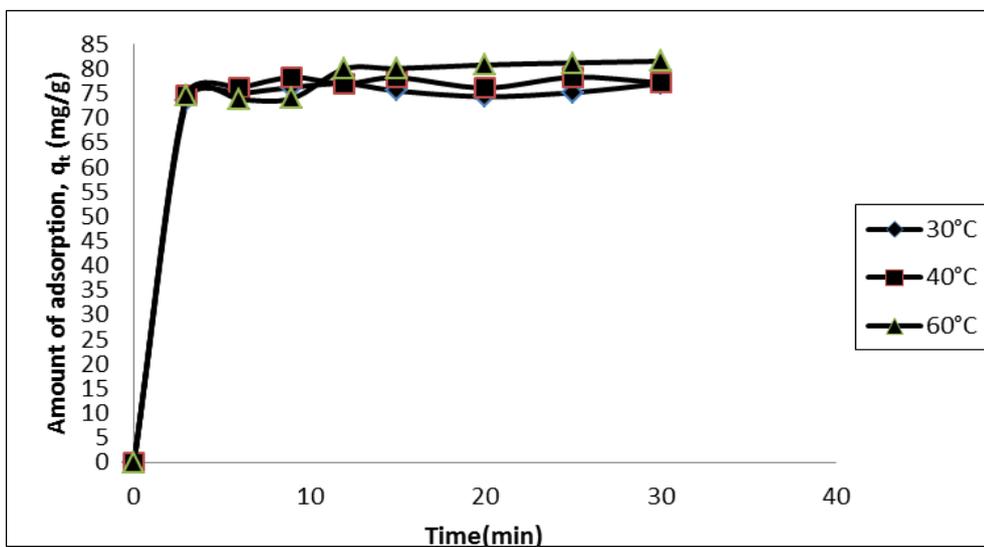
Figure 5.14 Effect of temperature on CR dye adsorption: pH solution 2.60, Volume of CR Solution 50 ml, Initial CR Concentration 20 ppm, Temp 30 °C , Shaker Speed 120 rpm and T= 30mins.

**Table 5.2 Thermodynamic parameters for adsorption of CR dye at different temperatures**

Temp (K)	ΔG° (kj/mole)	ΔH° (Kj /mole)	ΔS° (Kj /mole.K)
303	-7.087	7.924	0.050
313	-7.583	7.924	0.050
333	-8.574	7.924	0.050

5.3.4 Adsorption kinetic and mechanism of adsorption
5.3.4.1 Pseudo first order and Pseudo second order kinetic models

Batch adsorption kinetics results play a significant role in the design of industrial adsorption columns. The nature of the adsorption process depends on physical and chemical characteristics of the adsorbent system and also on the system conditions. The applicability of pseudo-first-order and pseudo-second-order models was tested to investigate the adsorption nature of CR dye on the synthesized biomass based activated carbon as per equation (2.5) and (2.7) respectively. Experimental data at various physico-chemical conditions were fitted to test the applicability of these models. Poor pseudo-first-order linear regression coefficient (R^2) values were in the range of 0.172 to 0.696 and calculated from the linearized form of the plot log (q_e _q_t) versus time (t) as shown in Table 5.3. Also, pseudo first-order kinetic model predicted a significantly lower value of the equilibrium adsorption capacity (q_e) than the experimental value thus indicated the inapplicability of this model. On the other hand, pseudo-second order model was fitted (Fig 5.15) where the (q_e) calculated values were very close to the experimental values. The (q_e) calculated values were obtained from the slope of the linearized form of the plots t/q_t verses time (t) (Fig 5.15). Pseudo-second-order kinetic plots for various physico-chemical conditions were shown in Fig 5.15. Also, the linear regression coefficients (R^2) values for pseudo second-order kinetic model were in the range of 0.989 to1 which suggest the applicability of this model as presented in Table 5.4. Chi square test (χ^2) was performed as per equation (5.1) where q_{calc} presents the calculated adsorption capacity (mg/g) and q_e is the equilibrium capacity (mg/g) from the experimental data. Low Chi square values (χ^2) indicated that the dye adsorption process followed pseudo-second-order model as presented in Table 5.3 and 5.4. It was also observed from Table 5.4, the adsorption capacity increasing with increase in initial dye concentration and temperature but decreases within initial solution pH and amount of adsorbent. Similar type of adsorption pseudo-second-order kinetic parameters such as k_2 was reported for the removal of CR dye by different adsorbents (Sen et al., 2011). Sample calculation of pseudo-first-order model is presented in appendix 5.7.

$$\chi^2 = \sum \frac{(q_e - q_{calc})^2}{q_{calc}} \qquad\qquad (5.1)$$

Table 5.3 Pseudo-first order model parameters for adsorption of CR dye on pine cone based activated carbon

System Parameters	q_e (mg/g), Experimental	K_1 (min^{-1})	q_e (mg/g), Calculated	R^2	χ^2
Initial dye Concentration (mg/L)					
20	77.09	0.33	4.65	0.468	1128.2
40	153.48	0.30	5.87	0.415	3711.6
50	186.67	0.25	4.85	0.514	6823.6
60	215.74	0.28	4.09	0.676	10957.6
Solution pH					
2.6	77.09	0.33	4.65	0.468	1128.2
3.5	77.94	0.28	6.97	0.620	722.4
5.5	20.25	0.23	3.29	0.507	87.3
8.2	5.68	0.14	2.29	0.222	5.0
Temperature					
30^{0}C	77.09	0.33	4.65	0.468	1128.2
40^{0}C	78.38	0.24	2.52	0.288	2282.7
60^{0}C	81.64	0.38	8.31	0.696	647.3
Initial dose (mg)					
10	77.09	0.33	4.65	0.468	1128.2
15	53.11	0.30	4.61	0.614	510.4
20	40.08	0.18	2.02	0.172	716.3
30	26.87	0.06	2.30	0.478	261.8

Table 5.4 Pseudo-second order model for adsorption of CR dye on biomass AC under various parameters

System Parameters	q_e (mg/g), Experimental	K_s (g/mg-min)	q_e (mg/g), Calculated	$t_{1/2}$ (sec)	R_2	χ^2
Adsorbent Dosage (mg)						
10	77.09	0.17	76.34	4.58	0.999	0.008
15	53.11	0.08	53.19	14.36	1.000	0.000
20	38.63	0.50	39.22	3.06	0.999	0.009
30	26.87	0.11	26.60	20.11	0.999	0.003
Initial dye Concentration (mg/L)						
20	77.09	0.17	76.34	4.58	0.999	0.008
40	153.48	0.04	153.85	11.08	1.000	0.001
50	186.67	0.05	185.19	6.67	1.000	0.012
60	215.74	0.21	217.39	1.30	1.000	0.013
Solution pH						
2.6	77.09	0.17	76.34	4.58	0.999	0.008
3.5	77.94	0.02	78.13	31.41	0.999	0.000
5.5	20.25	0.04	20.75	76.43	0.989	0.012
8.2	5.68	0.02	6.84	371.11	0.485	0.197
Temperature						
30^0C	77.09	0.17	76.34	4.58	0.999	0.008
40^0C	78.38	0.33	77.52	2.33	1.000	0.010
60^0C	81.64	0.03	82.64	26.78	0.999	0.012
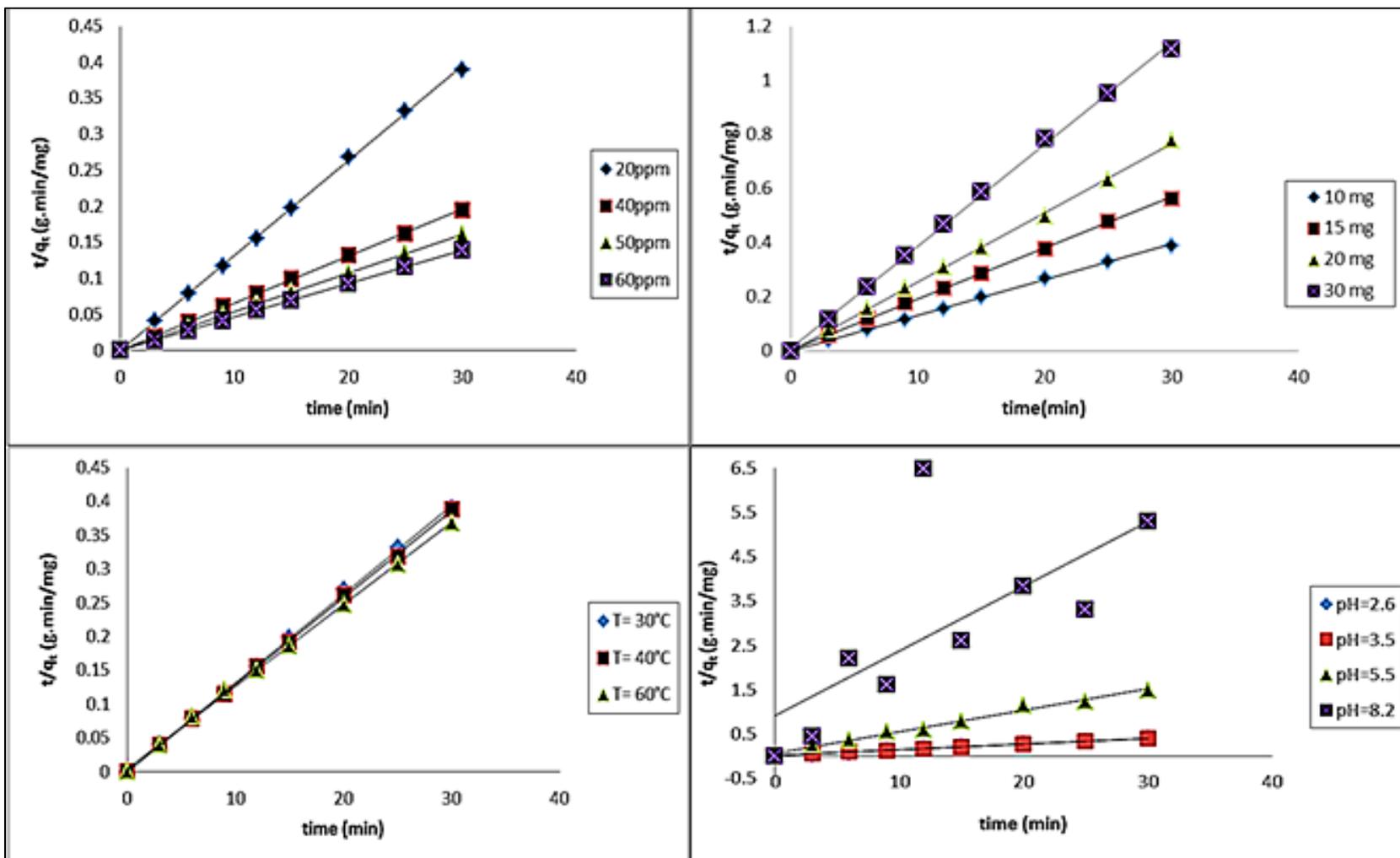
Figure 5.15 Pseudo- second –order plots for CR adsorption onto synthesized activated carbon under various physico-chemical conditions Volume of CR Solution 50 ml, , Shaker Speed 120 rpm and t=3mins time interval

5.3.4.2 Elovich model

Elovich equation was used in adsorption kinetics to describe the chemical adsorption mechanism in nature. From equation (2.8), the constant (x) (mg/(g.min)) was decreasing with increase in the initial dose and pH respectively while it increased at higher initial dye solution. The constant (y) (g/mg) exhibits the opposite nature of (x) constant. Increasing the temperature of the solution reflects a minor change in the constants values. Also, it was predicted the inapplicability of this model as the linear regression coefficients (R^2) values are less than 0.849. Full calculations are given in appendix 5.8.

Table 5.5 Elovich model for adsorption of CR dye on biomass AC under various parameters

Parameters	x (mg/(g min))	y (g/mg)	R^2
Adsorbent Dosage (mg)			
10	87.09	0.057	0.592
15	57.27	0.082	0.607
20	43.49	0.109	0.605
30	28.49	0.164	0.608
Initial dye Concentration (mg/L)			
20	87.09	0.057	0.592
40	173.40	0.028	0.593
50	224.31	0.024	0.570
60	259.82	0.020	0.574
Solution pH			
2.6	87.09	0.057	0.592
3.5	70.16	0.054	0.673
5.5	11.12	0.182	0.849
8.2	4.37	0.736	0.357
Temperature			
30^0C	87.09	0.057	0.592
40^0C	87.46	0.055	0.598
60^0C	75.13	0.051	0.670

5.3.4.3 Intra particles diffusion model and CR dye adsorption mechanism

Understanding the dynamic behaviour of the adsorption system is significant for process design. The removal of Congo red by adsorption on a biomass based activated carbon was found to be rapid at the initial period of three minutes then became slow and stable with increasing in contact time. Intra-particle diffusion mechanism for the sorption system of Congo red removal from its aqueous phase by activated carbon adsorption is assumed to consist of multi-stages where the dye molecules migrate from the bulk solution to the surface of the sorbent and penetrate through the boundary layer to the surface of the sorbent where adsorption and intra-particle diffusion take places (Vimonses et al., 2009). The experimental data were fitted as per equation (2.9) where k_{id} (mg/g min$^{0.5}$) is the intra-particle diffusion rate constant. The adsorption plot was not linear over the entire contact time and can be separated into two linear regions which confirmed the multi stages of adsorption as shown in Fig 5.16. Also, when adsorption steps are not dependent of one another, the plot of q_t against $t^{0.5}$ gives two or more intercepting lines depending on the actual mechanism (Bhattacharyya and Sharma, 2005). Furthermore, conclusion can be made that none of plot gave linear straight line segment passing through the origin showed that film diffusion and intra-particle diffusion occurred simultaneously. The diffusion coefficient (D_p) (cm^2/s) was calculated from equation (2.10) as shown in Table 5.6 for different parameters where r_o= 0.0033cm. These results agree with those of recently reported by Dogan et al., (2004), Sen et al., (2011). Intra-particle diffusion plots of varied process conditions are shown in appendix 5.9.

Table 5.6 Intra particle diffusion model parameters for adsorption of CR dye on biomass based AC under various conditions

System Parameters	K_{id} (mg/g min$^{0.5}$)	$t^{1/2}$ (sec)	D_p (cm^2 /s)	R^2
Initial dye Concentration (mg/L)				
20	10.74	3.41	9.5676E-08	0.534
40	22.27	9.52	3.4304E-08	0.537
50	26.63	5.77	5.6628E-08	0.518
60	30.99	1.33	2.4564E-07	0.518
Solution pH				
2.6	10.74	3.41	9.5676E-08	0.534
3.5	11.34	23.31	1.4018E-08	0.622
5.5	3.37	28.03	1.1656E-08	0.781
8.2	0.91	28.41	1.1498E-08	0.391
Temperature				
30^{0}C	10.74	3.41	9.5676E-08	0.534
40^{0}C	11.59	1.97	1.6607E-07	0.533
60^{0}C	12.44	19.66	1.6622E-08	0.594
Adsorbent dose (mg)				
10	10.74	3.41	9.5676E-08	0.534
15	7.52	10.73	3.0458E-08	0.557
20	5.60	2.24	1.4581E-07	0.547
30	3.75	15.08	2.1664E-08	0.560
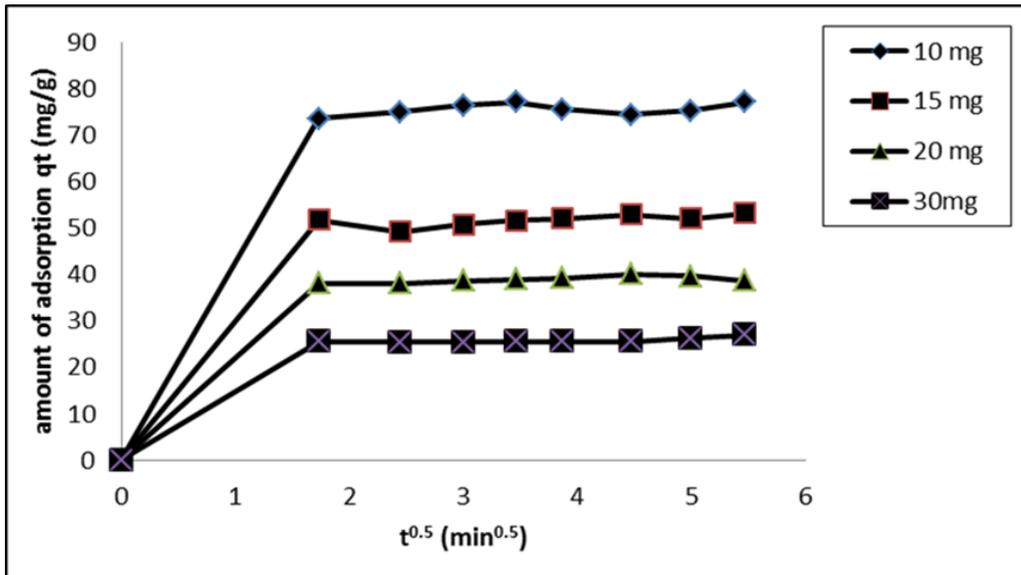
Figure 5.16 Intra-particle diffusion model on different initial CR concentrations

5.3.5 Adsorption equilibrium isotherm and mechanism of adsorption

The adsorption isotherm is important for the description of how the adsorbate will interact with the adsorbent and gives an idea of the adsorption capacity of the adsorbent (Salleh et al., 2011). Experiment data were fitted with different adsorption isotherm models to investigate the adsorbate and adsorbent interaction relationship. Freundlich model is developed to explain how multi-layers adsorption takes place by assuming a heterogeneous surface with interaction between adsorbed molecules with a non-uniform distribution of heat of sorption over the surface(Vimonses et al., 2009). The Freundlich equilibrium adsorption capacity of the system k_f (mg/g) and the Freundlich constant n were calculated from the linear equation of the plot Ln (qe) vs. Ln (Ce) as shown in Fig 5.17. Freundlich constant "n" is a measure of deviation from linearity of the adsorption and used to verify types of adsorption. The n value is more than the unity and this indicate a favourable and physical adsorption as shown in Table 5.7
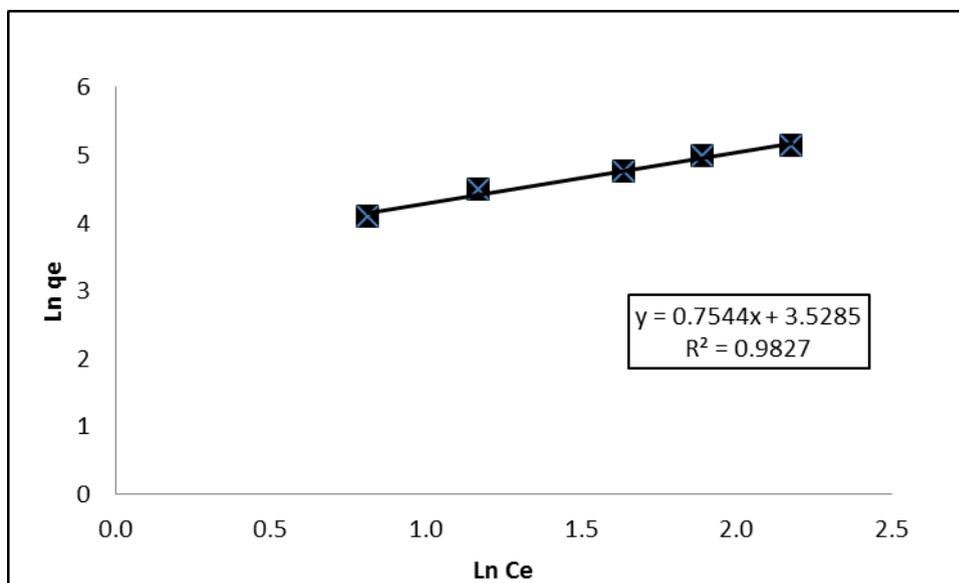
Figure 5.17 Freundlich plot: Amount of adsorbent 15 mg; Initial CR Concentration of 20, 30, 40, 50 and 60 ppm; pH 3.50, Temperature 40°C; Shaker Speed 120 rpm.

Langmuir isotherm model is valid for monolayer adsorption onto a surface containing a finite number of identical sites (Kaur et al., 2013). The maximum adsorption capacity, q_m (mg/g) and K_L values for Langmuir constants were obtained from the linear equations of different plots as shown in Table 5.7. Langmuir plot (type II) where $1/q_e$ versus $1/C_e$ is shown in Fig 5.18. The linear regression coefficients (R^2) for Freundlich and Langmuir models were in range of 0.93 to 0.99. These values indicate the applicability of both Freundlich and Langmuir model with the equilibrium data. The separation factor (R_L) is a dimensionless used to investigate the adsorption system feasibility at different initial dye concentration and it can be calculated from equation (2.16). The separation factor (R_L) values were listed in Table 5.8 and indicated a favourable adsorption process. Full calculations are presented in appendix 5.10
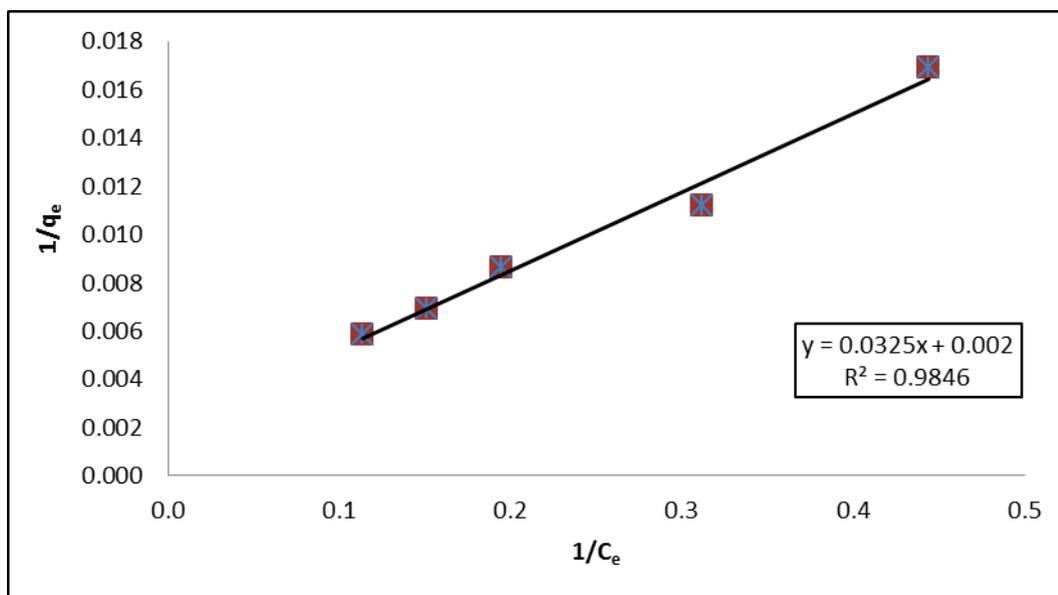
Figure 5.18 Langmuir plot(type II): Amount of adsorbent 15 mg; Initial CR Concentration of 20, 30, 40, 50 and 60 ppm; pH 3.50, Temperature 40∘C; Shaker Speed 120 rpm.

Furthermore, equilibrium data were also fitted with Tempkin isotherm model to describe the CR dye and the activated carbon indirect interactions as well as the sorption energy. Temkin model is fitted as shown in Fig 5.19. The constant K_T and B_1 are calculated as per equation (2.17). The linear regression coefficient (R^2) value was as 0.989 indicate the applicability of this model. Several studies also been reported on removal of dyes from aqueous solution using biomass based activated carbon under similar experimental conditions as shown in Table 2.6. From the comprehensive study of Table 2.6, it was found that pine cone derived activated carbon (present study) gives higher monolayer adsorption capacity compared to commercial biomass based activated carbon. Finally, Freundlich, Langmuir and Tempkin parameter values were summarised and presented in Table 5.7.

Table 5.7 Congo red dye isotherm model parameters

Freundlich		
K_f (mg/g)	n	R^2
34.07	1.33	0.983
Langmuir (Type I)		
q_m (mg/g)	K_L (L/g)	R^2
434.78	0.07	0.925
Langmuir (Type II)		
q_m (mg/g)	K_L (L/g)	R^2
500.00	0.06	0.985
Langmuir (Type III)		
q_m (mg/g)	K_L (L/g)	R^2
390.62	0.09	0.820
Langmuir (Type IV)		
q_m (mg/g)	K_L (L/g)	R^2
451.11	0.07	0.820
Tempkin		
B_1 (mg/g)	K_T (L/mg)	R^2
79.73	1.09	0.989

Table 5.8 The separation factor (R_L) of Langmuir (I, II, III, IV) model at different initial dye concentration

Initial dye concentration (mg/L)	R_L (I)	R_L (II)	R_L (III)	R_L (IV)
20	0.42	0.45	0.34	0.42
30	0.32	0.36	0.25	0.32
40	0.26	0.29	0.20	0.26
50	0.22	0.25	0.17	0.22
60	0.19	0.22	0.15	0.19

5.4 Design of single-stage batch adsorber from isotherm data

It was found that Freundlich, Langmuir and Tempkin isotherm models were all well fitted with the equilibrium data. Adsorption isotherms can be used to predict the design of single batch adsorption system (Sen et al., 2011). Due to lack of extensive experimental data, empirical design procedures based on adsorption isotherm studies are the most common method to predict the adsorber size and performance as shown in Fig 2.6. The design objective was to reduce initial Congo red dye concentration of C_0 to C_t (mg/L) for which total dye solution is V (L) (Sen et al., 2011). The amount of added adsorbent m (g) and the solute loading increasing from q_0 (mg/g) to q_e (mg/g) where $q_0 = 0$. The mass balance for the Congo red in the single-stage operation under equilibrium is presented as in equation (2.20). Freundlich adsorption isotherm data has been utilised to design a single-stage batch adsorption system as per method developed by Kumar et al. (2010). Rearranging equations 2.11 and 2.20 can be written as below

$$\frac{m}{V} = \frac{C_0 - C_e}{K_f\, Ce^{1/n}} \tag{5.2}$$

From Fig 5.19, it shows a series of plots derived from equation (5.2) between the predicted amount of activated carbon particles required to remove Congo red dye of initial concentrations of 20(mg/L) for 50%, 60%, 70% and 90% dye removal at different solution volumes (L) for a single-stage batch adsorption.
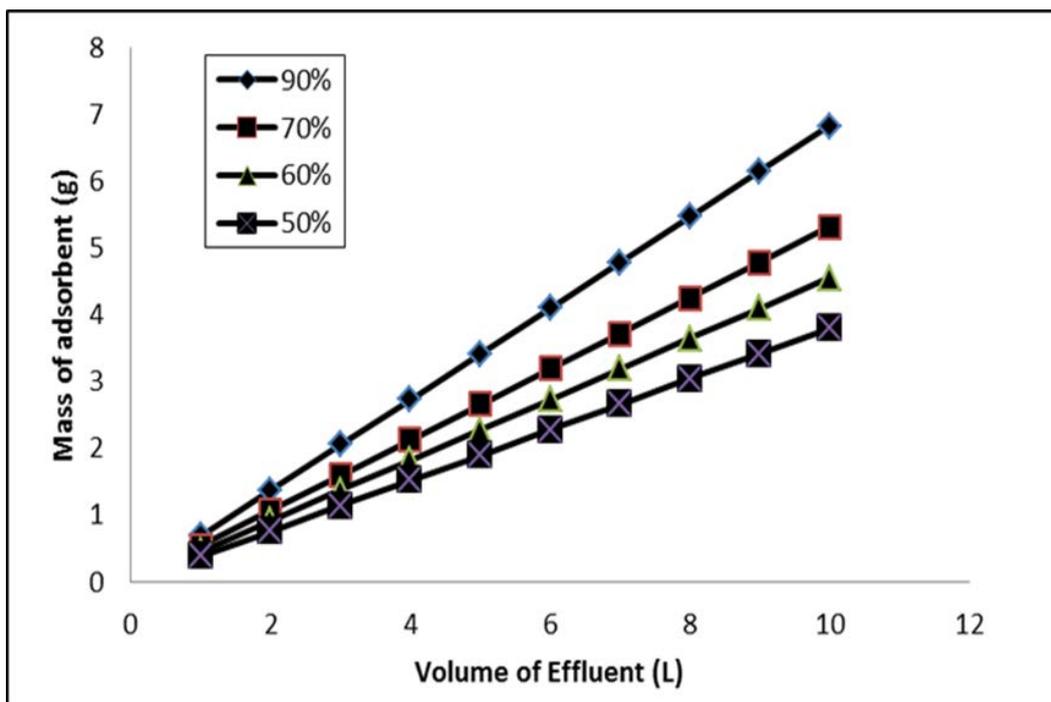
Figure 5.19 Adsorbent mass (m) against volume of solution treated (L).

5.5 Desorption study

Desorption studies help to elucidate the mechanism and recycling nature of the adsorbents. In the desorption studies, the loaded biomass based activated carbon adsorbent that was used for the adsorption of dye solution was separated from solution by centrifugation and then dried. The dried adsorbent was agitated with 50 ml of distilled water at various pH values (6.7 -12.2) for the predetermined equilibrium time of the adsorption process. It was found that the amount of dye released from the loaded adsorbent into the solution was minimal. This desorption study indicates that Congo red dye was strongly attached onto pine cone biomass based activated carbon through chemisorptions. To regenerate the activated carbon, further study is required to identify the suitable solvent for recovery.

5.6 Conclusion

In this present study, a biomass based activated carbon was used effectively to remove anionic Congo red dye from aqueous solution. Agricultural by-product pine cone waste was considered as precursor raw materials for the production of activated carbon. The physical and chemical properties (such as particle size, bulk density, CHNS, FTIR, etc.) of biomass based activated carbon vary with material used and the method of activation. This study was undertaken to synthesize a novel activated carbon from pine cone which is synthesized chemically at various concentrations of phosphoric acid under different temperature profiles in a tube furnace The amount of Congo red dye uptake on activated carbon was found to increase with an increase in initial dye concentration, temperature but decreased with increase in solution pH and amount of adsorbent. It was observed that Langmuir maximum adsorption capacity (q_m) was 500 mg/g at a pH of 3.5. Kinetic experiments clearly indicated that adsorption of Congo red on biomass based activated carbon are multi step processes: a rapid adsorption of dye onto the external surface followed by intra-particle diffusion into the interior of adsorbent which has also been confirmed by intra-particle diffusion model.

Overall, the kinetic studies showed that the Congo red dye adsorption process followed pseudo-second order kinetics models and the adsorption was controlled by chemisorptions process. Equilibrium data were fitted with Langmuir, Freundlich and Tempkin adsorption isotherm models. Based on the Thermodynamic Analysis and Freundlich Isotherm data, it was observed that the adsorption system was endothermic and physical processes in nature. The positive value of ΔS^0 indicated also greater stability of an adsorption process with no structural changes at the solid-liquid interface. The kinetics and thermodynamic data can be further explored for the design of an adsorbent for industrial effluent treatment. Finally, pine cone biomass is good and cheap precursor for the production of activated carbon which has versatile application including an effective adsorbent and an alternative to commercial activated carbon.

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6. CHAPTER SIX- CONCLUSION & RECOMMENDATION

6.1 Conclusion

Dyes are natural or synthetic organic compounds used to colour various materials such as fibres, leathers, papers, plastics, foods and rubbers. Natural dyes such as extracted from plants, animals, insects and minerals sources. However, due to the increase in population and industrial activities, natural dyes do not meet the industrial demand. Therefore the first synthesis dye was introduced in 1856.synthetic dye have complex molecular structures, thus decrease their ability to biodegrade. It has been estimated that about 10–15% of these dyes are released as effluents during the dyeing processes. Wastewater effluents contain synthetic dyes which may cause a potential hazard to human beings and to aquatic life. Dyes are broadly classified into cationic, anionic and non-anionic dyes. Interest for further investment opportunities in treating waste water is growing rapidly in the past few decades as the increase in the volume of dye effluents generated and discharged into the environment seems unavoidable. Therefore, this is crucially important for those industries in sustaining further development by managing their wastewater treatment operation efficiently. The removal of synthetic dyes in an economic and environmentally friendly way remains a very vital problem although a number of separation methods have been developed. Adsorption is found to be a very effective separation technique and now it is considered to be superior to other techniques for water treatment. Commercial activated carbon is widely used as an adsorbent in the removal of dyes from aqueous solution. The effectiveness of this versatile adsorbent is due to its external surface area, micro porous structure, high adsorption capacity and high degree of surface reactivity. However, commercial activated carbon (CAC) treatment processes have clear disadvantages including the high cost and difficulties with regeneration. Therefore, recent trend of research is to develop alternative cost effective and non-conventional potential adsorbents in the removal of dye from its aqueous solution such as clays, minerals, raw and modified agricultural solid waste and biomass based activated carbon.

In the recent years, growing research interest is focusing upon agricultural residual biomass based activated carbon. Biomass may offer inexpensive and renewable additional source of activated carbon which may help to reduce the cost of waste disposal and provide a potentially inexpensive alternative adsorbent into existing commercial activated carbons.

Therefore in this research work (1.5 years), a cost effective, environmentally friendly and readily available alternative agricultural by-product based sustainable novel adsorbent from agricultural solid has been reported. Pine Cone *(Pinus. Radiate)* has been developed its application in the removal of toxic anionic dye Congo Red from aqueous solution by adsorption. The present study shows that the raw pine cone and acid treated pine cone, an agricultural by-product waste both can be used as an effective alternative low cost adsorbent for the removal of anionic dye, Congo red from aqueous solutions. The amount of Congo red dye uptake on raw and treated pine cone biomass was found to increase with increase in initial dye concentration, contact time, temperature but was found to decrease with increase in solution pH and amount of adsorbent. It was further observed that the adsorption was pH dependent and the maximum adsorption of 32.65 mg/g occurred at pH of 3.55 for an initial dye concentration of 20 ppm by raw pinecone, whereas for acid treated pine cone the maximum adsorption of 40.19 mg/g for the same experimental conditions. Freundlich isotherm model gave better fittings with experimental data than Langmuir model. The maximum adsorption capacity of raw pine cone biomass from Freundlich model was found to be 19.18 mg/g. Freundlich constant, *n*, give an indication of favourable adsorption which was physical adsorption. The thermodynamic analysis indicates that system was endothermic and physical processes in nature. Kinetic data reveals that adsorption reaction was fast and it was a combination of multi-stage processes.

Furthermore, the current study was also undertaken to synthesize a novel activated carbon from pine cone *(Pinus. radiate)* which is synthesized chemically at various concentrations of phosphoric acid under different temperature profile in a tube furnace. The amount of Congo red dye uptake on activated carbon was found to increase with an increase in initial dye concentration, temperature but decreased with increase in solution pH and amount of adsorbent. It was observed that Langmuir maximum adsorption capacity (q_m) was 500 mg/g at a pH of 3.5. Equilibrium data were fitted with Langmuir, Freundlich and Tempkin

adsorption isotherm models. Based on the thermodynamic analysis data, it was observed that the adsorption system was endothermic and physical processes in nature. The positive value of ΔS^0 indicated also greater stability of an adsorption process with no structural changes at the solid-liquid interface. Kinetic experiments clearly indicated that adsorption of Congo red on pine cone and pine cone based activated carbon are multi step processes: a rapid adsorption of dye onto the external surface followed by intra-particle diffusion into the interior of adsorbent which has also been confirmed by intra-particle diffusion model. Overall, the kinetic studies showed that the Congo red dye adsorption process followed pseudo-second order kinetics models and the adsorption was controlled by chemisorption process. Finally, it can be concluded that pine cone *(Pinus. radiate)* biomass is good and cheap precursor for the production of raw, acid modified and biomass based activated carbon adsorbents and their adsorption capacity is much comparative with other adsorbents including commercial activated carbon in the removal of Congo red from aqueous solution.

6.2 Future Recommendations

6.2.1 Assessing the applicability of pine cone derived adsorbents in the removal of both cationic and anionic dyes

In this study, raw pine cone, acid modified pine cone and pine cone biomass based activated carbon were prepared and tested as low cost and effective adsorbents in the removal of dye such as Congo red dye. However, these studies may be extended in the removal of other organic / inorganic from its aqueous solution.

6.2.2 Scale up of batch adsorption system to pilot system

Much work is necessary to predict the performance of adsorption process for dye removal form real colour bearing effluents under various conditions. The scale up of batch adsorption system to pilot system is very important in order to evaluate and assess the applicability of this system for commercial use. In this research study, batch adsorption process was carried out in the removal of Congo red dye from aqueous solution by pine cone derived adsorbents. However more research is required for column study and pilot plant case study.

6.2.3 Working under natural conditions

Despite bright future of alternative cost effective adsorbents, there are some issues such as incapable to work effectively in natural conditions. Therefore there is great need to develop such adsorbents that can work almost at neutral pH, normal temperature with fast reaction time.

6.2.4 Mixed pollutant treatment

Despite the fact that industrial effluents contain several pollutants simultaneously and therefore less attention has been made to adsorption of dyes from mixed pollutants.

6.2.5   Optimization of the chemical activation process

In this research study, pine cone powder was mixed with phosphoric acid at an impregnation ratio of 1:2 respectively and kept at room temperature for 3 hrs. The mixture was placed in a horizontal tube furnace with constant flow of nitrogen gas to avoid oxidation. The temperature inside the tube furnace was increased at the rate of $10^oC/min$ until it was reached the set point then kept at the set temperature for a period of 2 hrs. Pine cone biomass based activated carbon was prepared under various initial phosphoric acid concentrations (0.5M – 14.7M) and temperature profiles of $120^oC – 350^oC$. Also, from the physical and chemical characterization, it was found that the percentage of carbon is less than 70% and the BET surface area is about $66m^2/g$. therefore, in order to increase the surface area and the percentage of the carbon element, the pine cone and phosphoric acid mixture should be left longer to allow the activation agent to increase the porosity and the surface area of the mixture. Also, pine cone based activated carbon should be synthesized under high temperature profiles ($400^oC – 900^oC$).

6.2.6   Surface reaction study
Adsorption of dye including Congo red dye mechanism on various adsorbents including cellulose biomass material is very complex and poorly understood. Surface reaction based dye adsorption mechanism is required for future research.

The above list is not meant to be complete. It only lists selected aspects that currently considered to be important.

APPENDIX

Appendix 4.1

Experimental Conditions 1: Amount of dye adsorbed q_t (mg/g)

time (min)	pH=3.55	pH=5.95	pH=7.45	pH=10.95
0	0	0	0	0
5	32.22222	8.575499	8.717949	0.45584
10	32.79202	10	8.005698	3.162393
15	32.07977	8.005698	9.430199	1.168091
20	32.36467	9.002849	8.717949	1.452991
30	31.93732	7.150997	9.430199	2.307692
40	31.22507	7.863248	8.575499	1.737892
50	32.22222	8.290598	9.57265	2.877493
60	31.93732	8.575499	9.002849	2.450142
80	32.64957	8.9	8.148148	1.880342
100	31.5	7.435897	8.433048	2.877493

Experimental Conditions 1: % Adsorption

time (min)	pH=3.55	pH=5.95	pH=7.45	pH=10.95
0	0	0	0	0
5	64.44444	17.151	17.4359	0.911681
10	65.58405	20	16.0114	6.324786
15	64.15954	16.0114	18.8604	2.336182
20	64.72934	18.0057	17.4359	2.905983
30	63.87464	14.30199	18.8604	4.615385
40	62.45014	15.7265	17.151	3.475783
50	64.44444	16.5812	19.1453	5.754986
60	63.87464	17.151	18.0057	4.900285
80	65.29915	20.5698	16.2963	3.760684
100	59.31624	14.87179	16.8661	5.754986

Experimental Conditions 2: Acid modified pine cone Amount of dye adsorbed q_t (mg/g)

Time, t (min)	pH=3.61	pH=5.85	pH=7.45
0	0	0	0
5	44.47293	9.57265	7.863248
10	43.19088	8.148148	8.005698
15	42.47863	11.4245	8.005698
20	41.19658	10.42735	6.153846
30	40.19943	10	9.430199
40	41.05413	11.7094	7.435897
50	39.77208	10	8.717949
60	35.78348	9.85755	7.720798
80	39.48718	10.8547	7.578348
100	37.20798	10.8547	8.433048

Experimental Conditions 2: % Adsorption

Time, t (min)	pH=3.61	pH=5.85	pH=7.45
0	0	0	0
5	88.94587	15.7265	19.1453
10	86.38177	16.0114	16.2963
15	84.95726	16.0114	22.849
20	82.39316	12.30769	20.8547
30	80.39886	18.8604	20
40	82.10826	14.87179	23.4188
50	79.54416	17.4359	20
60	71.56695	15.4416	19.7151
80	78.97436	15.1567	21.7094

	100	74.41595	16.8661	21.7094

Appendix 4.2

Experimental Conditions 1: Amount of dye adsorbed q_t (mg/g)

Time (min)	0.01 g	0.02g	0.03g
0	0	0	0
5	11.45299	8.575499	4.862298
10	14.87179	7.863248	5.622032
15	15.7265	9.287749	5.527066
20	16.8661	8.575499	6.666667
30	14.87179	9.287749	6.5717
40	14.30199	8.433048	6.951567
50	15.4416	9.430199	6.8566
60	14.1	8.860399	6.381766
80	14.01709	8.005698	6.5717
100	13.44729	8.290598	6.2868

Experimental Conditions 1: % Adsorption

Time, t (min)	0.01g	0.02g	0.03g
0	0	0	0
5	11.45299	17.151	14.58689
10	14.87179	15.7265	16.8661
15	15.7265	18.5755	16.5812
20	16.8661	17.151	20
30	14.87179	18.5755	19.7151
40	14.30199	16.8661	20.8547
50	15.4416	18.8604	20.5698
60	14.30199	17.7208	19.1453
80	14.01709	16.0114	19.7151
100	13.44729	16.5812	18.8604

Appendix 4.3

Experimental Conditions 1: Amount of dye adsorbed q$_t$ (mg/g)

Time (min)	20PPM	30PPM	40 PPM	50 PPM
0	0	0	0	0
5	8.717949	13.71795	16.8661	21.08262
10	8.005698	16.49573	18.5755	24.28775
15	9.430199	17.13675	16.8661	22.151
20	8.717949	16.48718	18.2906	25
30	9.430199	14.57265	17.151	21.79487
40	8.575499	15.8547	16.5812	24.28775
50	9.57265	18.63248	21.1396	21.79487
60	9.002849	15	18.8604	22.50712
80	8.148148	15	16.8661	22.86325
100	8.433048	16.06838	17.9	25.35613

Experimental Conditions 1: % Adsorption

Time (min)	20PPM	30PPM	40 PPM	50 PPM
0	0	0	0	0
5	17.4359	18.2906	16.8661	16.8661
10	16.0114	21.9943	18.5755	19.4302
15	18.8604	22.849	16.8661	17.7208
20	17.4359	25.98291	18.2906	20
30	18.8604	19.4302	17.151	17.4359
40	17.151	21.1396	16.5812	19.4302
50	19.1453	24.8433	21.1396	17.4359
60	18.0057	20	18.8604	18.0057
80	16.2963	20	16.8661	18.2906
100	16.8661	21.4245	16.5812	20.2849

Appendix 4.4

**Experimental Conditions 1: Amount of dye adsorbed q_t (mg/g)**

Time (min)	T = 30 °C	T = 40 °C	T = 60 °C
0	0	0	0
5	7.150997	8.717949	9.287749
10	6.866097	8.005698	9.145299
15	7.293447	9.430199	11.7094
20	6.723647	8.717949	10.42735
30	8.005698	9.430199	11.9943
40	7.435897	8.575499	11.28205
50	6.723647	9.57265	12.99145
60	7.9	8.6	12.2792
80	7.8	8.5	12.5641
100	7.02	8.43	11.7094

Experimental Conditions 1: % Adsorption

Time (min)	T = 30 °C	T = 40 °C	T = 60 °C
0	0	0	0
5	17.4359	14.30199	18.5755
10	16.0114	13.73219	18.2906
15	18.8604	14.58689	23.4188
20	17.4359	13.44729	20.8547
30	18.8604	16.0114	23.9886
40	17.151	14.87179	22.5641
50	19.1453	13.44729	25.98291
60	18.0057	18.0057	24.5584
80	16.2963	16.5812	25.12821
100	16.8661	14.01709	23.4188

Appendix 4.5

Intra particle diffusion model at various parameters

Different pH- Modified pine cone
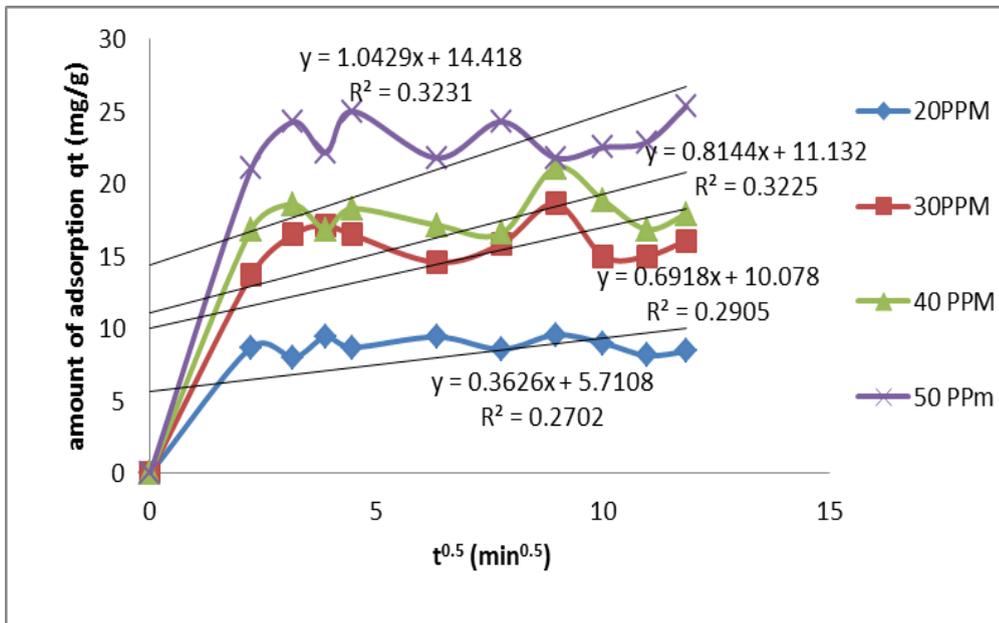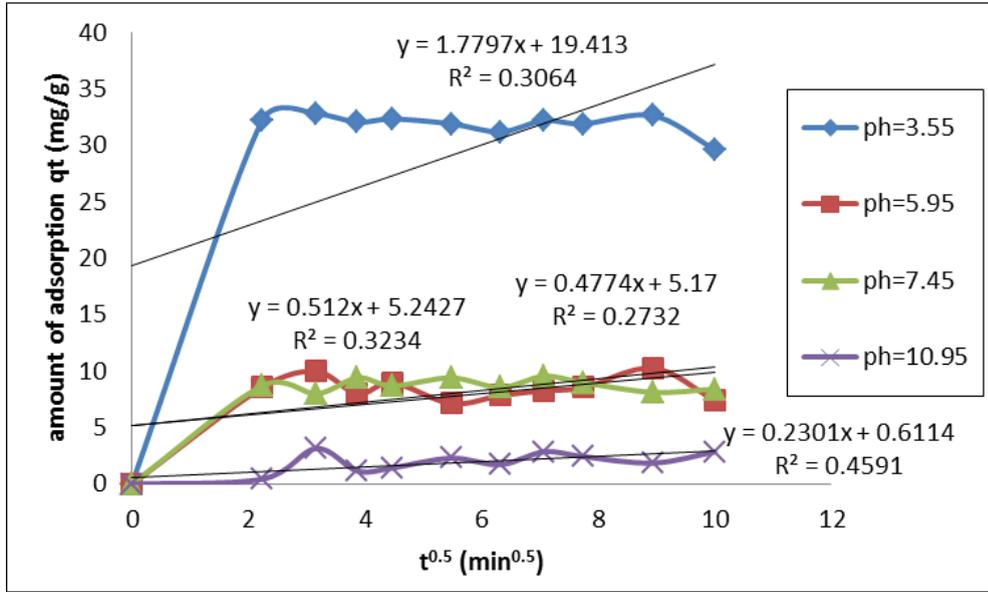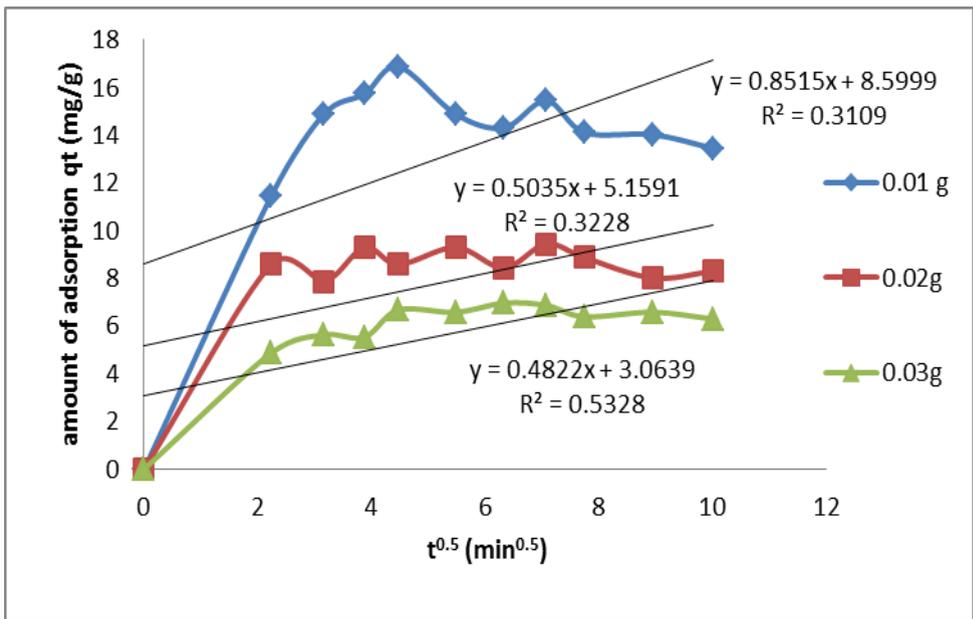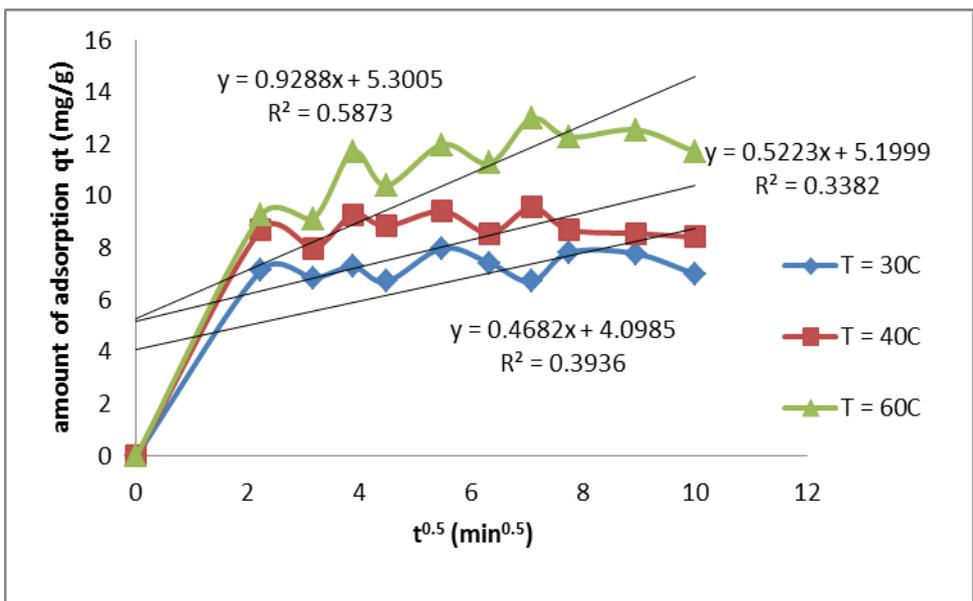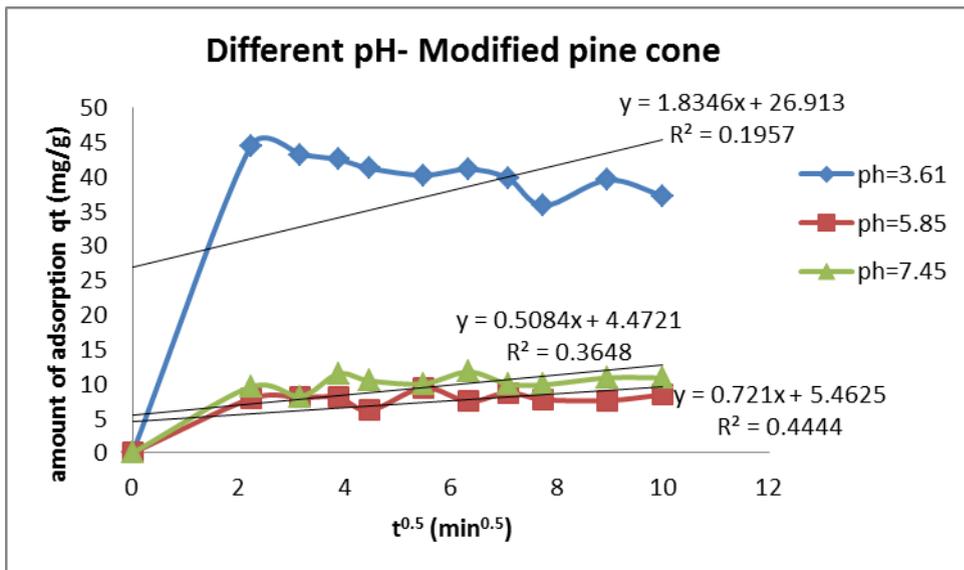
Appendix 4.6

Co (ppm)	Ce	qe (mg/g)	lnCe	lnqe	1/Ce	1/qe	Ce	Ce/qe
10	2.530	37.350	0.928	3.620	0.395	0.027	2.530	0.068
20	5.459	72.707	1.697	4.286	0.183	0.014	5.459	0.075
30	6.991	115.043	1.945	4.745	0.143	0.009	6.991	0.061
40	9.892	150.541	2.292	5.014	0.101	0.007	9.892	0.066
50	14.217	178.917	2.654	5.187	0.070	0.006	14.217	0.079
60	19.590	202.051	2.975	5.309	0.051	0.005	19.590	0.097

Freundlich		
K_f (mg/g)	1/n (L/g)	R^2
18.33478	1.1665	0.9588
Langmuir-1		
q_m (mg/g)	K_a (L/g)	R^2
0.06	2.9361	0.6492

Appendix 5.1

Experimental Conditions 1:

0.5M (AC)	Á=500 nm	C_t at 500nm	$C_t X$	q_t (mg/g)	% Adsorption
pH =2.2	0.169	1.05475	5.273752	73.63124	73.63
pH=3.5	0.193	1.441224	7.206119	63.9694	63.97
pH= 6.2	0.301	3.180354	15.90177	20.49114	20.49
pH=8.2	0.337	3.760064	18.80032	5.99839	5.99
1 M (AC)					
pH=2.2	0.1607	0.921095	4.605475	76.97262	76.98
pH=3.5	0.174	1.135266	5.676329	71.61836	71.62
pH= 6.2	0.2999	3.162641	15.8132	20.93398	20.93
pH=8.2	0.3357	3.73913	18.69565	6.521739	6.52
3 M (AC)					
pH=2.2	0.159	0.89372	4.468599	77.657	77.66
pH=3.5	0.169	1.05475	5.273752	73.63124	73.63
pH= 6.2	0.2969	3.114332	15.57166	22.14171	22.14
pH=8.2	0.331	3.663446	18.31723	8.413849	8.41
14.7M(AC)					
pH=2.2	0.15	0.748792	3.743961	81.28019	81.28
pH=3.5	0.1467	0.695652	3.478261	82.6087	82.61
pH= 6.2	0.2962	3.10306	15.5153	22.42351	22.42
pH=8.2	0.3226	3.52818	17.6409	11.79549	11.80

Experimental Conditions 2:

1M/180°C	Λ=50nm	C_t at 500.67 nm	C_t X	q_t (mg/g)	% Adsorption
pH =2.6	0.169	1.05475	5.273752	73.63124	73.63124
pH=3.5	0.164	0.974235	4.871176	75.64412	75.64412
pH= 6.2	0.311	3.341385	16.70692	16.46538	16.46538
pH=8.2	0.3437	3.867955	19.33977	3.301127	3.301127
1 M /250°C					
pH =2.6	0.1604	0.916264	4.58132	77.0934	77.0934
pH=3.5	0.1583	0.882448	4.412238	77.93881	77.93881
pH= 6.2	0.3016	3.190016	15.95008	20.2496	20.2496
pH=8.2	0.3378	3.772947	18.86473	5.676329	5.676329
1M / 350°C					
pH =2.6	0.1607	0.921095	4.605475	76.97262	76.97262
pH=3.5	0.174	1.135266	5.676329	71.61836	71.61836
pH= 6.2	0.2999	3.162641	15.8132	20.93398	20.93398
pH=8.2	0.3357	3.73913	18.69565	6.521739	6.521739
1M/120°C					
pH =2.6	0.1701	1.072464	5.362319	73.18841	73.18841
pH=3.5	0.1732	1.122383	5.611916	71.94042	71.94042
pH= 6.2	0.3161	3.42351	17.11755	14.41224	14.41224
pH=8.2	0.3315	3.671498	18.35749	8.21256	8.21256

Experimental Conditions 3:

0.5 M/ 350 °C	Λ=50nm	C_t at 500 nm	C_t X	q_t (mg/g)	% Adsorption
10 mg	0.169	1.055	5.274	73.631	73.63
15 mg	0.175	1.151	5.757	47.477	71.22
20 mg	0.181	1.248	6.240	34.400	68.80
30 mg	0.185	1.312	6.562	22.397	67.19
1 M /350 °C					
10 mg	0.1607	0.921	4.605	76.973	76.97
15 mg	0.1655	0.998	4.992	50.027	75.04
20 mg	0.172	1.103	5.515	36.212	72.42
30 mg	0.1732	1.122	5.612	23.980	71.94
3M / 350 °C					
10 mg	0.159	0.894	4.469	77.657	77.66
15 mg	0.1699	1.069	5.346	48.846	73.27
20 mg	0.1785	1.208	6.039	34.903	69.81
30 mg	0.1799	1.230	6.151	23.081	69.24
14.7 M/350 °C					
10 mg	0.15	0.749	3.744	81.280	81.28
15 mg	0.1504	0.755	3.776	54.079	81.12
20 mg	0.156	0.845	4.227	39.432	78.86
30 mg	0.1581	0.879	4.396	26.006	78.02

Appendix 5.2

**Particle size distribution of various synthesized activated carbon samples**
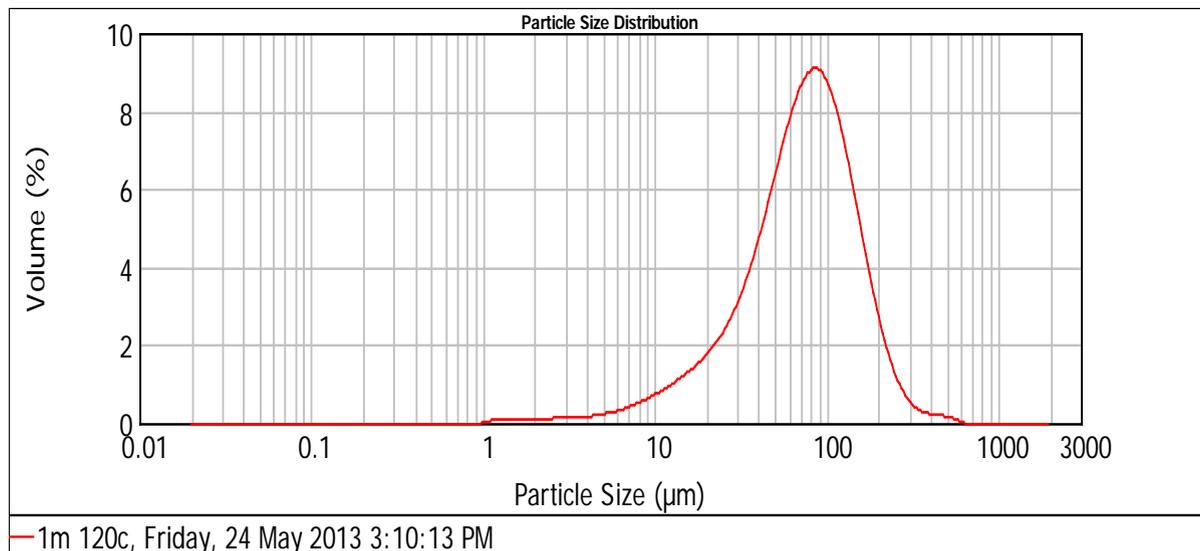
**Figure 1. Particle size distribution of (1M/120 °C) pine cone AC**
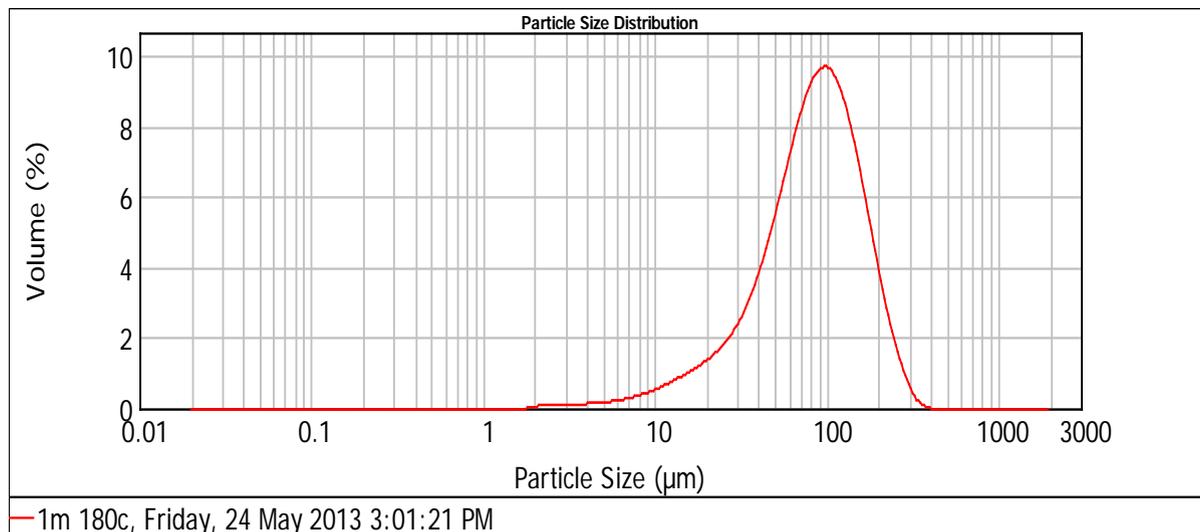
Figure 2 Particle size distributions of (1M/180 °C) pine cone AC
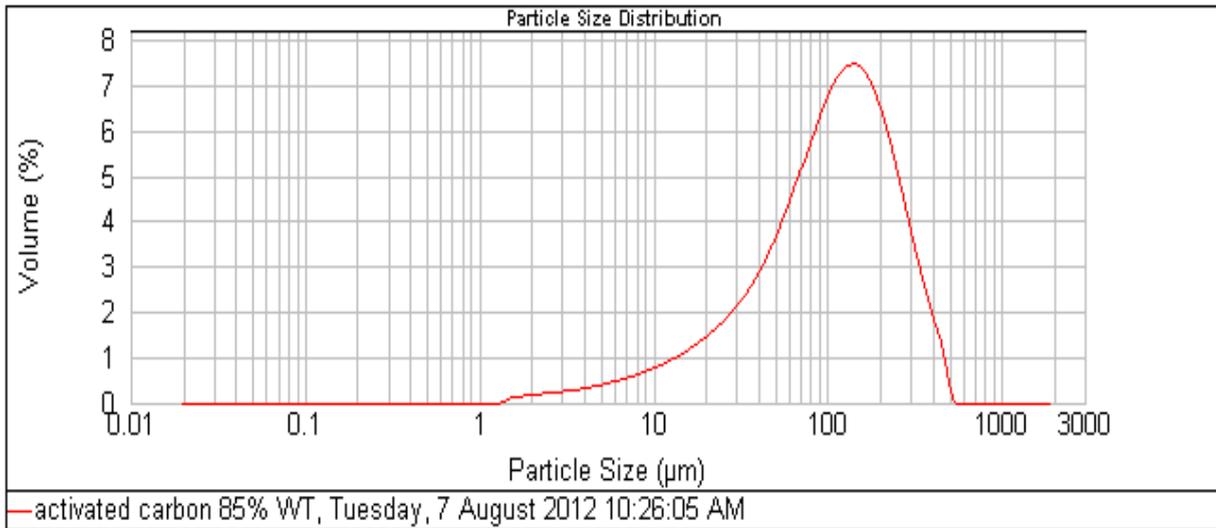
Figure 3 Particle size distributions of (14.7 M/350 °C) biomass activated carbon
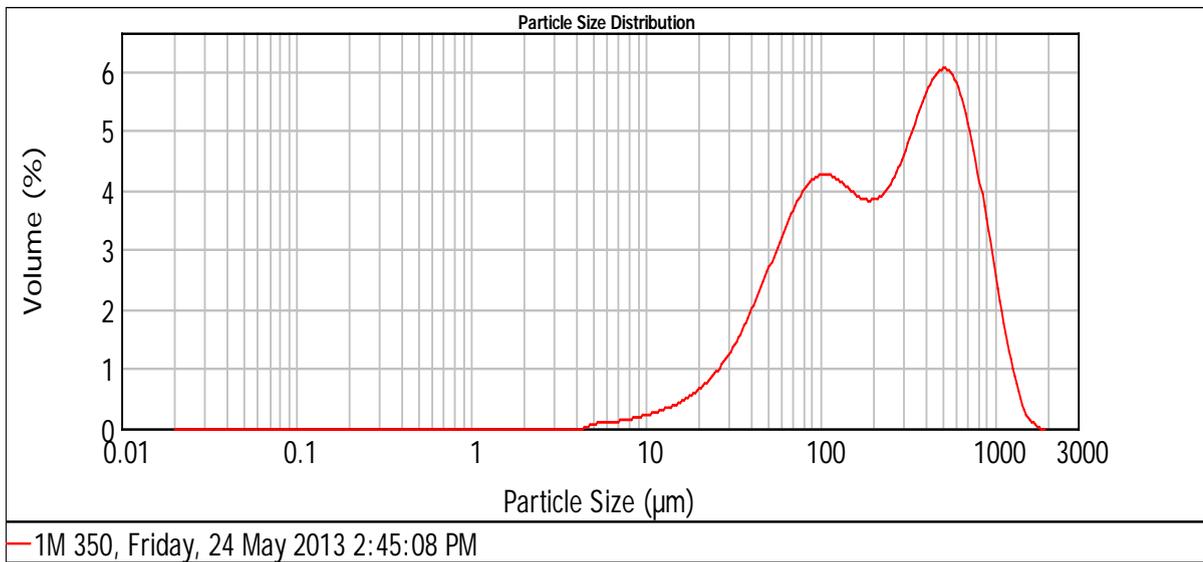

**Figure 4 Particle size distributions of (1M/350 °C) biomass activated carbon**
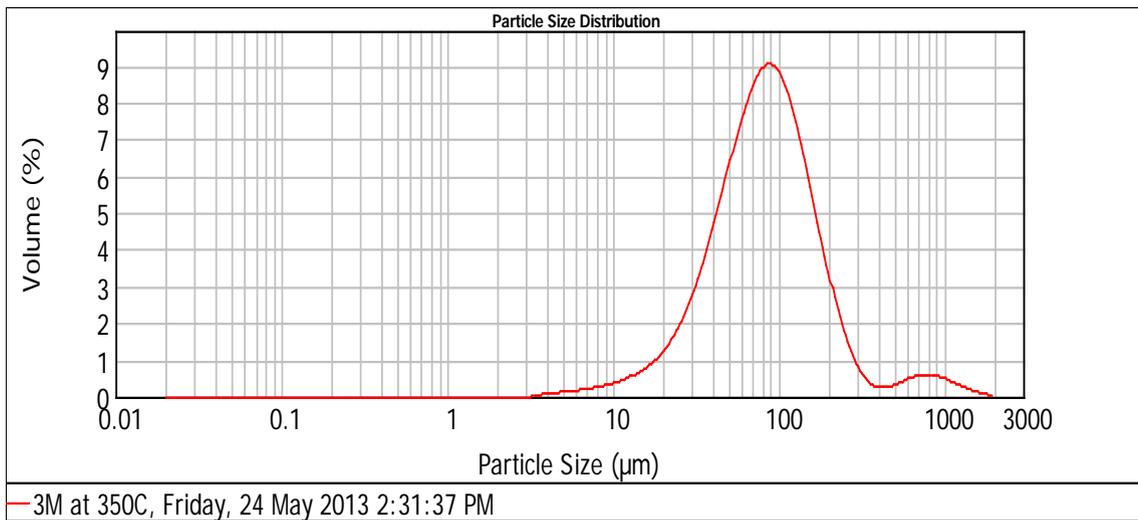
**Figure 5 Particle size distributions of (3M/350 °C) biomass activated carbon**
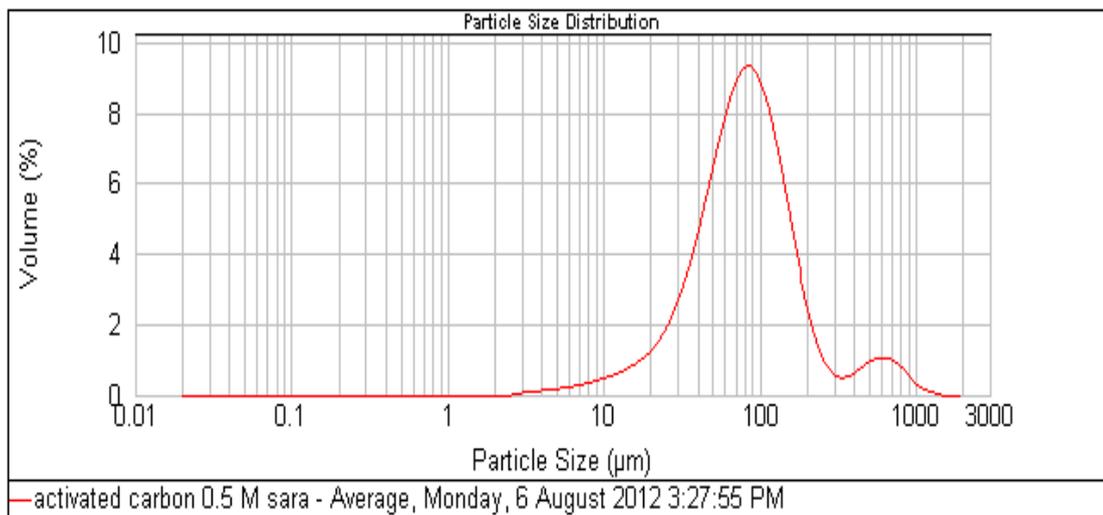
Figure 6 Particle size distributions of (0.5 M/350 °C) biomass activated carbon

Appendix 5.3

Experimental Conditions 1: Amount of dye adsorbed q_t (mg/g)

Time (min)	pH=2.6	pH=3.5	pH=5.5	pH=8.2
0	0	0	0	0
3	73.55	69.16	12.16	6.80
6	75.00	69.57	16.83	2.74
9	76.33	73.55	16.91	5.60
12	77.05	73.15	20.29	1.85
15	75.60	72.62	19.28	5.80
20	74.44	75.28	17.79	5.23
25	75.24	76.25	20.41	7.61
30	77.09	77.94	20.25	5.68

Experimental Conditions 2:

pH	Zeta potential (mV)
2	3.75
3	-16.4
4	-23.6
5	-25.1
6.2	-31.9
8	-46.2
10	-56.2

Zeta potential (mV) of synthesized activated carbon at pH=3

| Records View | Zeta potential (M) | Electrophoretic Mobility (M) | Phase Plot (M) | Zeta quality report (M) |

Sample Name: Activated carbon, ph=3
SOP Name: zetaDarwood.sop
File Name: 20120529.dts
Record Number: 195
Date and Time: Monday, 29 October 2012 10:44:07 AM

Dispersant Name: Water
Dispersant RI: 1.330
Viscosity (cP): 0.8872
Dispersant Dielectric Constant: 78.5

Temperature (°C): 25.0
Count Rate (kcps): 2994.3
Cell Description: Clear disposable zeta cell

Zeta Runs: 22
Measurement Position (mm): 2.00
Attenuator: 9

		Mean (mV)	Area (%)	Width (mV)
Zeta Potential (mV): -16.4	Peak 1:	-16.4	100.0	6.33
Zeta Deviation (mV): 6.33	Peak 2:	0.00	0.0	0.00
Conductivity (mS/cm): 0.625	Peak 3:	0.00	0.0	0.00

Zeta Potential Distribution

Record 195: Activated carbon, ph=3

Appendix 5.4

Experimental Conditions 1: Amount of dye adsorbed q_t (mg/g) and % adsorption

Time (min)	10 mg	15 mg	20 mg	30mg
0	0	0	0	0
3	73.55	51.77	38.02	25.443
6	75.00	49.22	38.10	25.322
9	76.33	50.70	38.59	25.416
12	77.05	51.64	38.95	25.497
15	75.60	52.04	39.17	25.470
20	74.44	52.82	40.08	25.537
25	75.24	52.04	39.63	26.288
30	77.09	53.11	38.63	26.865

Dose(mg)	q_t (mg/g)	% Dye removal
10	77.093	77.09
15	53.113	79.67
20	40.076	80.15
30	26.865	80.60

Appendix 5.5

Experimental Conditions 1: Amount of dye adsorbed q_t (mg/g) and % adsorption

Amount of dye adsorbed q_t (mg/g)

Time (min)	20ppm	40ppm	50ppm	60ppm
0	0	0	0	0
3	73.55	150.07	185.52	214.275
6	75.00	150.00	185.70	215.008
9	76.33	145.87	182.42	214.799
12	77.05	151.88	180.48	214.589
15	75.60	149.71	182.60	214.799
20	74.44	150.72	185.61	215.113
25	75.24	153.77	184.90	215.531
30	77.09	153.48	186.67	215.741

| Initial dye concentration (ppm) or (mg/L)	q_t (mg/g)	% Dye removal
20	77.09	77.09
40	153.768	76.88
50	186.675	74.67
60	215.741	71.91

Appendix 5.6

Experimental Conditions 1: Amount of dye adsorbed q_t (mg/g)

| Time (mins)	30°C	40°C	60°C
0	0	0	0
3	73.551	74.597	74.718
6	75.000	76.248	73.833
9	76.329	78.341	74.074
12	77.053	77.053	80.072
15	75.604	78.301	80.153
20	74.436	76.208	80.878
25	75.242	78.382	81.280
30	77.093	77.254	81.643

Thermodynamic properties

Temp(C°)	Temp (k)	1/T	log (qe/Ce)
30	303	0.0033	1.23
40	313	0.0032	1.26
60	333	0.0030	1.35
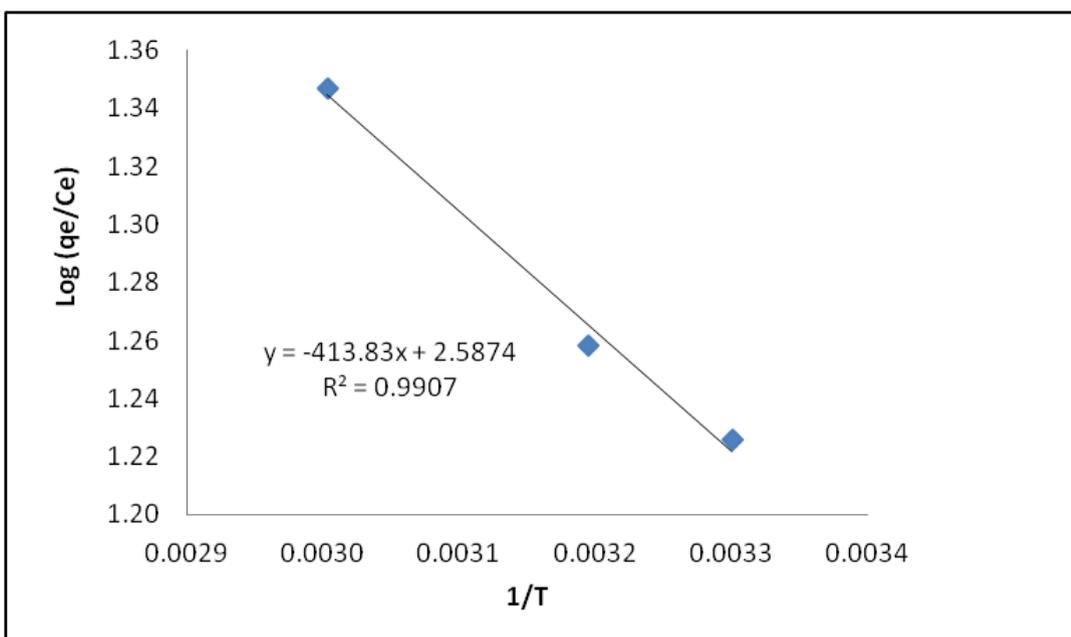
Appendix 5.7

Sample calculation of pseudo-first-order model

$$\text{Log } (q_e\text{-}q_t)$$

| Time (min)	20ppm	40ppm	50ppm	60ppm
0	1.887	2.187	2.271	2.334
3	0.549	0.568	0.061	0.166
6	0.321	0.576	-0.011	-0.135
9	-0.116	0.898	0.629	-0.026
12	-1.395	0.275	0.792	0.061
15	0.173	0.608	0.610	-0.026
20	0.424	0.483	0.027	-0.202
25	0.268	-5.392	0.248	-0.679
30	-5.647	-0.538	-3.550	-3.586
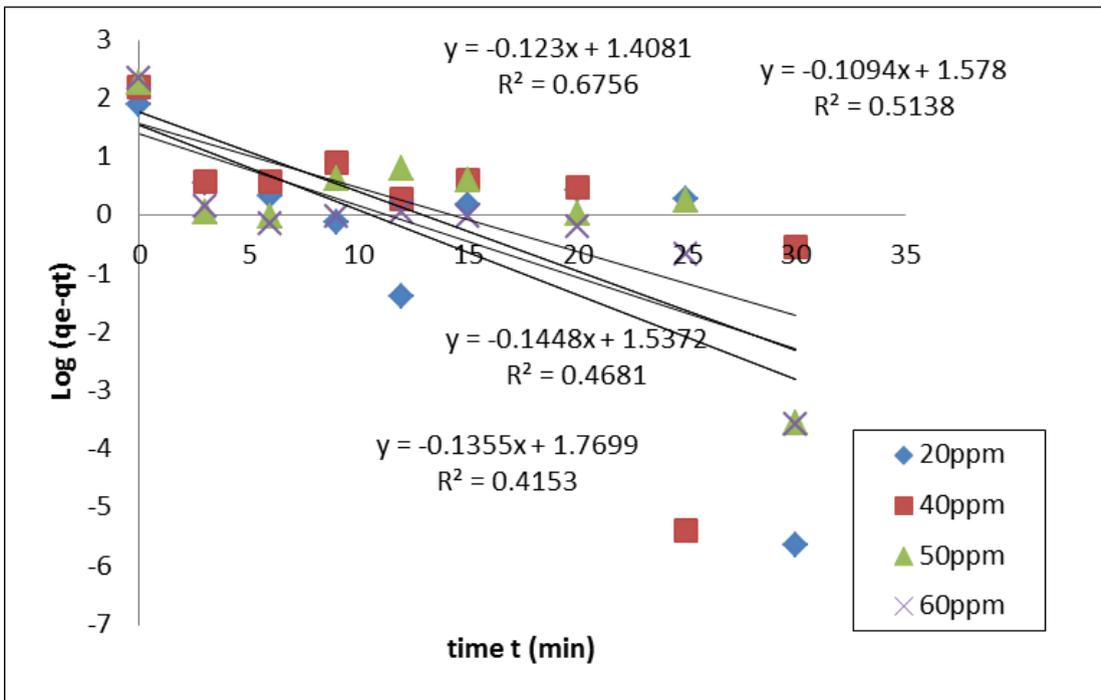
Appendix 5.8

Parameters	x (mg/(g.min))	y(g/mg)	R^2	Formula from the graphs	** /*	Ln b	(1/b)*	(1/b)Ln(ab)**
Adsorbent Dosage (mg)								
10	87.09	0.057	0.592	y=17.633 x +28.163	1.597	-2.870	17.633	28.163
15	57.27	0.082	0.607	y=12.233 x +18.883	1.544	-2.504	12.233	18.883
20	43.49	0.109	0.605	y=9.1806 x +14.279	1.555	-2.217	9.181	14.279
30	28.49	0.164	0.608	y=6.0943 x +9.3981	1.542	-1.807	6.094	9.398
Initial dye Concentration (mg/L)								
20	87.09	0.057	0.592	y=17.633 x +28.163	1.597	-2.870	17.633	28.163
40	173.40	0.028	0.593	y= 35.2 x +56.128	1.595	-3.561	35.200	56.128
50	224.31	0.024	0.570	y=42.192 x +70.495	1.671	-3.742	42.192	70.495
60	259.82	0.020	0.574	y=49.358 x +81.978	1.661	-3.899	49.358	81.978
solution pH								
2.6	87.09	0.057	0.592	y=17.633 x +28.163	1.597	-2.870	17.633	28.163
3.5	70.16	0.054	0.673	y=18.391 x +24.623	1.339	-2.912	18.391	24.623
5.5	11.12	0.182	0.849	y=5.4805 x +3.8754	0.707	-1.701	5.481	3.875
8.2	4.37	0.736	0.357	y= 1.3585 x+1.5862	1.168	-0.306	1.359	1.586
Temperature								
30^0C	87.09	0.057	0.592	y=17.633 x +28.163	1.597	-2.870	17.633	28.163
40^0C	87.46	0.055	0.598	y= 18.086 x+28.505	1.576	-2.895	18.086	28.505
60^0C	75.13	0.051	0.670	y= 19.585 x+26.332	1.344	-2.975	19.585	26.332

Appendix 5.9

Intra particle diffusion model at various physico-chemical parameters
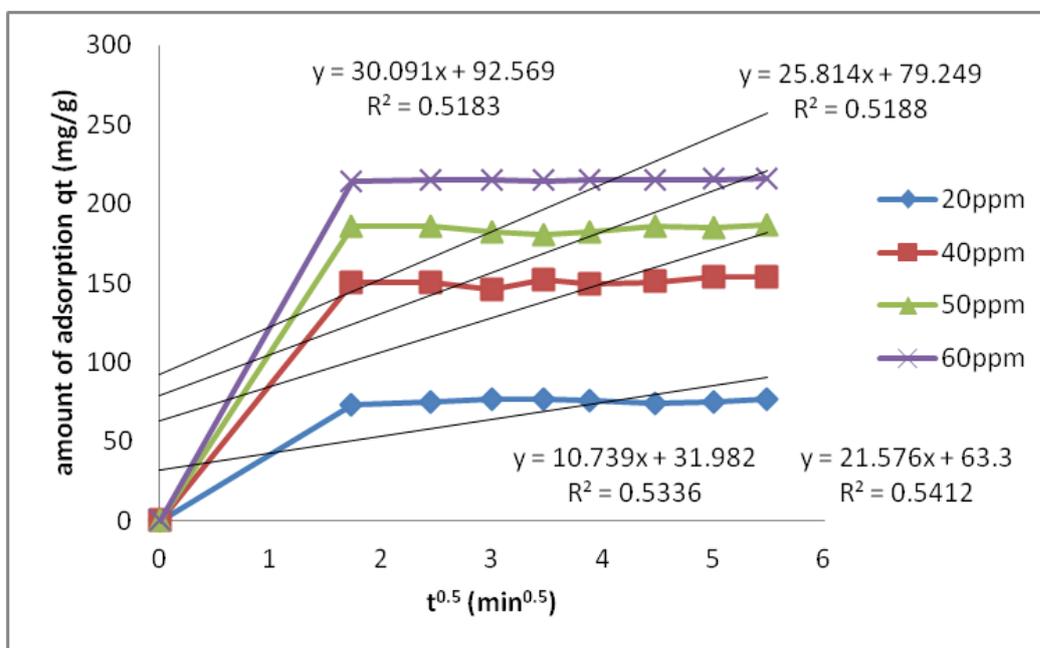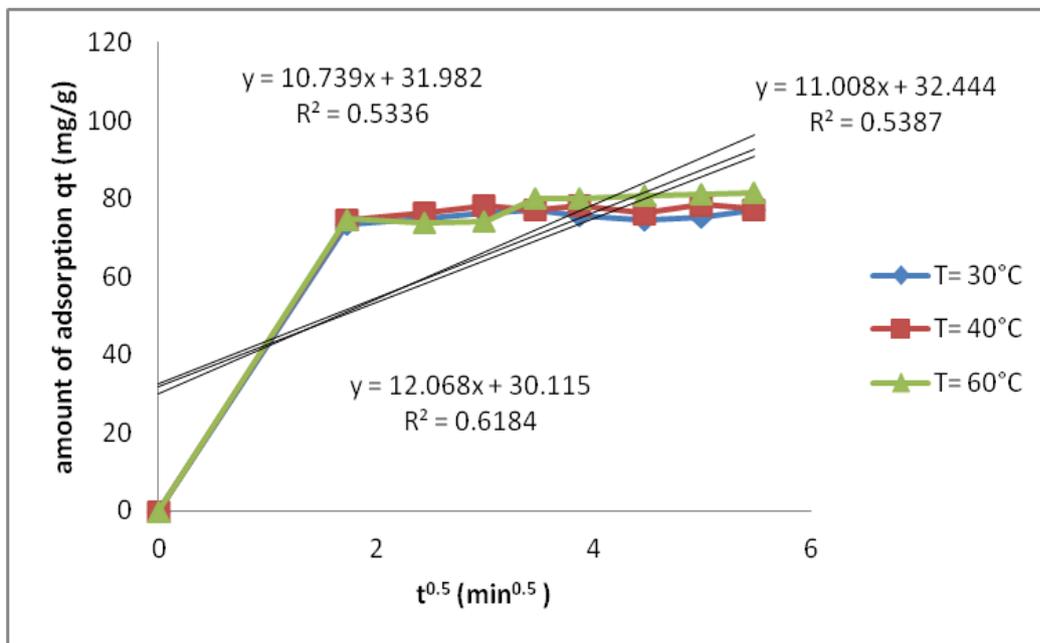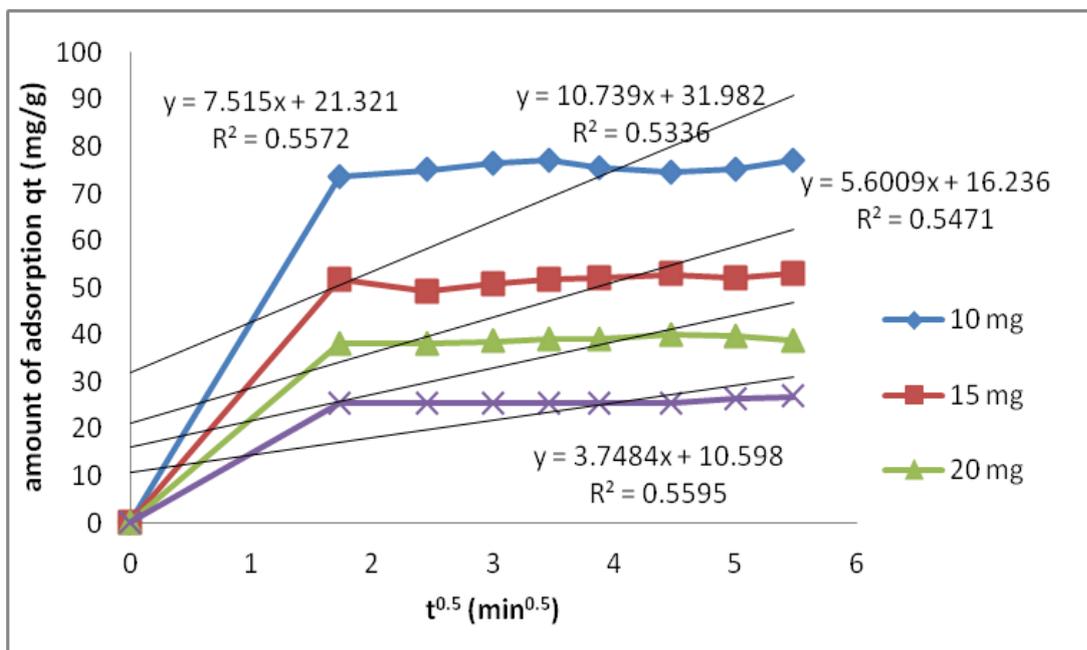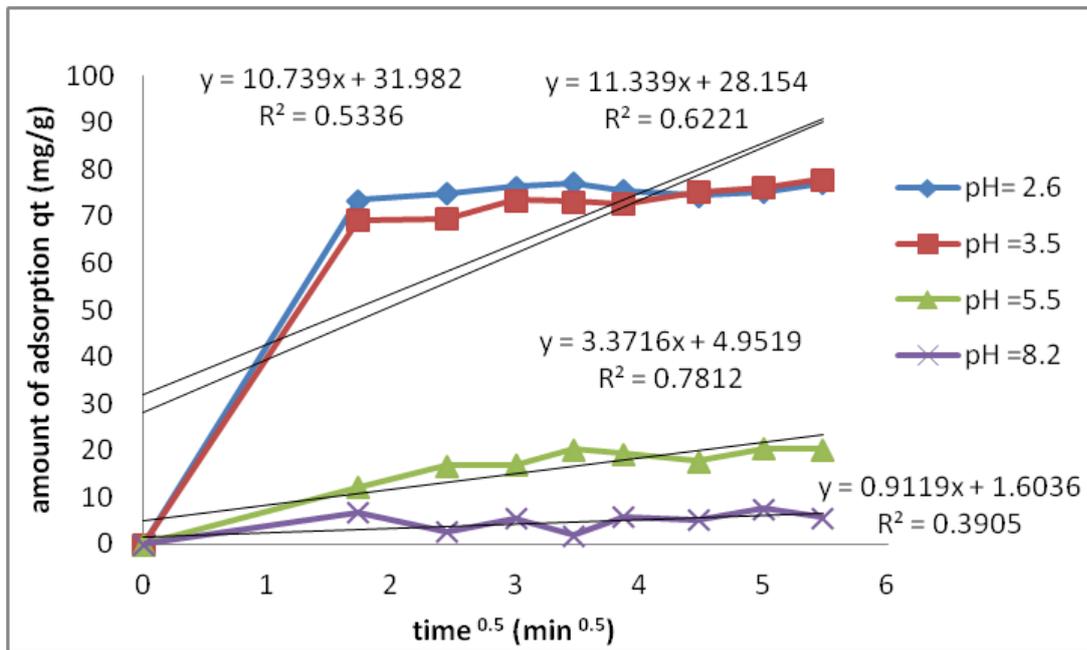
Appendix 5.10

Adsorption isotherm experiment

Initial dye Concentration (ppm)	Ce	qe (mg/g), Experimental	lnCe	lnqe	1/Ce	1/qe (g/mg)	Ce	Ce/qe	qe/Ce
20	2.254	59.152	0.813	4.080	0.444	0.017	2.254	0.038	26.238
30	3.213	89.291	1.167	4.492	0.311	0.011	3.213	0.036	27.794
40	5.145	116.184	1.638	4.755	0.194	0.009	5.145	0.044	22.582
50	6.625	144.584	1.891	4.974	0.151	0.007	6.625	0.046	21.825
60	8.813	170.623	2.176	5.139	0.113	0.006	8.813	0.052	19.360