MATHEMATICAL MODELING OF ADSORPTION FOR WASTEWATER TREATMENT

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Thesis submitted in fulfillment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering in Chemical Engineering

Faculty of the Chemical Engineering and Natural Resources
UNIVERSITI MALAYSIA PAHANG

JANUARY 2012

ABSTRACT

Textile industries produced huge volume of wastewater which is contains synthetic dyes. Synthetic dye is a toxic dye and can cause harm to the aquatic ecosystem as well as to human being because it is poisonous and have carcinogenic and mutagenic. Therefore, dyes must be removed from wastewater before discharged to the drain or river. The method which is widely used is adsorption because this method requires simple operation procedures, low cost compared to the other separation process and no sludge formation. The potential of tea dust as low cost adsorbent to remove color from dye solution was studied. The equilibrium and kinetic of adsorption were studied in batch mode and then mathematical model of adsorption for wastewater treatment was developed. The experiment was conducted under batch mode with various parameters such as initial concentration, pH, adsorbent dose and contact time. The equilibrium study, kinetic study and effect of pH and effect adsorbent dosage were conducted under batch mode constant temperature. The equilibrium data were fitted with Langmuir isotherm, Freundlich isotherms and modified Langmuir model while for kinetic data were fitted with pseudo-first-order, pseudo-second-order and Unified Approach model. Tea dusts have potential to adsorbed crystal violet very well when solution was basic. The adsorption data were fitted better in Langmuir Isotherm which mean this adsorption of crystal violet onto tea dust was monolayer system and the structurally homogeneous sorption surface of adsorbent. The Lagergren pseudo-first order and pseudo-second order were dependent on initial concentration and adsorbent dosages but the Unified Approach Model does not depend on this two parameters. Thus, Unified Approach Model was described the kinetic well and it was useful for modeling the adsorption of crystal violet using tea dust.

ABSTRAK

Industry tekstil menghasilkan isipadu air tercemar yang sangat tinggi dimana air tercemrt ini mengandungi pewarna sintetik. Pewarna sintetik sangat merbahaya kerana ia adalah sejenis toksik dan boleh menyebabkan kemudaratan kepada ekosistem air dan juga manusia. Oleh sebab itu, pewarna sintetik perlu dinyahkan dari air tercemar sebelum dilepaskan ke sungai-sungai. Penjerapan ialah salah satu kaedah dan digunakan secara meluas kerana kaedah ini mempunyai prosedur yang mudah, murah dan tiada penghasilan enapcemar. Serbuk teh ialah jenis penjerab yang mampu menjerab pewarna dari air dan penjerab ini murah berbanding jenis lain. Keseimbangan dan kinetic untuk kaedah ini telah dijalankan dalam kumpulan kemudian model untuk penjerapan telah dibuat. Eksperimen telah dilakukan dengan parameter-parameter seperti berbeza kepekatan, pH, berat penjerab dan masa dibawah suhu yang tetap. Model Langmuir, Freundlich dan ubah-suai model Langmuir telah digunakan untuk uji data-data untuk keseimbangan manakala model Lagergren pseudo-first order, pseudo-second order dan Unified Approach Model digunakan untuk data-data kinetic. Serbuk teh ialah penjerab yang berpotensi dan lebih berkesan dalam larutan crystal violet lebih beralkali. Keseimbangan data sesuai diuji mengunakan model Langmuir bermakna sistem penjerapan ini ialah satu lapisan molekul dan mempunyai struktur penjerab dalam keadaan homogen. Model Lagergren pseudo-first order dan pseudo-second order kurang sesuai kerana model-model ini bergantung kepada kepekatan awal larutan tetapi Unified Approach Model sesuai untuk data kinetik dan berguna untuk model penjerapan crystal violet mengunakan serbuk teh.

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$1/n$	Adsorption intensity
Ce	Equilibrium concentration of dye solution (kg/m^3)
Co	Initial concentration (mg/L)
K	Langmuir constant (m^3/kg)
k	Rate constant of pseudo-second order kinetic (min^{-1})
k_{ad}	Rate constant of pseudo-first order kinetic (min^{-1})
K_f	Adsorption coefficient
$q\infty$	Maximum adsorption capacity (mg/g)
qe	Amount of adsorbed at equilibrium (kg adsorbate/kg adsorbent)
q_t	Amount of dye adsorbed at time (mg/g)
R_L	Indicate type of isotherm

LIST OF ABBREVIATIONS

Al^{3+}	Aluminum
BOD	Biological oxygen demand
C=O	Carbonyl group
Ca^{2+}	Calcium
CO_2	Carbon dioxide
COD	Chemical oxygen demand
COOH	Carboxylic acid
CV	Crystal violet
Fe^{3+}	Ferric
FTIR	Fourier Transform Infrared Spectroscopy
GAC	Granular activated carbon
H_2O	Water
H_2O_2	Hydrogen peroxide
PAC	Powder activated carbon
pH_{zpc}	Zero point charge for various system pH
TD	Tea dust
UV	Ultra Violet

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Dyes are the major of the wastewater produced by industries such as textile, paint, cosmetics, etc (Adak *et al*., 2004; Hameed 2009; Bhattacharyya and Sarma, 2003; Hu *et al*., 2007). The productions of dyes are over $7x10^5$ metric tons based on worldwide research and 5 - 10% of the dyes lost in industrial effluents (Bajpai and Jain, 2010). Since textile industries consume large quantity of water, the wastewater produced large volume of dyes (Hameed, 2009). Moreover, the type of dyes used in textile industries are synthetic dyes which is toxic dye and cause harm to the aquatic ecoystem (Hameed, 2009; Bajpai and Arti, 2010; Adak et al., 2005). Other than that, dyes consist of carcinogenic and mutagenic effects which can affect aquatic life and human (Bhattacharyya and Sarma, 2003).

To avoid this kind of disease, researchers have found some method to remove dyes from the wastewater. There are a few methods used in dye removal such as sedimentation, chemical treatment, oxidation, biological treatment, electrochemical methodology and last but not least adsorption (Gupta *et al*., 2009). Adsorption is widely used because this method requires simple operation procedures, low cost compared to the other separation process and no sludge formation (Mohanty *et al*., 2006). Adsorption method will use adsorbent as a medium to adsorb dyes from the wastewater. There are several types of adsorbents which are alumina, zeolites, activated carbon and natural adsorbents (Gupta and Suhas, 2009). Natural adsorbents are widely used because these materials are low cost. The natural adsorbents usually used as adsorbent for dye removal are peat, chitosan, natural coal, cotton, orange peel, and etc (Gupta and Suhas, 2009).

In this study, tea dust will be used to remove crystal violet dye from wastewater Effective parameters such as adsorbent dosage, initial dye concentration, pH, and contact time were investigated for dye removal. The Langmuir and Freundlich isotherms were used to fit the equilibrium study. The adsorption rates of dyes for kinetic study will be determined by pseudo-first-order and pseudo-second-order. Other than that, unified approach model will be use to test the experiment data.

1.2 PROBLEM STATEMENT

Textile industries produce very huge volume of wastewater which is consists of synthetic dyes. Dyes are soluble in water and cannot be removed easily from water. Removal of dye from wastewater by adsorption widely used because adsorption is a simple method and low cost. In adsorption process, adsorbent will be used to adsorb the dyes from wastewater. Tea dust is one of the potential adsorbent to remove dyes from wastewater. The data from experiment such as potential initial concentration, pH, adsorption dosage and contact time will be test by computing the kinetic and equilibrium data. From the previous study, Langmuir isotherm usually used to fit the equilibrium isotherm. The each molecule of adsorbate assumed as monolayer coverage of the homogenous surface of the adsorbent. However, molecule of adsorbate on the surface of adsorbent can be multilayer because the layer cannot be seen with naked eye. For Freundlich isotherm, the adsorbate layer will be assuming as multilayer and heterogeneous. For kinetic study, rate constants were determined by initial concentration ($-r=kCAo$). Unfortunately, rate constants depend on reaction temperature and catalyst activities but independent of initial concentration, the adsorbent mass and solution volume.

1.3 RESEARCH OBJECTIVES

This research has three main objectives which are:

I. To study the potential of tea dusts as adsorbent for adsorption of dyes removal from wastewater
II. To study the equilibrium and kinetic of adsorption in batch mode
III. To study mathematical models of adsorption for wastewater treatment

1.4 RESEARCH QUESTIONS

After the experiment, some questions need to be answered to achieve the objectives of this research. The questions are:

I. How efficient tea dust is as the adsorbent in dye removal from wastewater?
II. How to study the equilibrium and kinetic study of adsorption in batch mode?
III. How to develop mathematical modeling of adsorption for wastewater treatment?

1.5 SCOPE OF STUDY

In order to achieve the objectives as of this experiment, the following scopes had been identified and to be studied:

I. The effect of adsorbent dose on dye adsorption
II. The effect of solution pH on dye adsorption
III. The effect of temperature on dye adsorption
IV. Development of mathematical model of adsorption for wastewater treatment

1.6 SIGNIFICANCE OF STUDY

Based on the research scopes mentioned above, the significance of the study had been outlined:

I. Tea dust can be used as a potential adsorbent for dye removal from wastewater.
II. The equilibrium study must be consistent with kinetic study
III. Mathematical modeling of adsorption can be developed for wastewater treatment.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Water is the most important in human life and this utility is use in many industries such as food processing, metal produce industry, paper and wood process, chemicals, oil and gases, textile industry, laundry services and other industries. Before this, most of the industries just release the wastewater to the drain or river and the wastewater can induces water pollution. To decrease the water pollution, the wastewater should be treated to get the pure water back or before the wastewater release to the drain or river. Other than that, cost for water utility can be decrease because the treated water can be reuse.

Most of wastewater was pollute by dye removal. This has resulted in the discharge of highly polluted effluents. Normally, colour is noticeable at a dye concentration more than 1 mg/L and the textiles industries have an average concentration of 300 mg/L dye. More than 7 x 10^5 tonne per year and approximately 100,000 different dyes and pigments are produced from worldwide. Overall it is about 10% of the dyes may be found in wastewater (Bajpai *et al*, 2009). Manu and Chaudhari (2002) said a proficient and low cost treatment is required because of lacking in water source and more legal action by the authorities to decrease water pollution.

There is more than one method which can use as dye removal treatment. Adsorption is one of the methods to treat the wastewater. Water can be reuse after through the adsorption process by using absorbent such as activated carbon, silica gel, activated alumina, molecular sieve zeolites, and synthetic polymer or resins

(Geankoplis, 2003). However, this method is influenced by several factors which is can affect the rate of adsorption such as amount of adsorbent taken, pH of adsorbate, concentration of the adsorbate, contact time and temperature of batch system. There are several materials used as adsorbent such as activated carbon, alumina etc. and spent tea leaves is one of the suitable adsorbent for dye removal from wastewater based on previous studies. The behaviour of adsorption can be characterizing according to the both kinetics and equilibrium isotherms as well as the adsorption mechanism (Mozammel *et al*, 2010).

2.2 DYE

Dye can be said to be coloured, ionising and aromatic organic compounds which shows an affinity towards the substrate to which it is being applied. It is generally applied in a solution that is aqueous. Dyes more used in industries such as food, pharmaceutical, cosmetic, printing, textile and leather industries. Synthetic dyes are easier and low cost in synthesis, firmness, more stable in light, detergent and microbial attack. Other than that, synthetic dyes are made in varieties of colour compared to natural colour. There are 100 000 or more commercial dyes which is available and the production of dyes annually is over $7x10^5$ ton (Robinson *et al.*, 2001; Bajpai *et al.*, 2010).

Although dyes are useful, but it can be classified as problematic compounds because can pollute the environment otherwise it been treated nicely. Dyes are resistant to washy when it is exposing to the water, light or any chemicals according to the chemical structure (Robinson *et al.*, 2001). Dyes are withstood to biological attack, light, heat and oxidation (Manu and Chaundari, 2002). Dyes are soluble in water and cannot be remove easily from the waste water although using biological wastewater treatment (Panswad *et al.*, 2000) and dyes removal using municipal aerobic treatment were found to be inefficient (Moran *et al.*, 1997). According to Manu and Chaudhari (2002) and Chu (2001), although dyes are very low concentration, it needs to be remove before water can be discharged or disposal. Dye is an effluent characteristic which is easily detected. Some dyes are stable to biological degradation and metal containing dyes are toxic (McKay *et al.*, 1984).

There are two key of dye molecule which is the chromophores and auxochromes. Chromophores are use for produce the colour and auxochromes to give the molecule soluble in the water and increased affinity toward the fibres (Gupta and Suhas, 2009). Figure 2.1 shows the chromophore group and auxochrome group contain in chemical structure of dye.

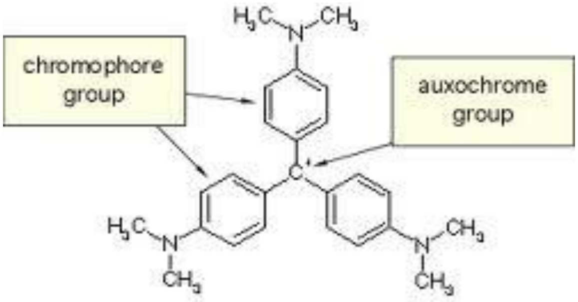
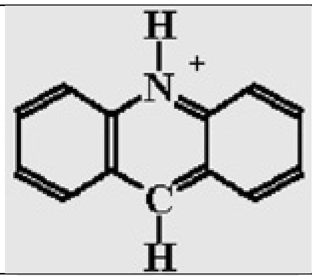
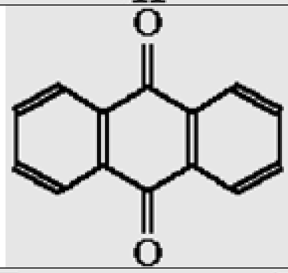
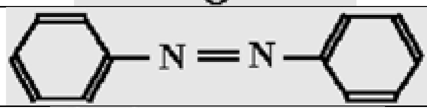
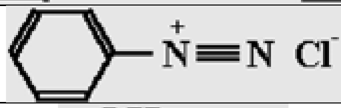
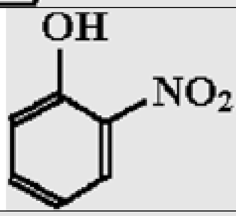
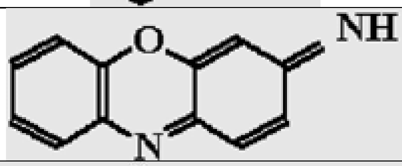
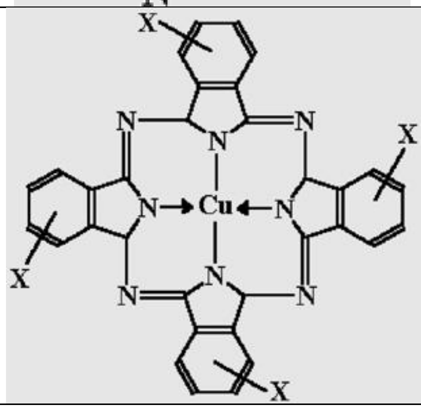


Figure 2.1: Chromophores and auxochromes in dye.

Source: Goggle.com

Many types of dyes are poisonous and have carcinogenic and mutagenic effects that can affect aquatic lives and also humans being (Bhattacharyya and Sarma, 2003). The carcinogenic was prepared from known carcinogens such as benzene or other aromatic compound (Robinson *et al*., 2001) that might be formed as a result of microbial metabolism. Different dyes will have different chromophoric group. Several studies shows that different class of dyes will be remove using different methods such as azo and nitro compound were reduced in sediment (Weber *et al*., 1987) and anthroquinone compound was degrade due to the fused of aromatic ring structure (Baughman *et al*., 1988). Table 2.1 shows class of dyes with the general formula of each dye.

Table 2.1: Dyes structure according to their chromophores

Class	General Formula
Acridine	
Anthraquinone	
Azo	
Diazonium	
Nitro	
Oxazin	
Phthalocyanine	

Source: Goggle.com

There is more than one type of dyes in the industries. Some properties of dyes can be classified based on the usage of the dye. Table 2.2 shows the usage of dyes and the chemical class.

Table 2.2: Properties of dye and usage

Type of dye	Usage	Principle chemical classes
Acid dyes	Nylon, wool, silk, modified acrylics, and also to some extent for paper, leather, ink-jet printing, food, and cosmetics.	Azo (including premetallized), anthraquinone, triphenylmethane, azine, xanthene, nitro and nitroso.
Cationic dyes	Paper, polyacrylonitrile, modified nylons, modified polyesters, cation dyeable polyethylene terephthalate and to some extent in medicine.	Diazahemicyanine, triarylmethane, cyanine, hemicyanine, thiazine, oxazine and acridine.
Disperse dyes	Mainly on polyester and to some extent on nylon, cellulose, cellulose acetate and acrylic fibers.	Azo, anthraquinone, styryl, nitro, and benzodifuranone groups.
Direct dyes	Dyeing of cotton and rayon, paper,leather, and, to some extent to nylon.	Polyazo compounds, along with some stilbenes, phthalocyanines and oxazines.
Reactive dyes	Cotton and other cellulosics, but are also used to a small extent on wool and nylon.	Azo, anthraquinone, triarylmethane, phthalocyanine, formazan, oxazine, etc
Solvent dyes	Plastics, gasoline, lubricants, oils, and waxes.	Predominantly azo and anthraquinone, but phthalocyanine and triarylmethane are also used.
Sulphur dyes	Cotton and rayon and have limited use with polyamide fibers, silk, leather, paper, and wood.	Have intermediate structures

Source: Gupta and Suhas., 2009

2.2.1 Crystal Violet

Crystal violet is monovalent cationic dye (Jian-min *et al*, 2010) is used for various purposes such as biological stain, dermatological agent, veterinary medicine, and additive to poultry feed to inhibit propagation of mold. Furthermore, the used of Crystal Violet is widespread in textiles and printing industries (Adak *et al*, 2005). Besides that, crystal violet is the most dye used of dyeing for cotton, wool, silk, nylon, leather etc. (Bajpai *et al*, 2010). This type of dye is a mutagen and mitotic poison (Mohanty *et al*, 2006). Crystal violet becomes hazardous in case of eye contact or irritation, ingestion, inhalation and skin contact.

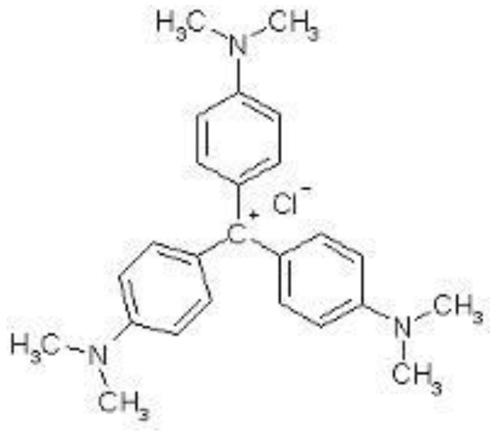


Figure 2.2: Chemical structure for Crystal Violet

Source: Goggle.com

2.3 METHODS OF DYE REMOVAL

Synthetic dye is very harmful to environment and human being. It is easily soluble in the water and if human drinks that water, the water can dangerous human body system. For the workers who work in dye industries, they are more exposed to the dye poisoning. Dye can cause disease such as tumours, several cancers, cerebravascular disease and lung disease. All of this disease and problems can be avoid if wastewater consist of dye was treated well before it is discharge to the river. Due to this problem, people have been aware about the negative impact which is caused by dye industries on the environment. The colour manufacturing industry represents a relatively small part of the overall dye industry. All the industries which are using dyes for their manufacturing should be aware of this problem. Dyes are harmful and hazardous will affected aquatic life and environment although in low concentration. Removal of colour from wastewater or waste effluent is very important for environmental and also for human.

There are a few methods of dye removal such as physical, chemical and biological methods. For physical method, the treatment used such as sedimentation, filtration, adsorption, ion exchange, irradiation, and electrokinetic coagulation (Robinson *et al*., 2001and Gupta and Suhas, 2009). Oxidative process, electrochemical destruction, photochemical and cucrbituril are types of methods which is using chemical to treat effluent while anaerobic textile-dye bioremediation system is one of treatment in biological method (Robinson *et al*., 2001).

2.3.1 Physical method

Physical method in wastewater treatment is a process applied in which no chemical change occurred. The unit operation involves in this method such as screening process, preliminary treatment and primary treatment. Adsorption, filtration, ion exchange, irradiation and electrokinetic coagulation are such of physical method which is widely used for dye removal in wastewater treatment (Robinson *et al*., 2001). Physical processes have advantages rateable to biological and other treatment processes (Gupta and Suhas, 2009). Physical treatments remain unaffected by the presence of toxic substances such as metal whereas biological systems fail to operate in case of water foremost inorganic or non-biodegradable in nature. Table 2.3 below are shows the advantages and disadvantages some of the treatment in physical method.

Table 2.3: Advantages and disadvantages of physical methods for dye removal from industrial effluents.

Chemical methods	Advantages	Disadvantages
Activated carbon	Good removal for variety of dyes	High cost
Peat	Good adsorbent due to cellular structure	Limited surface area
Wood chips	Good sorption capacity for acid dye	Required long retention time
Silica gel	Effective for basic dye removal	Side reaction prevent commercial application
Membrane filtration	Remove all dyes type	Concentrated sludge production
Ion exchange	Can be regenerate : no adsorbent loss	Not effective for all dyes
Irradiation	Effective oxidation at lab scale	Required a lot of DO
Electrokinetic coagulation	Economically feasible	High sludge production

Source: Robinson *et al*. (2001)

2.3.1.1 Sedimentation

Sedimentation is any solid or particle which is transported by the fluid and at the end the particle will deposited as a layer as a solid on the bed or bottom of the body of water. Sedimentation is such as physical treatments to maintain the pH, total dissolved solid (TDS) and total suspended solid (TSS) of the dispose water. This method is basic method which is widely use by the industrial wastewater to remove dye from waste water (Cheremisinoff, 2002). There are some factors which are affecting the ability of solid to settling in water which are size of particles to be removed, temperature of water, types of water, sedimentation basin zone, selection of basin, rate of settlers, and contact of solid combine in the basin. The applications of sediment in wastewater treatment are preliminary treatment, primary treatment, secondary treatment, sludge treatment and physical-chemical treatment (Sperling, 2007).

2.3.1.2 Filtration

Filtration is a technique to remove the impurities from the solution. This filtration technology is an application for integral component of drinking water and wastewater treatment. The applications are microfiltration, ultrafiltration, nanofiltration and reverse osmosis and already investigate for colour removal (Avlonitis *et al*, 2008; Cheremisinoff, 2002). Cheremisinoff (2002) again said each membrane process is suitable for the function of particular water treatment. Compare each of the process, microfiltration is not really use much for water treatment because it has huger pore size followed by ultrafiltration and nanofiltration (Cheremisinoff, 2002). Nanofiltration is an effective process to remove all classes of dyestuffs and dye molecules because frequent clogging of the membrane pores making the separation systems of limited use for textile liquid waste treatment. In industries less use this treatment because this method are high working pressure, significant energy consumption, high cost of membrane and relatively short membrane life. Under the pressure, reverse osmosis water will force water through a membrane which is impermeable to most contaminants. The membrane is better in rejecting salts than it is rejecting non-ionized weak acids and bases and also in rejecting smaller organic molecules usually molecular weight under 200. This reverse osmosis is effective decolouring and desalting process compare to most diverse range of dye wastes, and has been successfully employing for recycling (Sostar-Tark *et al.*, 2005). The water discharge by reverse osmosis will be close to pure water.

2.3.1.3 Adsorption

Adsorption is physical separation which the attractive forces between adsorbed molecules and the solid surface are van der Waals forces and being weak in nature result in reversible adsorption. Adsorption does not require another chemical compound in the process (Ulson de Souza and Peruzzo, 2008). The advantages of adsorption are it is simple operation, low cost and absence of sludge formation (Mohanty *et al.*, 2006). Adsorption is most method used in removal of dye from water effluent because this method inexpensive but still depends on adsorbent used. Today, there are many types of low cost adsorbent used for dye removal including charcoal, wood, silica gel, agricultural waste, cotton waste etc. (Mohanty *et al*, 2006). Adsorption with activated carbon was broadly used in dye removal and other hazardous chemicals but cannot be commercialized since the high cost of activated carbon (Hameed, 2009).

In adsorption process, solid adsorbent will adsorb one or more component of a gas or liquid on the surface of solid. Adsorbent used is usually in the form of small particles in fix bed. The fluid will pass through the adsorbent in the bed and that solid particles which have porous will adsorb the liquid particle. The adsorbent can be regenerated after the solid particles become saturated by heating up the solid particles. The adsorbent will recover and that adsorbent can be use again (Geankoplis, 2003). Adsorption process was affected by many factors such as sorbent interaction, sorbent surface area, particle size, temperature, pH and contact time (Kumar *et al*., 1998).

2.3.1.4 Ion exchange

Ion exchange is one of treatment used to remove dye from wastewater but this method not widely used because this method cannot accommodate a wide range of dyes (Robinson *et al*., 2001). The process used in ion exchange is reversible process where an ion from solution is exchange for a similar charged ion which is attached to an immobilized solid particle (Gupta and Suhas, 2009). In this process, wastewater is passed through the resin until the availability of exchange site is saturated. Both cation and anion dyes can be removed from effluent using this method (Mishra *et al*., 1993).

2.3.1.5 Irradiation

In irradiation treatment, requirement of dissolved oxygen in sufficient amount for broke down the organic substances effectively by radiation. Oxygen need to supply continuously since this process required rapidly supplement of dissolve oxygen. This method shows that some dyes can be oxidised effectively but in lab scale only (Robinson *et al*., 2001).