FIXED BED ADSORPTION FOR WASTEWATER TREATMENT

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ABSTRACT

This study is about the comparison of flow arrangement in fixed bed adsorption for wastewater treatment and also to study the equilibrium adsorption in batch mode, to study the column adsorption for dye removal, and to study the effect of flow pattern, flow rate and initial dye concentration. The adsorption of methylene blue from wastewater onto granular activated carbon (GAC) in fixed bed was investigated and breakthrough data of the dyes was determined. This research is run in small scale column at constant temperature and pH value. The equilibrium study was done on batch mode and the data fitted with Langmuir model so that the design parameter will be evaluated. The column mode was studied by considering varies parameter to find suitable flow pattern (up-flow and down-flow) and optimum flow condition. Both the flows will be subject to static mode adsorption studies. The effects of bed height, initial concentration and flow rate on breakthrough curve were investigated. It is found that breakthrough time and adsorption capacity increases by increasing flow rate, increasing initial concentration and decreasing bed height. The results show that the up-flow arrangement is better performance than the down-flow arrangement. This is due to the higher of the breakthrough time and the equilibrium capacity for up-flow column in all experimental conditions.

ABSTRAK

Kajian ini adalah tentang perbandingan arah aliran terhadap penjerapan di dalam bekas tetap untuk rawatan air kumbahan. Ia juga untuk mengkaji keseimbangan penjerapan secara berkelompok, mengkaji penjerapan ruangan untuk penyingkiran pewarna, dan mengkaji kesan arah aliran, kadar kelajuan aliran dan kepekatan awal pewarna. Penjerapan metilena biru dari air kumbahan menggunakan karbon berbutir yang diaktifkan (GAC) untuk penjerapan bekas tetap disiasat dan data bulus (breakthrough) daripada pewarna telah ditentukan. Penyelidikan ini dijalankan dalam skala yang kecil tanpa perubahan pada suhu dan nilai pH. Kajian keseimbangan yang telah dilakukan secara berkelompok dan data yang diperolehi disesuaikan dengan model Langmuir supaya parameter yang hendak dikaji dapat dinilai. Penjerapan dalam keadaan turus telah dikaji dengan memfokuskan pelbagai parameter untuk mencari arah aliran yang sesuai (aliran ke atas dan aliran ke bawah) dan keadaan aliran yang optimum. Kedua-dua aliran akan tertakluk kepada kajian penjerapan statik. Kesan ketinggian bekas, kepekatan awal pewarana dan kadar kelajuan aliran terhadap lengkung bulus disiasat. Ia didapati bahawa masa bulus dan kapasiti penjerapan meningkat apabila kadar kelajaun aliran meningkat, kepekatan awal pewarna meningkat dan ketinggian katil berkurang. Hasil kajian menunjukkan bahawa prestasi arah aliran ke atas lebih baik daripada arah aliran ke bawah. Ini adalah kerana masa bulus dan keupayaan keseimbangan untuk arah aliran ke atas lebih tinggi dalam semua keadaan uji kaji.

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LIST OF SYMBOLS

O_2	Oxygen
%	Percentage
C_{ad}	Adsorbed dye concentration
C_0	Initial dye concentration
C	Outlet dye concentration
C_x	Exhaustion point
V_{eff}	Effluent volume
Q	Volumetric flow rate
t	Total flow time
A	Area above the breakthrough curve
w	Amount of adsorbent
K_c	Adsorption rate constant
N_0	Adsorption capacity
X	Bed depth
V	Linear flow velocity
q_m	Maximum adsorption capacity
C_e	Equilibrium concentration
K	Adsorption equilibrium constant
R^2	Correlation coefficient
q_{total}	Total adsorbed dye quantity
m_{Total}	Total amount dye
t_b	Breakthrough time
t_e	Exhaust time
H_{UNB}	Unused length

LIST OF ABBREVIATIONS

ABS	Absorption
BDST	Bed Depth Service Time
GAC	Granular Activated Carbon
MB	Methylene Blue
PAC	Powder Activated Carbon
PCBs	Polychlorinated Biphenyls
PVC	Polyvinyl Chloride
TCE	Trichloroethylene

CHAPTER 1

INTRODUCTION

1.1 Research Background

Decolourisation of wastewater has become one of the major issues in wastewater pollution. This is because many industries used dyes to colour their products, such as textiles, rubber, paper, plastics, leather, cosmetics, food and mineral processing industries. Especially, the textile finishing industry has a specific water consumption part of which is due to dying and rinsing processes. Every year, the production of dyestuffs about 10 million kg/ year between 1 and 2 million kg of active dye enter the biosphere, either dissolved or suspended in water. About 10,000 different commercial dyes and pigments exist, and over 7 x 10^5 tons are produced annually world-wide. It has been estimated that about 10–15% of these dyes are release in effluents during dyeing process (Yener *et al*., 2008).

Dyes and pigments are very visible material. Although just a little of dyes or are release into the environment, they can cause colour appearance, for example in open water, that striking critical public and local authorities. Dyes exhibit considerable structural diversity. Colour of textile effluents cause environmental problem mainly because of its non-biodegradable characteristics. For example, acute exposure of methylene blue can cause some harmful effects such as increasing the heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans (Hameed and Ahmad, 2008). Scientists recommend that dyes need to remove completely from effluents prior to their final discharge (El Qada *et al*., 2008).

Various methods for dye removal were divided to three categories, which biological, physical and chemical methods such as oxidation, electrochemical destruction, adsorption by activated carbon, ion exchange, membrane filtration and coagulation. The choice of dye removal treatment is depends on effluents characteristics such as concentration of dye, pH, temperature, flow volume, the economics involves and the social factor (Dwivedi *et al.*, 2008). The current study is based on exploring its removal method based on adsorption technique. Adsorption is a process by which molecules or ions retained on the surface of solids by physical or chemical bonding. Adsorption compared with other methods appears to be an attractive process because it's high efficiency, low cost, easy handling and available for different absorbents (El Qada *et al.*, 2008). Interestingly, the adsorption technique also removable the inorganic and organic complex metal effectively that would not be removed by other treatment methods. The adsorption technique has proven successful on lowering dye concentration from industrial effluents by using activated carbon as an adsorbent.

The present research work deals with the design parameters of fixed bed adsorption column. Fixed bed column were widely use in many chemical industries because of their simple operation and can be scaled-up from laboratory process. Al-Degs *et al.*, (2009) was studied the adsorption characteristics of reactive dyes in columns of activated carbon. Fixed-bed adsorption of reactive azo dye onto granular activated carbon prepared from waste has been reported by Ahmad and Hameed (2010). Before testing the performance of an adsorbent in fixed bed column, equilibrium isotherm should be studied to determine the properties of adsorbent such as surface area, density and pores structure. Due to the high cost of commercial activated carbon, it is advisable to run small scale column. In addition, the scale column studies will be give accurate prediction for dye removal (within an acceptable size of error) from real wastewater systems (Al-Degs *et al.*, 2009).

1.2 Problem Statement

Lot of research reported well done for adsorption of dye in the column. Usually, the flow inlet to the column is given from the top or from the bottom of column. But, none of study reported the comparison of the flow pattern. This study should be done to find suitable flow pattern and optimum flow condition. Both the flows (up-flow and down-flow) will be subject to static mode adsorption studies and then compare them based on isotherm analysis.

1.3 Research Objectives

There are four main purposes of this research;

i. To study the equilibrium of adsorption in batch mode.
ii. To study the column adsorption for dye removal.
iii. To study the effect of flow pattern, flow rate and initial dye concentration.
iv. To develop up-flow and down-flow arrangement for fixed bed study.

1.4 Scopes of Study

This study investigates the column adsorption abilities for the removal of methylene blue (MB) dye from aqueous solutions. There are four parameters to be studied which are the characteristic and effects of flow patent, bed height, flow rate and initial concentration of MB dye.

1.5 Rational and Significance of Study

This study should be done to find suitable flow pattern and optimum flow condition. Usually, the flow inlet to the column is given from the top or from the bottom of column. Hence, this research can help treatment industrial to develop a good adsorption column module to improve the treatment such as wastewater treatment, dye removal or to remove heavy metal and nocuous ion.

In this study, granular activated carbon (GAC) is used to remove dye from wastewater. Basically, commercial available GAC are quite expensive due to use of non-renewable and relatively expensive raw material such as coal, which is not justified in pollution control application (Yener *et al*., 2008). However, this research still uses GAC as an adsorbent because it is more effective than other adsorbent media and will give optimum data to this research. Both factors are so important to achieve the objective of research. Besides, this research is run in small scale column. Thus, it only use small amount of GAC to run it.

CHAPTER 2

LITERATURE REVIEW

2.1 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 (R.Couto, 2009).

Although dyes are useful, but it can be classified as problematic compounds because can pollute the environment otherwise it been treated nicely. Dye is water soluble and cannot be remove easily from the waste water although using biological wastewater treatment (Panswad and Luangdilok, 2000; Forgacs *et al.*, 2004 and Rai et al., 2005). Dye usually withstand to biological attack, light, heat and oxidation (Manu *et al*, 2002). According to Manu (2002) and Chu (2000), dye has very low concentration and need to remove before water can be discharged or disposal. 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.

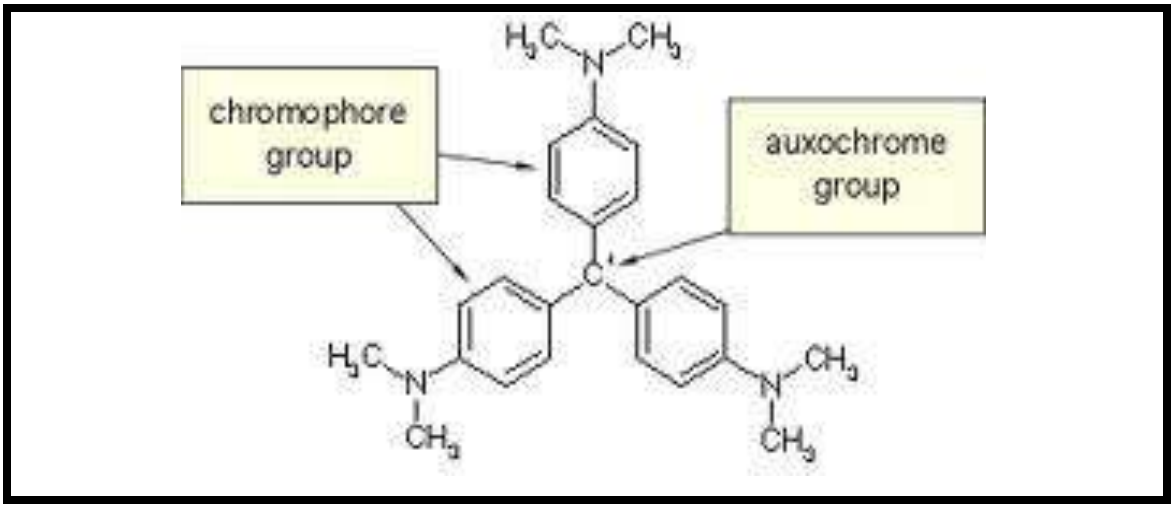

Figure 2.1: Chromophores and auxochromes in dye

Many types of dyes are poisonous and have carcinogenic and mutagenic (McKay and Otterburn, 1985; Dutta, 1994; R. Couto, 2009) effects that can affect aquatic lives and also humans being (Gregory, Elliot and Kluge, 1991). The carcinogenic was prepared from known carcinogens such as benzene or other aromatic compound that might be formed as a result of microbial metabolism (Novotny *et al*, 2006; Kariminiae-Hamedaani *et al*, 2007). Different dyes will have different chromophoric group. Besides, 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 (Christie, 2007).

Table 2.1: Properties of dye and usage

Adapted from (Christie, 2007)

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.
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
Vat dyes	Cotton mainly to cellulosic fibers as soluble leuco salts and for rayon and wool too.	Anthraquinone (including polycyclic quinones) and indigoids.
Azoic dyes	Cotton and other cellulosicmaterials, fluorescent brighteners having stilbene, pyrazoles, coumarin and naphthalimides used for soaps and detergents, fibers, oils, paints, and plastics.	Azo group
Mordant dyes	Wool, leather, natural fibers after pretreating withmetals and anodized aluminium.	Azo and anthraquinone

2.2 Methods of Dye Removal

Generally, dye is water soluble and has very low concentration. So, dye need to remove before water can be discharged or disposal by dye although this activity is very difficult. Otherwise, the environment and human body will be affecting by dye industries. Due to this problem, human now have concern on potential adverse effects to the chemical industry in environment. Hence, for protecting the environment and to meet the stringent government law, many researchers try to find out this problem. There are many ways to remove the dye, which are classified into three main categories namely physical, chemical and biological methods. All of them have advantages and disadvantages respectively. Considerable amount of research has been undertaken on the treatment to decrease the impacts of the environment.

2.2.1 Biological Method

Biological treatment method can be defined as a process in which microorganisms such as bacteria are used to biochemically decompose the dye wastewater and stabilize the end of product (Aizenchtadt *et al*., 2008). Biological treatment methods usually more cheap and simple to apply and currently used to remove dye wastewater. Most of existing process includes an initial step of activated sludge treatment to remove the organic matters, follow by oxidation, membrane, activated carbon and so on.

Biological treatment methods that used for wastewater treatment can be classified into two types, which are aerobic and anaerobic method. The commonest treatment of wastewater has been based on aerobic biological process that involved mainly conventional and extended activated sludge process. In activated sludge process, the wastewater flows into a tank after primary settling. The microorganism in activated sludge is suspended in the wastewater as aggregates. The operation of activated sludge process likes of mixing and stirring raw sewage with recycled by activated sludge. Aerobic degradation of the pollution takes place by thoroughly mixing the purifying the microorganism to be treated. Then, the purified water and purifying sludge phases are separated. Meanwhile, an anaerobic process is an organism that does not need oxygen as based metabolism. There is an interest in anaerobic bacteria used for bioremediation of polychlorinated biphenyls (PCBs) in river sediments, chlorination of the solvent trichloroethylene (TCE), and chloroform (Vidali, 2001).

Sometimes, aerobic and anaerobic processes have been use together or separately for the treatment of dye wastewater. Conventional biological treatment methods are not effective for removal dye because many commercial dyestuffs are toxic to organism being used and also because of low biodegradability of many textile chemicals and dyes.

2.2.2 Physical Method

Physical methods different also widely used, such as membrane-filtration processes (nanofiltration, osmosis relapse, electrodialysis) and adsorption techniques. Physical methods use strictly physical processes to improve or treat the wastewater and no gross chemical or biological changes. The major weaknesses of membrane processes is they have lifetimes limited before membrane cancel is happen and the periodic replacement cost must be became included in any their economic viability analysis. In line with enormous literature data, liquid phase adsorption is one of methods that most popular for pollutant isolation of material from wastewater since suitable design adsorption process will produce one high quality treat effluent. This process provides an alternative pulled to the treatment polluted waters, especially if sorbent inexpensive and does not require an additional pre-treated stepped before the application.

Adsorption is famous balance separation process and one of the effective processes for water purification applications. Adsorption has been found in order to be great for other techniques for deep water salvage in term of initial cost, flexibility and design moderation, operations facility, and not sensitive for toxic pollutants. It is an effective of lowering the concentration of solution in the effluent water. Adsorption also did not result in dangerous materials formation. Decolourisation is a result of two mechanisms that included adsorption and ion exchange, and is influenced by many physiochemical factors, such as, dye or material interaction, material surface area, particle size, temperature, pH, and contact time (Kumar *et al*., 2006). Flotation also is a method of physical wastewater treatment processes. Flotation is used to remove suspended matter and to concentrate biological sludge. Flotation uses air exclusively as the floating agent so that particles can be removed faster and smoothly.

2.2.3 Chemical Method

Chemical treatment method is used the chemical reactions to achieved treatment. This chemical technique is often expensive, and although dyes are removed, concentrated sludge collection holds a disposal problem. There is also possible that one is a secondary pollution problem will be submerged due to excess chemistry use. The most common using chemical treatment is chlorination. Chlorine is used to kill the bacteria which lead to decomposition of water and to decrease the rate of decomposition. It is important to note that chlorination will not remove toxic by products because it has already been produced. Coagulating chemicals in wastewater treatment is a conventional treatment method to remove of high turbidity and this is more consistent performance. This method is suitable to treat the water employed in dyeing (Lin *et al*., 2004). Metals that have more than one valence (e.g. lime and aluminium sulphate) are some commonly used coagulants. The main advantage of the conventional coagulation is removal of the waste stream due to the removal of dye molecules from the dye bath effluent and not due to partial decomposition of dyes.

Besides, disinfection involves in chemical treatment process. Disinfection with aggressive chemicals like chlorine or ozone is normally the last step in purifying water. Water is disinfected to destroy any pathogens which passed through the filters. Chemical oxidation is the most commonly used method of decolourization by specific chemical to its simplicity. Chemical oxidation uses strong agents which are hydrogen peroxides, chlorine and others to force degradation of resistance organic pollutant. An advantage of oxidation is the volume of wastewater and sludge does not increase.

Physical and chemical treatment techniques are effective for dye removal but use more energy and chemicals substance than biological technique. They also focussed to the additional treatment disposal to treat liquid or solid pollution that through into the rivers.

2.2.4 Summary of Methods for Dye Removal

Table 2.2: Advantages and disadvantages of methods of dye removal from industrial effluent
(Robinson, 2001)

Methods	Advantages	Disadvantages
Ozonation	Applied in gaseous state: no alteration of volume	Short half-life (20 min
Photochemical NaOCl	No sludge production Initiates and accelerates azo-bond cleavage	Formation of by-product Release of aromatic amine
Cucurbituril	Good sorption capacity for various dyes	High cost
Electrochemical destruction	Breakdown compounds are non-hazardous	High cost of electricity
Activated carbon	Good removal of wide variety of dyes	Very expensive
Peat	Good adsorbent due to cellular structure adsorption	Specific surface area for are lower than
Wood chips	Good sorption capacity for acid dyes	Requires long retention times
Silica gel	Effective for basic dye removal	Side reactions prevent commercial application
Membrane filtration	Remove all dye types	Concentrated sludge production
Ion exchange	Regeneration: no adsorbent loss	Not effective for all dyes
Irradiation	Effective oxidation at lab scale	Requires a lot of dissolved O_2
Coagulation	Economically feasible	High sludge production

2.3 Adsorption Method

Adsorption is a process of collecting soluble substances in a solution on a surface. In adsorption processes, one or more components of a gas or liquid stream are adsorbed on the surface of a solid adsorbent and a separation is accomplished. This separation process use a solid phase with large surface area, which selectively retains the components to be separated. Adsorption is simple to apply and currently use for the removal of wastewater and dye. For many industrial treatment applications, it has proved to be the least expensive treatment option. Adsorption is particularly effective in treating low concentration waste streams and in meeting stringent treatment levels (Diwakar *et al*., 2007).

The adsorbing phase is known as adsorbent and the material concentrated adsorbed at the surface of the phase is called adsorbate. Adsorption process is operative in natural physical, chemical, and biological systems. Adsorption operations with an activated carbon and synthetic are widely used in industrial applications for the purification of water and wastewater. In the bulk material, all the bonding requirements ionic, covalent or metallic of the constituent atoms of the material are filled. The exact nature of the bonding depends on the details of the species involved, which the process is generally classed as physisorption or chemisorption. In physisorption, adsorbed molecules are held by the weaker Van der Waals' forces (Geankoplis, 2003). Physisorption is generally considered to be an effective method for quickly lowering the concentration of dissolved dyes in an effluent. For chemisorption, the molecules undergo a chemical bonding with the solid molecules, and this attraction may be stronger than the forces holding the solid together.

The configuration of the adsorption system, which is the fluid (feed) and solid (adsorbent) are contacted, is divided into two main categories. There are batch and column adsorption. Batch adsorption is often used for amount of quantities treated are small, as in the pharmaceutical. In this process, the volume of feed solution contact with a quantity of adsorbent in a vessel. For column adsorption, a column is used to hold the adsorbent in a fixed position. In column, adsorbate is always continuously in contact with an adsorbent thus providing the required concentration (Al-Degs *et al.*, 2009).

Mechanism of adsorption occurs in three steps. First step, the adsorbate diffuses from the major body of the stream to the external surface of the adsorbent particle. Second step, the adsorbate migrates from the relatively small area of the external surface to the pores within each adsorbent particle. The bulk of adsorption usually occurs in these pores because there is the majority of available surface area. And final step, the contaminant molecules go to the surface in the pores.

Application of liquid-phase adsorption includes removal of organic compound from water or organic solution, coloured impurities from organic, and various fermentation products from fermentor effluence. While, application for gas-phase adsorption include removal of water from hydrocarbon gases, sulphur compounds from natural gas, solvents from air and other gases, and odours from air. However, solid can be a good adsorption if it has a surface composed of molecules which provide a good attractive force.

2.4 Column Study

In commercial processes, the adsorbent is usually in the form of small particles in a fixed bed column. A fixed-bed column is often to bring the wastewater into contact with activated carbon. The water to be treated is usually passed down through the packed bed from the top of the column at a constant flow rate also knows as down flow column. However, this research also to study the up flow column, where the water applied to the bottom of the column and withdraw at the top. It is because to compare which one is better, optimum flow condition. The process in the fixed-bed columns is unsteady state. So, mass transfer resistances are important in the column (Geankoplis, 2003). In fixed-bed column, adsorbate is continuously in contact with a given quantity of fresh adsorbent thus providing the required concentration gradient between adsorbent and adsorbate for adsorption. The column may be arranged either in series or parallel. There are some advantages and disadvantages in this method.