DYNAMIC ADSORPTION AND REGENERATION STUDIES OF ACID YELLOW 17 USING ACTIVATED CARBON

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by

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Rosmaliza Zuraida Binti Yaacob

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LIST OF SYMBOLS

	Symbol	Unit
pH	-	-
B_a	Wolborska model kinetic coefficient of the external mass transfer	1/min
C	Effluent concentration	mg/L
C_b	Breakthrough concentration	mg/L
C_o	Influent concentration	mg/L
C_t	Effluent dye concentration	mg/L
F	linear velocity	cm/min
K_a	BDST rate constant	1/min
k_{AB}	Bohart–Adams rate constant	L/mg min
k_{TH}	Thomas rate constant	mL/min.mg
k_{YN}	Yoon–Nelson rate constant	1/min
N_o	Adsorption capacity	mg/L
t_b	Breakthrough time	min

t_s	Saturation time	min
t_e	Exhaustion time	min
Q	Flow rate	mL min^{-1}
$q_{e,ave}$	Average of calculated adsorption capacity	mg/g
$q_{e,cal}$	Calculated adsorption capacity	mg/g
$q_{e,exp}$	Experimental adsorption capacity	mg/g
q_o	Maximum adsorption capacity	mg/g
q_{oYN}	Yoon-Nelson adsorption capacity	mg/g
q_{total}	Total amount of solute adsorbed	mg/g
t	Contact time	min
τ	Time required for 50% adsorbate breakthrough	min
τ_{exp}	Experimental time required for 50% adsorbate breakthrough	min
x	Adsorbent mass	g
W_{total}	Total amount of the solute passing through the column	mg

Y	Ratio of the maximum capacity of the column	-
Z	Bed depth of column	cm
Z_o	Critical bed depth	cm

LIST OF ABBREVIATIONS

AC	Activated Carbon
AY 17	Acid yellow 17
BDST	Bed depth service time
BGAC	Bamboo waste based granular activated carbon
C_2H_6O	Ethanol
GAC	Granular activated carbon
GCSAC	Granular coconut shell based activated carbon
HCl	Hydrochloric acid
IUPAC	International Union of Pure and Applied Chemistry
JLP	Jackfruit leaf powder
MB	Methylene blue
NaCl	Sodium chloride
NaOH	Sodium hydroxide
NGY	Novacron golden yellow dye
PAC	Powdered activated carbon
PAN	Polyacrylonitrile
PZC	Point zero charge
RB5	Reactive black 5 dye

RE	Removal efficiency
Re	Regeneration efficiency
r^2	coefficient of determination
SSE	Sum square of the errors

KAJIAN PENJERAPAN DINAMIK DAN PENJANAAN SEMULA PEWARNA ASID KUNING 17 MENGGUNAKAN BUTIRAN KARBON TERAKTIF BERASASKAN TEMPURUNG KELAPA

ABSTRAK

Penjerapan di dalam turus lapisan tetap telah dicadangkan sebagai kaedah yang berkesan untuk rawatan air kumbahan daripada bidang perindustrian. Kajian ini bertujuan untuk mengkaji keberkesanan penyingkiran pewarna Asid Kuning 17 (AY 17) menggunakan butiran karbon teraktif berasaskan tempurung kelapa (GCSAC) di dalam turus lapisan tetap. Kesan parameter penting seperti kepekatan awal pewarna (10-50 mg/L), kadar kelajuan aliran (10-30 mL/min) dan ketinggian butiran karbon teraktif berasaskan tempurung kelapa (2-4 cm) di dalam turus lapisan tetap terhadap lengkung bulus dan prestasi penjerapan disiasat. Hasilnya menunjukkan bahawa lengkung bulus bergantung kepada kepekatan awal pewarna, kadar kelajuan aliran AY 17 dan ketinggian lapisan. Kapasiti penjerapan direkod pada kadar kelajuan aliran terendah, kepekatan pewarna awal tertinggi dan ketinggian tertinggi didapati sebanyak 5.58 mg/g. Model Thomas, Adams-Bohart, Yoon-Nelson, Wolborska dan BDST dipilih untuk menganalisis prestasi penjerapan di dalam turus lapisan tetap. Kapasiti penjerapan, kadar pemalar dan kadar penentuan bukan linear (r^2) bagi setiap model telah dikira. Model Thomas, Yoon-Nelson dan BDST damat serasi dengan data penjerapan berbanding model Adams-Bohart atau Wolborska. Hasilnya menunjukkan bahawa GCSAC adalah penjerap yang sesuai untuk penjerapan pewarna AY 17 di dalam turus lapisan tetap.

DYNAMIC ADSORPTION AND REGENERATION STUDIES OF ACID YELLOW 17 USING GRANULAR COCONUT SHELL ACTIVATED CARBON

ABSTRACT

The continuous fixed bed adsorption has been proposed as an effective method for the removal of pollutants from the waste water in industrial applications. In this work, the real intention of the study was to investigate the effectiveness of Acid Yellow 17 (AY 17) dye removal onto non-modified granular coconut shell activated carbon (GCSAC) in fixed-bed column. The influence of important parameters such as initial dye concentration (10-50 mg/L), feed flow rate (10-30 mL/min) and bed height (2-4 cm) on the behaviour of the breakthrough curves and adsorption performance was studied. The results indicated that the breakthrough curves were dependent on initial concentration, feed flow rates of AY 17 dye solution and bed height. The adsorption capacity was recorded at lowest flow rate, highest initial concentration and bed height and was found to be 5.58 mg/g. Thomas, Adams-Bohart, Yoon-Nelson, Wolborska and BDST model were selected to analyse the performance of the column adsorption. The adsorption capacity, rate constant and non-linear coefficient of determination (r^2) of each model was calculated. Thomas, Yoon-Nelson and BDST model fitted well the adsorption data compared to Adams-Bohart or Wolborska model. The results indicated that the GCSAC was shown to be suitable adsorbent for adsorption of AY 17 dye using fixed-bed adsorption column.

CHAPTER 1

INTRODUCTION

1.1 Research Background

1.1.1 Water Pollution

The growth of mankind, society, science and technology has created a corresponding increase of Earth's limited supply of fresh water. According to United Nations World Water Development Report UNESCO, the fresh water demand for agricultural, industrial and domestic sectors has increased tremendously consuming 70, 22 and 8% of the available fresh water respectively (Gupta and Suhas, 2009). However, with large amount of fresh water consumption by different sectors has significantly led to generation of large amounts of waste water with various type of pollutants. The nature of the industrial, agricultural and municipal waste water releasing activities determine the type of pollutants present in the waste water. The type of pollutants found in the waste water can be classified as inorganic, organic, and biological in nature (Gupta, 2012)

One of the most common inorganic waste water contaminants is heavy metals which are highly toxic and carcinogenic in nature. Additionally, nitrates, sulphates, phosphates, fluorides, chlorides and oxalates also have some serious hazardous effects. The toxic organic pollutants are from pesticides which includes insecticides, herbicides, fungicides; polynuclear hydrocarbons (PAHs), phenols, polychlorinated biphenyls, halogenated aromatic hydrocarbons, formaldehyde, polybrominated biphenyls, biphenyls, detergents, oils, greases etc. In addition to these, normal hydrocarbons, alcohols, aldehydes, ketones, proteins, lignin, pharmaceuticals etc. are also found in wastewater (Gupta, 2012).

Among all the pollutants contain in waste water, dyes are the most important class of the pollutants and the most recognizable and undesirable one. They are also considered to be the particularly dangerous organic compounds for the environment (Demirbas, 2009) as they impart colour besides toxicity to fish and other aquatic organism (Jain et al., 2003). The colour is the first contaminant to be recognized in waste water. The presence of even very small amounts of dyes in water at 1 ppm is enough to give colour changes to the affected stream (Rafatullah et al., 2010). Moreover, dyes are widely used in industries such as various kinds of textile (Sokolowska-Gajda et al., 1994), paper (Ivanov et al., 1996), leather tanning (Kabdaşli et al., 1999), food processing, plastics, cosmetics, rubber , printing and dye manufacturing industries (Bensalah et al., 2009). As a result, they generate a considerable amount of coloured waste water. Therefore, their removal from dyes bearing effluent is tremendously essential due to much concern regarding its use.

1.1.2 Dyes

Dyes are defined as coloured substances that when applied to fibers give them a permanent colour that is resistant to action of light, water and soap (Rai et al., 2005). Since the use of dyes in industries and households has increased remarkably, nearly 40,000 dyes and pigments are listed which consist of over 7000 different chemical structures (Demirbas, 2009). Based on recent data, it was estimated that more than 100,000 commercial dyes are being produced with annual production of over 7×10^5 tonnes/year and the total dye consumption in the textile industry worldwide is more than 10,000 tonnes/year and approximately 100 tonnes/year of dyes is discharged into water streams (Yagub et al., 2012).

Dyes are widely used in various industries such as textile, tannery, paper and pulp and electroplating. They are also being used in the food, pharmaceutical and cosmetic industries. During the dyeing process, it is estimated about 5-10% of the dyes is lost in the effluent while about 50% of the initial load of reactive dyes is found in the dye bath effluent (Sierra-Alvarez and Lettinga, 1991). Discharging large amount of dyes into the water streams can cause severe water pollution as they can reduce light penetration, retards photosynthetic activity and inhibits the growth of biota, etc (Han et al., 2009a). Thus, loss of dyes to the environment has become an environmental hazard.

Many classes of dyes has been reported in the literature (Clarke and Anliker, 1980, Gupta and Suhas, 2009, Demirbas, 2009, Yagub et al., 2014). One of the dye classes is the azo dye. There are approximately 2000 azo dyes on the market (Demirbas, 2009) and over half of the commercial dyestuffs are azo dyes. Previous researches show that the conventional waste water treatment plants such as activated sludge process does not decompose azo dyes causing a serious disposal problem. Some azo dyes and their dye precursors have been shown to be or are suspected to be human carcinogens (Shu and Huang, 1995). Acid Yellow 17 (AY 17) is the one example of azo dyes. Therefore, studying the destruction of AY 17 in wastewater treatment processes is of utmost importance. Consequently, alternative technologies which can decompose the non-biodegradable azo dyes have to be explored in order to ensure the effective removal of AY 17 from waste water streams.

1.1.3 Adsorption Process

Among all these methods available for the removal of pollutants from the waste water, adsorption has been reported as the most efficient and promising technique compared to other methods such as electrocoagulation, membrane filtration, chemical precipitation. Adsorption is suitable for many types of dyes with lower cost treatment (Azadeh et al., 2015) and it is has long been used in the removal of heavy metals and other hazardous materials (Chafi et al., 2015). Adsorption is defined as a separation process by which certain components of a fluid phase are attracted to the surface of a solid adsorbent and form attachments via physical or chemical bonds, thus removing the component from the fluid phase (McKay et al., 1997).

Adsorption process possess several advantages such as high efficiency, efficient methodology, high adsorption capacity, low cost, simple design and ease of operation (Jafari et al., 2017, Hu et al., 2011). Normally, pre-filtration of the effluent is required before the adsorption process due to the presence of suspended particles and oils that reduce the efficiency of the adsorption (Gupta, 2012).

The most common adsorbent used in the adsorption process is the activated carbon (AC). A vast number of references reporting on the adsorption of dyes, heavy metals and antibiotics using activated carbon. For instant, research about adsorption of phenol on activated carbon produced from olive stones conducted by Nouri and Ouederni (2013) and adsorption of basic dyes including methylene blue, basic red and basic yellow onto activated carbon operated by El Qada et al., (2006). Activated carbon is suitable as the adsorbent because it displays excellent adsorption performance, high adsorption capacities, extremely high surface areas, micropore volumes, fast adsorption kinetics, relative ease of regeneration and amphoteric properties, which enable the adsorption of both cationic and anionic pollutants in effluent (Djilani et al., 2015).

1.2 Problem Statement

Traditionally, back to 3500 BC, dyes are extracted from vegetables, fruits, flowers, certain insects and fish (Özacar and Şengil, 2005). However, in 1856 WH Perkins discovered the synthetic dyes overcome the limitations caused by the natural dyes that gave a dull range of colours and had lower fastness to light and washing (Nawaz et al., 2014). About 2% of dyes produced annually are for manufacturing treatments and 10% was discharged from textile and associated industries (Demirbas, 2009) causing water pollution.

Pollution due to dye contamination in the water stream has become a serious problem nowadays. Dye pollution can affect the physicochemical properties of fresh water when discharging dye together with organics, bleaches and salt (Chafi et al., 2015). Making it worse, dye pollution reduced light penetration, retarding the photo-synthesis process in aquatic flora and may also toxic leading to increasing biochemical oxygen demand (Qureshi et al., 2017). Since AY 17 is a reactive mono-azo dye, it is also considered to be highly carcinogens and toxic making its removal is necessarily important.

Adsorption is known to be a promising technique for dye removal. Although commercial activated carbon is reported as the widely used adsorbent for adsorption process in waste water treatment, its high cost has prevented its application. Keeping that in mind, numerous approaches have been made in order to find the alternative for cheaper adsorbents. Therefore, many study has reported the conversion of agricultural solid wastes, industrial solid wastes, agricultural by-products, and biomass to activated carbon in the removal of dyes from aqueous phase. Their conversion to activated carbon would add economic value to the waste materials. Furthermore, help to reduce the cost of waste disposal (Rafatullah et al., 2010). Hence, this study is to present and investigate an efficient methodology for AY 17 dye by using adsorption process in fixed bed column with granular coconut shell based activated carbon (GCSAC) as the adsorbent. Finally, analyse the adsorption data obtained using the selected dynamic adsorption models.

1.3 Research Objectives

1. To investigate the effectiveness of granular coconut shell based activated carbon (GCSAC) in removing AY 17 dye from waste water using continuous adsorption process in fixed-bed column.
2. To study the effect of different bed height, initial dye concentration and flow rates of dye solution onto breakthrough curve of AY 17 dye adsorption on GCSAC.
3. To analyse the adsorption data using selected dynamic adsorption models which are Thomas Model, Adams and Bohart Model, Yoon-Nelson Model, Wolborska Model and BDST Model.

1.4 Organization of thesis

This thesis consists of five main chapters and each chapter contributes to the sequence of this study. The following are the contents for each chapter in this study:

Chapter 1 introduces the definition of dye, application of AY 17 in industries, the toxicity of AY 17 in wastewater, definition of adsorption, activated carbon and, problem statement, research objectives, organization of thesis and research scope.

Chapter 2 discusses the literature review of this study. An insight into the classification dyes, methods for dye removal, dye removal by adsorption process, type of activated carbon and non-conventional low cost adsorbent.

Chapter 3 covers the experiment materials and the details of methodology. It discusses on the description of equipment and materials used, continuous adsorption experiment, experimental procedure, parameters being studied in this research and the selected dynamic adsorption models to analyse the experimental data.

Chapter 4 clarifies about the result of this research. The performance comparison between the adsorption experimental data and the dynamic adsorption model of Acid Yellow 17 on granular coconut shell based activated carbon in terms of initial concentration, flow rates and the bed height will be discussed.

Chapter 5 gives a brief about overall conclusion about our research studies based on result and discussion in Chapter 4 whether the research objectives have been achieved successfully or not. Recommendation and improvement of this study will be conducted prior to the conclusion.

1.5 Research scope

In this research, adsorption of AY 17 process is carried out in a fixed bed glass column. It is a continuous adsorption process study instead of batch process. The GCSAC obtained from Kekwa Indah Sdn. Bhd is used as the adsorbent. Besides, pH screening is conducted to obtain the best pH value favours for the adsorption process. Point of zero charge of adsorbent is also investigated by solid addition method. The important operational parameters such as inlet concentration of dye solution, fluid flow rate and column bed height were explored on removal percentage of dye from aqueous phase. The main concern of the design of adsorption column is the prediction of the breakthrough curve. Generally, the time for the breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining the operation and the dynamic response of adsorption column. Therefore, four kinetic models, Thomas, Adams-Bohart, Yoon-Nelson, and Wolborska are applied to the experimental data to predict the breakthrough curve. Bed Depth Service Time (BDST) model is used to studied the effect of bed depth on breakthrough curves. The aim of this present work is to test the possibility of utilizing GCSAC as the adsorbent for the removal of AY 17 from waste water. Modelling on the adsorption dynamics of the fixed bed is presented and finally the correlation between the model and the experimental data is compared.

CHAPTER TWO

LITERATURE REVIEW

2.1 Classification of Dyes

Dyes are basically chemical compounds that can connect themselves to surfaces or fabrics to impact colour (Yagub et al., 2014). The colour of a dye is provided by the presence of a chromophore group. A chromophore group is a radical configuration consisting of conjugated double bonds (Demirbas, 2009). Dyes can be classified into several different classes. The classification of dyes are according to theirs chemical structure, colour and application methods (Clarke and Anliker, 1980). However, the classification of dyes in term of structure is the most favourable by synthetic dye chemist and dye technologist. The classification based on application is useful whenever having the difficulty in identifying the chromophore due to its complex chemical structure. Table 2.1 shows the classification of common class of the dyes based on chemical structure.

Table 2.1: Classification of dyes according to chemical structure (Yagub et al., 2014)

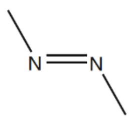
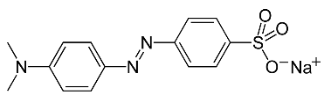
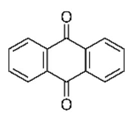
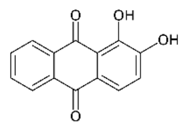
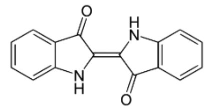
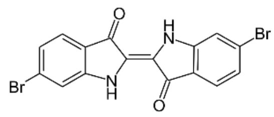
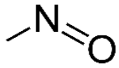
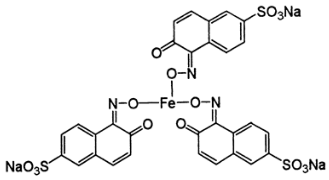
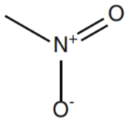
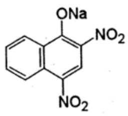
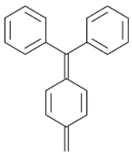
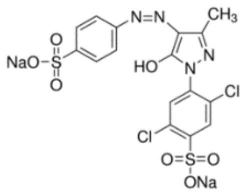
Class	Chromospheres	Example
Azo Dyes		 Methyl Orange
Anthraquinone dyes		 Alizarin (Turkey Red)
Indigoid dyes		 Tyrian Purple

Table 2.1: Continued

Nitroso Dyes		 Acid Green 1
Nitro Dyes		 Acid Yellow 24
Triarylmethane dyes		 Ethyl Violet

Moreover, dyes also may be classified on the basis of their solubility. Soluble dyes includes acid, mortant, metal complex, direct, basic and reactive while insoluble dyes involves azoic, sulphur, vat and disperse (Gupta and Suhas, 2009). There are three types of dyes which are cationic, anionic and non-ionic dyes. Anionic dyes are the direct, acid and reactive dyes (Mishra and Tripathy, 1993). The most problematic dyes are the brightly coloured, water-soluble and acid dyes because they have the possibility to pass through the conventional treatment system unaffected (Willmott et al., 1998). Non-ionic refers to disperse dyes as they do not ionise in aqueous phase (Robinson et al., 2001). The classification of dyes according to its application is presented in Table 2.2.

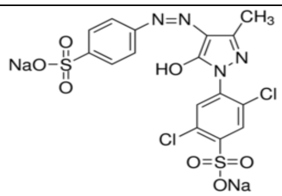
Table 2.2: Properties of dyes classified on their usage (Gupta and Suhas, 2009).

Class	Applications and properties	Chemical types
Acid Dyes	For nylon, wool, silk, modified acrylics, paper, leather, ink-jet printing, food and cosmetics. Water-soluble dyes.	Azo, anthraquinone, triphenylmethane, azine, xanthene, nitro and nitroso.
Cationic (Basic) Dyes	For paper, polyacrylonitrile, modified nylons, modified polyesters, cation dyeable polyethylene terephthalate and to some extent in medicine too. Water-soluble dyes. Yield coloured cations in solution.	Diazahemicyanine, triarylmethane, cyanine, hemicyanine, thiazine, oxazine and aridine.
Disperse Dyes	Mainly used on polyester, nylon, cellulose, cellulose acetate and acrylic fibers. Water-insoluble non-ionic dyes used for hydrophobic fibers from aqueous dispersion.	Azo, anthraquinone, styryl, nitro and benzodifuranone groups.
Direct Dyes	Used in dyeing of cotton and rayon, paper, leather and nylon Water-soluble dyes.	Polyazo compounds, along with some stilbenes, phthalocyanines and oxazines.
Reactive Dyes	Used for cotton and cellulosic, wool and nylon.	Azo, anthraquinone, triarylmethane, phthalocyanines, formazan and oxazines.
Solvent Dyes	Used for plastics, gasoline, lubricants, oils and waxes. Water-insoluble. Generally non-polar or little polar.	Azo, anthraquinone, triarylmethane, phthalocyanines.
Sulphur Dyes	Used for cotton and rayon and have limited use with polyamide fibers, silk, leather, paper and wood	
Vat Dyes	Used for cotton, rayon and wool too.	Anthraquinone (including polycyclic quinones) and indigoids.

2.1.1 Acid Yellow 17

According to the molecular structure of AY 17 as shown in Table 2.3 by having colouring azo function (N=N) as the chromophoric configuration, AY 17 is a mono-azo dye. There are approximately 2000 azo dyes on the market (Demirbas, 2009). Azo dyes can be broken down to aromatic amine, arylamine. This could be achieved by chemically, through reductive cleavage or through the body's own enzyme system. Some azo dyes can also be broken down to arylamines during storage due to light and high temperature (Jinqi and Houtian, 1992).

Table 2.3: Chemical structure of Acid Yellow 17

Dye Name	Molecular Formula	Structural Formula	Molar Mass (g/mol)	$\Lambda_{max\ (nm)}$
Acid Yellow 17	$C_{16}H_{10}Cl_2N_4Na_2O_7S_2$		551.29	400

2.1.2 Toxicity of Acid Yellow 17

AY 17 is a reactive, anionic dye which is also known with other names such as fluorescein or its salt and uranin. It is usually utilized in detergent, soap, textile, printing and cosmetic industries (Ashraf et al., 2013). Discharging large amount of dyes into the water streams can cause severe water pollution as they can reduce light penetration, retards photosynthetic activity and inhibits the growth of biota (Han et al., 2009a). As azo dyes can be broken down to aromatic amine, it is dangerous because of the presence of amines in the effluent which is toxic (Yagub et al., 2014).

Moreover, AY 17 is harmful for respiratory system resulting dyspnoea, dermatitis and cause irritation to eyes. Not only that, it can also give negative effects on cardiovascular and nervous system of human beings and living organisms. It produces toxic fumes of oxides of carbon and nitrogen during thermal decomposition. It also has mutagenic and tumorigenic effects on bacteria, yeast, and somatic cells of mammalian, leading to problem during reproduction and growth by affecting genetic material (Ashraf et al., 2013). Therefore, removal of reactive mono-azo dye AY 17 from waste water is very crucial due to much concern regarding its use.

2.2 Methods of dye removal

There are various technologies to treat dye bearing effluent have been reported. Each of these method have their own limitations. They can be divided into three different categories: biological, physical and chemical (Robinson et al., 2001). Conventional methods for treating dye wastewater were not widely adapted in large scale applications due to the high cost and disposal problem (Ghoreishi and Haghighi, 2003). Table 2.4 expresses the advantages and disadvantages of dye removal methods.

Table 2.4: Principal existing and emerging processes for dyes removal (Crini, 2006)

	Technology	Advantages	Disadvantages
Conventional treatment processes	Coagulation Flocculation	Simple, economically feasible	High sludge production, handling and disposal problems
	Biodegradation	Economically attractive, publicly acceptable treatment	Slow process, necessary to create an optimal favourable environment, maintenance and nutrition requirements

	Adsorption on activated carbons	The most effective adsorbent, great, capacity, produce a high-quality treated effluent	Ineffective against disperse and vat dyes, the regeneration is expensive and results in loss of the adsorbent, non-destructive process
Established recovery processes	Membrane separations	Removes all dye types, produce a high-quality treated effluent	High pressures, expensive, incapable of treating large volumes
	Ion-exchange	No loss of sorbent on regeneration, effective	Economic constraints, not effective for disperse dyes
	Oxidation	Rapid and efficient process	High energy cost, chemicals required
Emerging removal processes	Advanced oxidation process	No sludge production, little or no consumption of chemicals, efficiency for recalcitrant dyes	Economically unfeasible, formation of by-products, technical constraints
	Selective bioadsorbents	Economically attractive, regeneration is not necessary, high selectivity	Requires chemical modification, non-destructive process
	Biomass	Low operating cost, good efficiency and selectivity, no toxic effect on microorganisms	Slow process, performance depends on some external factors (pH, salts)

2.2.1 Biological treatments

Biological treatments technology include methods such as fungal decolourization, microbial degradation, adsorption by (dead or living) microbial biomass and bioremediation systems. They can be aerobic (in presence of oxygen), anaerobic (without oxygen) or combined aerobic-anaerobic. This technology is the most economical techniques compared to other physical and chemical processes (Crini, 2006, Demirbas, 2009). Biodegradation methods uses the role of many microorganisms such as bacteria, yeasts, algae and fungi to treat the waste water system because these organisms can accumulate and degrade different pollutants (McMullan et al., 2001). The limitations that hold back the application of these methods in industry is the technical constraints such as the requirement of large land area. This methods also did not give the desired result expected and it cannot degrade azo dyes (Crini, 2006).

2.2.2 Chemical treatments

These chemical treatments are often expensive, and the sludge produced from these dyes removal methods form a disposal problem. Chemical treatments include coagulation or flocculation combined with $Fe(II)/Ca(OH)_2$, electrofloatation, electrokinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), irradiation or electrochemical processes. Emerging techniques known as advanced oxidation processes has been introduced and successfully applied for pollutant degradation. These techniques involving simultaneous use of more than one oxidation processes producing hydroxyl radical which is very reactive (Gupta and Suhas, 2009). Unfortunately, they are very costly and commercially unattractive. The concern of these emerging techniques are the high electrical energy demand and consumption of chemical reagents (Crini, 2006).

2.2.3 Physical treatments

Physical treatments consist of membrane-filtration processes (nanofiltration, reverse osmosis, electrodialysis and adsorption techniques. Membrane processes have not been widely applied in industry because they have a limited lifetime before membrane fouling occurs. Not only that, they are also highly cost due to their periodic replacement. Many literature have reported that liquid-phase adsorption is one of the most popular methods for the removal of pollutants from the effluents (Dąbrowski, 2001). Adsorption has found to be the most efficient methods when compared to the others in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Indeed, adsorption does not produce any harmful end products (Crini, 2006).

2.3 Dye removal by adsorption

Gupta and Suhas (2009) define adsorption process as a process where a material is concentrated at a solid surface from its liquid or gaseous surroundings. Furthermore, according to (McKay et al., 1997) adsorption is defined as a separation process by which certain components of a fluid phase are attracted to the surface of a solid adsorbent and form attachments via physical or chemical bonds, thus removing the component from the fluid phase. The substance that accumulates at the solid surface is called adsorbate while the solid on which adsorption occurs is adsorbent. Figure 2.1 illustrate the adsorption process scheme of a surface.

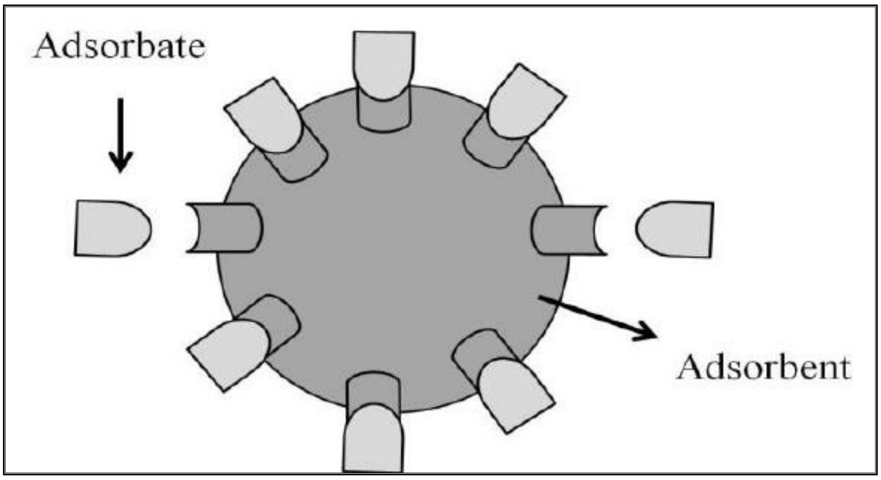


Figure 2.1: Adsorption process scheme of a surface (De et al., 2014)

Adsorption can be classified into two types: chemical sorption and physical sorption. The adsorption is referred to as physical adsorption if the attraction between the solid surface and adsorbed molecules is physical in nature. Generally, physical adsorption or physorption involves the formation of weak van der Waals bonds between adsorbate and adsorbent and it is reversible in most cases. The main physical forces involve in the physorption are the van der Waals forces, hydrogen bonds, polarity and dipole-dipole interaction (Yagub et al., 2014). On the other hand, chemical sorption or chemisorption is the formation of strong chemical associations between molecules or ions of adsorbate to adsorbent surface which is generally due to the exchange of electrons. Thus, chemisorption is irreversible. Based on the operation mode, adsorption process is classified into two modes which are batch adsorption or dynamic adsorption

2.3.1 Batch adsorption

Batch adsorption, occurs in a closed system containing a desired amount of adsorbent contacting with a certain volume of adsorbate solution (Xu et al., 2013). Batch adsorption is commonly used to measure the effectiveness of adsorption for removing specific adsorbates and also to investigate the maximum adsorption capacity. The limitation of batch operation is it is not suitable when dealing with high flow rates (Chafi et al., 2015). Batch mode studies usually conducted with certain amounts of adsorbents in which are shaken separately at a known speed and volume with also fixed or varying adsorption parameters such as concentration, contact time, pH, temperature and adsorbent dosage.

A vast number of references reporting on batch adsorption of pollutants including dyes, antibiotics, heavy metals, organic contaminants are available from printed or electronic database. For instant, batch adsorption study of AY 17 dye from aqueous solution using eco-friendly bio-sorbent has been reported by (Ashraf et al., 2013). They reported the highest dye uptake capacity at 303K, initial pH value of 2, the initial dye concentration of 150 mg/L, bio-sorbent dosage of 0.5g and contact time of 40 min. Table 2.5 summarize the previous batch adsorption studies of different adsorbates with various experimental conditions and adsorbents.

Table 2.5: The result of previous batch adsorption studies reported for various adsorption systems

Adsorbents	Adsorbates	Isotherms models	Kinetics	References
Peanut hulls	Novacron golden yellow dye	Frendlich	Pseudo-second order	(Nawaz et al., 2014)
Typha angustata L	Acid yellow 17 dye	Frendlich	Pseudo-second order	(Ashraf et al., 2013)
Acid treated kenaf fibre char	Methylene blue dye	Langmuir	Pseudo-second order	(Mahmoud et al., 2012)
Waste acorn of Quercus ithaburensis	Chromium(VI)	Elovich	Pseudo first-order	(Malkoc and Nuhoglu, 2007)
Magnesium oxide (MgO) nanoparticles	Cephalosporins	Langmuir	Pseudo-second order	(Fakhri and Adami, 2014)
Coir pith	Cobalt (II) Chromium (III) Nickel (II)	Langmuir	Pseudo-second order	(Parab et al., 2006)

2.3.2 Dynamic adsorption

Dynamic adsorption usually occurs in an open system where adsorbate solution continuously passes through a column packed with adsorbent (Xu et al., 2013). The dynamic or continuous adsorption study is much favourable from industrial point of view as it is simple and can be scaled-up from a laboratory process. In addition, it also can be used for high flow rates (Chafi et al., 2015). Moreover, in batch operation the adsorbent effectiveness for removing solute from solution decreases as the adsorption proceeds, whereas in column operation the adsorbent is continuously in contact with a fresh solution and, consequently, the concentration in the solution in contact with a given layer of adsorbent in the column is relatively constant (El Qada et al., 2006).

Since the adsorption in a fixed bed columns using activated carbon as the adsorbents, do not require the addition of chemical compounds in the separation process, therefore the method has been widely used in industrial processes for the removal of contaminants from aqueous textile industry effluents. Table 2.6 shows the previous dynamic adsorption study of various pollutants onto different type of adsorbent.

Table 2.6: The result of previous dynamic adsorption studies reported for various adsorbate and adsorbent.

Adsorbents	Adsorbates	Max adsorption capacity (mg/g)	Dynamic models	References
Pre-treated red algae with formaldehyde	Lead	774	Thomas	(Hanbali et al., 2014)
Pre-treated red algae with $CaCl_2$	Lead	1089.6	Thomas	(Hanbali et al., 2014)
Bamboo waste granular activated carbon	Reactive black 5	39.02	Thomas Yoon-nelson	(Ahmad and Hameed, 2010)
Resin	Phenol	98.3	Adams-Bohart Yoon-Nelson Thomas	(Soto et al., 2017)
Peanut hulls	Novacron golden yellow	7.28	Adams-Bohart	(Nawaz et al., 2014)
Rubber wood sawdust	Lead	38.56	Thomas	(Biswas and Mishra, 2015)
Tamarind seed powder	Acid Yellow 17	978.5	Adams-Bohart	(Patel and Vashi, 2012)

2.4 Adsorbent used in adsorption process

One of the important factors to ensure an efficient adsorption process is the adsorbent itself. An excellent adsorbent must has a porous structure which leads to higher surface area. Additionally, the time taken for the adsorption process to achieve equilibrium should be small as possible so it can be used to remove dye in shorter time. Some of the adsorbents which are commonly used for dye removal in wastewater treatment, are:

i. **Alumina**

Alumina is basically a synthetic porous crystalline gel. It is available in the form of different sizes of granules having surface area (Gupta and Suhas, 2009) ranging from 200 to 300 m^2g^{-1}. The application of alumina in dyes removal have been studied by many researchers (Huang et al., 2007, Adak et al., 2006).

ii. **Silica Gel**

Silica gel is produced by the coagulation of colloidal silicic acid resulting formation of porous and non-crystalline granules of different sizes. It has slightly higher surface area (Gupta and Suhas, 2009) compared to alumina which ranging from 250 to 900 m^2g^{-1}. The studies of adsorption of basic dyes onto silica have been conducted by a number of workers (Alexander, 1977). However, silica gel is not widely being applied in industry because they are expensive even though the adsorption capacities were high (McKay et al., 1999).

iii. **Zeolites**

Zeolites are highly porous aluminosilicates with different cavity structures. Zeolites consist of more than 40 natural species. The most frequently used zeolite is clinoptilolite, a mineral of the heulandite group. Zeolites have relatively high surface areas and low cost adsorbent. The study about zeolite has been investigated by Ghobarkar et al. (1999). Unfortunately, the problem with zeolites is their low permeability (Ghobarkar et al., 1999). Hence, an artificial support is required when used in column operations (Crini, 2006).

iv. Activated carbon

Activated carbon (AC) is the oldest and popular adsorbents used to remove pollutants from wastewater. It is usually prepared from coal, coconut shells, lignite, wood etc. There are two basic activation methods existed which are physical and chemical (Lillo-Ródenas et al., 2007, Phan et al., 2006). High temperature and longer activation time is needed in physical activation as compared to chemical activation. Figure 2.2 shows the diagram of the process of producing activated carbon.

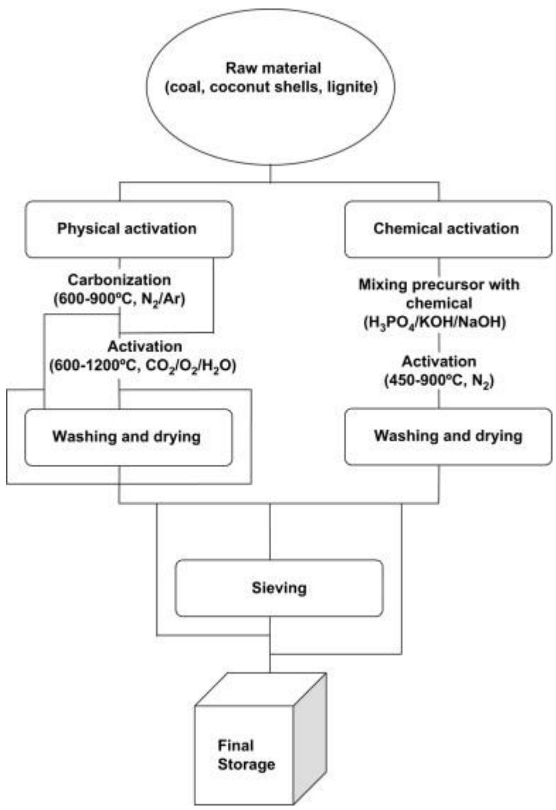


Figure 2.2: Schematic diagram of the process of producing activated carbons generally (Gupta and Suhas, 2009)

2.4.1 Activated carbon

Activated carbon (AC) is the most common adsorbent used in removal of pollutants from the waste water by adsorption. They are available in two main forms which are powdered activated carbon (PAC) and granular activated carbon (GAC). The two main forms have their own advantages and limitations. The most common form of activated carbon being used is the granular form. This is due to the easier separation between adsorbent and adsorbate after the adsorption process. Not only that, GAC is more adaptable to continuous contacting and there is no need to separate the carbon from the bulk fluid (Gupta and Suhas, 2009). The advantages of using PAC are the low capital cost and lesser contact time. However, the problems arise when using PAC is the requirement to separate the adsorbent from the fluid after use.

Studies have shown AC are good adsorbent for the removal of different type of dyes. Surface area is one of the important characteristics of activated carbon for its adsorption capacity. The adsorption capacity of activated carbon is directly proportional to its surface area. Thus, increasing the surface area leading to higher adsorption capacity of activated carbon (Djilani et al., 2015). High adsorption capacity resulted in higher efficiency of adsorbate removal from the system. Table 2.7 exhibits the adsorption capacities of AC made from agricultural by-prodct for various dyes.

Table 2.7: Adsorption capacities for carbon materials made from raw agricultural by-product for various dyes

Raw material	Dye	q_m (mg/g)	Sources
Pine sawdust	Acid Yellow 123	398.8	(Özacar and Şengil, 2005)
Coffee residues	Basic Blue 3G	179	(Kyzas et al., 2012)
Grapefruit peel	Crystal Violet	254.16	(Saeed et al., 2010)
Peanut hull	Methylene Blue	68.06	(Gong et al., 2005)

Table 2.7: Continued

Banana peel	Methylene Blue	20.8	(Annadurai et al., 2002)
Pineapple stem	Methylene Blue	119.05	(Hameed et al., 2009)
Garlic peel	Methylene Blue	82.54	(Hameed and Ahmad, 2009)
Coconut bunch waste	Methylene Blue	70.92	(Hameed et al., 2008)
Coffee husk	Methylene Blue	90.1	(Oliveira et al., 2008)
Rice husk	Methylene Blue	40.59	(Vadivelan and Kumar, 2005)
Coconut coir	Methylene Blue	15.59	(Sharma et al., 2009)
Orange peel	Methylene Blue	18.6	(Annadurai et al., 2002)
Canola hull	Basic Red 46	49.00	(Mahmoodi et al., 2010)
Peanut hull	Reactive Black 5	55.55	(Tanyildizi, 2011)
Chitosan	Acid Orange 10	922.9	(Wong et al., 2004)
Peat	Acid Blue 25	14.4	(Ho and McKay, 2003)

2.5 Analysis and design of column adsorption

One important information gained from dynamic or continuous adsorption in fixed bed operation is the breakthrough curve. Breakthrough determines bed height and operating life span of the bed and regeneration times (Martin et al., 2003). In this process, the composition of a solution changed as it is continuously being pumped into the column and passes through a bed of adsorbent. The effluent composition or concentration of the solution is influenced by the properties of the adsorbent, the composition of the feed and the operating conditions (flow rate, initial concentration, temperature, pH of the solution and also the height of the adsorbent in column) (Barros et al., 2013). The typical concentration profile as well as the S-shape of breakthrough curve as the ratio of the effluent concentration (C_e) to the influent concentration (C_i) versus time or throughput volume is shown in Figure 2.3.

According to Barros et al. (2013) the mass transfer zone is the region where most of the change in concentration occurs. As the run starts, most of the mass transfer takes place near the inlet of the bed, where the first fluid contact the adsorbents. As the run proceeds, the adsorbent near the inlet is almost saturated. After a lapse of time, a breakthrough point will occur at breakthrough time, $t_{b.}$ The breakthrough point determined the breakthrough concentration, $C_{b.}$ and the process proceed until the effluent concentration reached the saturation point, where the ratio of the effluent concentration (C) to the influent concentration (C_o) achieved a value of 1.0. Meaning that the effluent concentration becomes equal to the feed concentration increases with time and the adsorbent is said to be exhausted. The breakthrough point is normally assumed when C/C_0 reached 0.1; while the saturation point is defined ideally when C/C_0 reach 1.0 (generally at 0.90-0.95) (Asberry et al., 2014). When the concentration reached the saturation point, the flow of the solution is stopped and the column undergoes regeneration process using a suitable regenerant for the next cycle of adsorption.

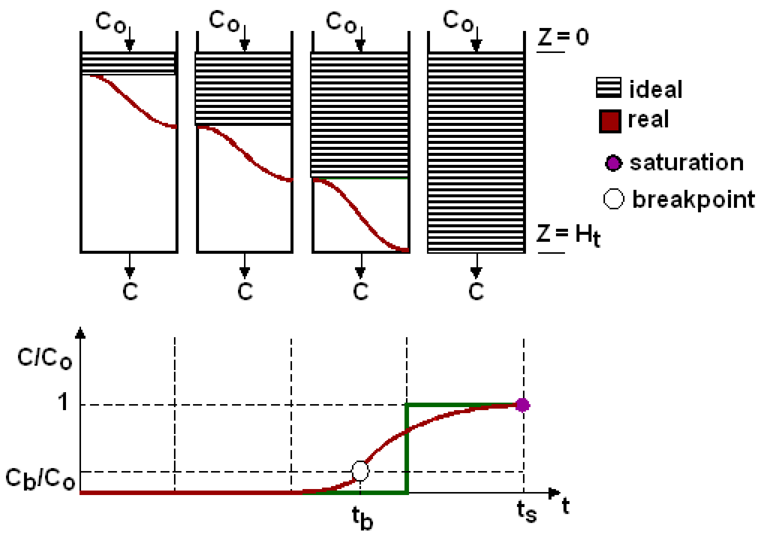


Figure 2.3: Typical breakthrough curves for the adsorption process in fixed bed operation (Barros et al., 2013)

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2.5.1 Factors affecting adsorption of dye

An efficient dye removal method by dynamic adsorption is influenced by many factors. The factors include the solution pH, temperature, flow rate, initial concentration and bed height of the column. Hence, the effect of these factors must be taken into account when constructing the development of industrial-scale dye removal treatment processes. In the next section, some of the factors mentioned above are further discussed.

A) Effect of initial dye concentration

One of the most important factors affecting the dye adsorption is the initial dye concentration. In general, the percentage of dye removal decreases on increasing initial dye concentration due to the saturation of adsorption sites on the adsorbent surface. Whereas, the capacity of the adsorbent increases with increasing initial dye concentration due to the high driving force for mass transfer at a high dye concentration (Yagub et al., 2014).

Nawaz et al. (2014) studied the adsorption of Novacron Golden Yellow (NGY) dye on the peanut hulls. They found out that when the concentration of NGY increased from 50 mg/L to 100 mg/L the column adsorption capacity also increased. The adsorption capacity for the mentioned dye concentrations are 6.07, 7.2 and 7.28 mg/g, respectively. Not only that, they also observed the decreasing breakthrough time upon increasing initial dye concentration that resulted in a decrease in the length of adsorption zone. Figure 2.4 shows the breakthrough curves of NGY dye adsorption on peanut hulls at different dye concentration and constant flow rate, bed height and also temperature of the dye solution.