SIMULATION AND VALIDATION OF ADSORPTION PROCESS FOR ACRYLIC ACID REMOVAL FROM WASTE WATER

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Report submitted in partial fulfilment of the requirements for the award of the degree of
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SUPERVISOR'S DECLARATION

I hereby declare that I have checked this project and in my opinion, this project is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

Signature   :

Name of Supervisor   : DR. ANWARRUDIN HISYAM

Position   :

Date   : 25th January 2013

STUDENT'S DECLARATION

I hereby declare that the work in this project is my own except for quotations and summaries which have been duly acknowledged. The project has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature

Name   : NURSAKINAH BINTI MAT SAAD

ID Number   : KA09144

Date   : 25th January 2013

DEDICATION

Special dedication to my supervisor, Dr. Anwarrudin Hisyam for your Time, Guidance, and Support.

And,

To my beloved parents (Mat Saad bin Hashim & Salmiah binti Khalid), Mr. Hanif and friends, that encouraged and fully supports me throughout completing this thesis.

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SIMULATION AND VALIDATION OF ADSORPTION PROCESS FOR ACRYLIC ACID REMOVAL FROM WASTE WATER

ABSTRACT

The objectives of this study were to develop the mathematical model of the adsorption process of the acrylic acid removal and also to validate the simulation of the adsorption process by using the previous experimental data. The adsorption process is used in the waste water treatment to remove toxic or organic pollutants. Simulation of the adsorption process is necessary to understand the acrylic acid removal using adsorption process. Acrylic acid is removed from the waste water because it can cause serious damage to the environment due to its high toxicity for the aquatic organisms. As a conclusion, the objective is achieved. The new mathematical model of the adsorption process of the acrylic acid by using the activated carbon can created based on the mass balance on the continuous fixed bed column. The validation of the simulation is carried out to compare the simulation data with the experiment data. This research is to improve the understanding of adsorption process of acrylic acid removal from waste water by created the mathematical modeling.

SIMULASI DAN PENGESAHAN PENJERAPAN PROSES UNTUK PENYINGKIRAN ASID AKRILIK DARI AIR SISA RAWATAN

ABSTRAK

Objektif kajian ini adalah untuk membangunkan model matematik proses penjerapan penyingkiran asid akrilik dan juga untuk mengesahkan simulasi proses penjerapan dengan menggunakan data sebelumnya eksperimen. Proses penjerapan digunakan dalam rawatan air sisa rawatan untuk membuang bahan pencemar toksik atau organik. Simulasi proses penjerapan adalah perlu untuk memahami penyingkiran asid akrilik menggunakan proses penjerapan. Akrilik asid dikeluarkan daripada air sisa rawatan kerana ia boleh menyebabkan kerosakan yang serius kepada alam sekitar akibat ketoksikan yang tinggi untuk organisma akuatik. Sebagai kesimpulannya, objektif dicapai. Model baru matematik proses penjerapan asid akrilik dengan menggunakan karbon diaktifkan boleh diwujudkan berdasarkan imbangan jisim pada turus tetap berterusan. Pengesahan simulasi dijalankan untuk membandingkan data simulasi dengan data eksperimen. Kajian ini adalah untuk meningkatkan pemahaman proses penjerapan penyingkiran asid akrilik dari air sisa oleh mencipta pemodelan matematik.

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LIST OF SYMBOLS

a_p	Radius of the adsorbent pellets, m
b	Langmuir isotherm parameter, ml/mg
c	Solute concentration in the liquid phase inside the pores, mg/l
C_b	Bulk phase dye concentration, mg/ml
C_s	Liquid phase concentration in equilibrium with qs on the surface, mg/ml
C_{bo}	Inlet adsorbate concentration, mg/ml
D_L	Axial dispersion coefficient, m^2/s
k_f	External film mass transfer coefficient, m/s
L	Column length, m
q	Average adsorbed phase dye concentration, mg/g
q_m	Langmuir isotherm parameter, mg/g
q_p	Concentration on the surface of the pellet, mg/g
r	Radial coordinate, m
t	Time, sec
V	Superficial velocity, m/s
z	Axial coordinate, m
ε	Bed porosity

CHAPTER 1

INTRODUCTION

1.1   Background

Adsorption is typically used in wastewater treatment to remove toxic or recalcitrant organic pollutants (especially halogenated but also non-halogenated), and to a lesser extent, inorganic contaminants, from the wastewater. Adsorption finds applications in tertiary wastewater treatment as a polishing step before final discharge. Adsorption is commonly used in the treatment of industrial wastewaters containing organic compounds not easily biodegraded during secondary (biological) treatment or toxic. In the adsorption process, acrylic acid is removed from waste water by using the activation carbon. The activation carbon has ability to remove the contaminants from the water. Acrylic acid is removed from waste water because it contain high toxicity that can harmful the aquatic organism. The adsorption process is used in the waste water treatment because it has low cost operation and has high efficiency.

Acrylic acid is also known as propenoic acid which has a colorless transparent liquid which a pungent smell. The boiling point of acrylic acid is 141.0

^{o}C and the melting point is 13.5 ^{o}C. Its density is 1.045 g/ml. Acrylic acid is produced from propene which is a byproduct of ethylene and gasoline production. This corrosive chemical is miscible in water, alcohol, and esters and polymerizes readily in the presence of oxygen forming acrylic resins. Acrylic acid is a strong corrosive agent to many metals, such as unalloyed steel, copper and brass. Acrylic acid undergoes reactions characteristics of both unsaturated acids and aliphatic carbolic acids or esters. Acrylic acids also can be polymerizing very easily. The polymerization is catalysed by heat, light, and peroxides and inhibited by stabilizers, such as monomethyle ether of hydroquinone or hydroquinone. These phenolic inhibiters are effective only in the presence of oxygen. The highly exothermic, spontaneous polymerization of acrylic acid is extremely violent. Acrylic acid is widely used in several industries such as painting, chemical fibers, adhesives, paper, oil additives and also detergent. When the acrylic acid released in effluents serious damaged to the environment can be cause because it has high toxicity for aquatic organisms.

The industries nowadays gives severe impact to our nature by producing a lot of pollution that have the tendency to brings more harmful than good such as air pollution, sound pollution and water pollution. Water pollution is one of the serious environmental issues because it can cause problem to the clean water production and also can contributes to the shortage of clean water supplies. Water pollution occurs when the physicals and chemicals properties of the water are change or in the other word is, there is a contamination in the water such as lakes, rivers, oceans and also ground water.

Wastewater pollution is always consider as dangerous because it has been affected by the hazardous or dangerous chemicals and release to the water source

such as rivers, lakes and oceans. The lack of clean water has always been an issue of environmental concern all over the world. This environmental issue is mainly stressed in developing countries today. Just imagine what would happen for the future life if no action will take to control the wastewater pollution. It can affect our sustainable nature and at the same time our source of clean water is not enough to meets the needs of the human from days to days. The wastewater pollution is commonly produced by domestic residences, commercial properties, industry, and agriculture. The unwanted contaminant in the wastewater can be dangerous to the aquatic and human health. It might contain the heavy metal in different concentrations and pH values that are dangerous. There are many industries that contribute to the wastewater pollution and textile industry is a part of it.

There are several ways to treat the waste water. It consists of physical, chemical and biological method. Microbial degradation, activated sludge and bio film process are the examples of biological method, which accepted for its potentialities but applicable only to lower concentration range. Meanwhile, the chemical and physical methods such as solvent extraction, precipitation, filtration, adsorption, and chemical oxidation are normally used to treat pollutants especially organic compounds and heavy metals. Every particular method is based on the application to the solute concentration range, capacity, cost, reusability and the reproducibility (Kentish & Stevens, 2001; Sarkar et al., 2003; Abburi, 2003).

1.2   Problem Statement

The acrylic acid is need to remove from waste water because it contains high amount of toxicity that can harmful the aquatic organism. Therefore, the suitable method of separation process needs to select. The adsorption process is chosen as the suitable separation process because it has high efficiency of the product and low cost of production. It is necessary to understand the adsorption process of acrylic acid using certain kind of adsorbent in order to create the mathematical modeling by using Mat Lab software.   Several parameters of the adsorption process need to be investigated including adsorption time and the concentration of the adsorbate which is acrylic acid.

1.3   Research Objectives

1.3.1   To develop the mathematical modeling of the adsorption process of the acrylic acid removal.

1.3.2   To validate the simulation of the absorption process by using the experimental data.

1.4   Research Questions/Hypothesis

1.4.1   How to develop the mathematical model of the adsorption process of the

acrylic acid?

1.4.2   How to validate the simulation of the absorption process by using the

experimental data?

1.5   Scope of Proposed Study

This research project is focusing on the simulation and the mathematical model based on the several parameters of the adsorption process such as the adsorption time and the concentration of the adsorbate that depends on the initial controller which is the initial concentration of the adsorbate itself. The simulation is run by using the Mat Lab software that is running in the ordinary differential equation (ODE). Then, the validation of the adsorption process for acrylic acid removal from waste water is simulating by using the previous experimental data that has been done by senior UMP.

CHAPTER 2

LITERATURE REVIEW

2.1   Adsorption Process

Adsorption is a process where a solid is used for removing a soluble substance from the water. In this process active carbon is the solid (Richardson et al, 2002). Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid which is called as adsorbent or the material doing adsorbing, forming a molecular or atomic film which is called as the adsorbate or material that being adsorbed (Richardson et al, 2002). It is different from absorption, in which a substance diffuses into a liquid or gases. The term sorption encompasses both adsorption and absorption processes, while desorption is the reverse process. Many adsorptions of organic substances by activation carbon results foam specific interactions between functional groups on the adsorbate and on the surface of the sorbent. These interactions may be designated as 'specific adsorptions' (Walter, 2012).

Adsorption is the process through which a substance, originally present in one phase, is removed from that phase by accumulation at the interface between that

phase and a separate (solid) phase. (Armenante, 2012). Adsorption process has been proved to be an excellent way to treat industrial waste water treatment because the adsorption process has the low-cost, availability, profitability, easy of operation and efficiency（Ayhan Demirbas, 2008).

Adsorption is more approachable and easy to run due to the price of adsorbent that usually is cheap and does not require a pre-treatment step before its application (Wang et al., 2005). A lot of researchers believes this treatment is to be far more superior than others due to variety reasons ((Sanghi and Bhattacharya, 2002; Meshko et al., 2001;Bulut and Aydin, 2006); including the simple design, low cost, and of course easy to handle.

The continuous adsorption in fixed-bed column is often desired from industrial point of view. It is simple to operate and can be scaled-up from laboratory process. The flow behavior and mass transfer aspects become peculiar beyond a particular length to diameter ratio of the column. Adsorption in fixed bed columns using activated carbon has been widely used in industrial effluent, since it does not require the addition of chemical compounds in the separation process (J.M Chern and Y.W Chiem, 2003).

2.2   Types of Adsorption

There are several types of adsorption and each of them has their own different characteristics. Exchange adsorption, physical adsorption and chemical adsorption are examples of types of adsorption.

2.2.1 Exchange Adsorption

Exchange adsorption or ion exchange is the electrostatic due to charged sites on the surface. Adsorption goes up as ionic charge goes up and as hydrated radius goes down. Ion exchange is a highly popular and has been widely practiced in industrial waste water treatment (Sheng et al, 2000).

2.2.2 Physical Adsorption

While in the physical adsorption or physisorption, it focuses on the Van der Waals (weak intermolecular) attraction between adsorbate and adsorbent, which are also responsible for the non-ideal behavior of real gases. The attraction is not fixed to a specific site and the adsorbate is relatively free to move on the surface. This is relatively weak, reversible, adsorption capable of multilayer adsorption. The physical adsorption takes place between all molecules on any surface providing the temperature is low enough. Physical adsorption phenomena were already well known in the early years of the twentieth century, where the various attempts were made to explain the underlying principles (Kenneth, 2008).

2.2.3 Chemical Adsorption

In chemical adsorption or chemisorption, some degree of chemical bonding between adsorbate and adsorbent are characterized by strong attractiveness.

Adsorbed molecules are not free to move on the surface. There is a high degree of specificity and typically a monolayer is formed. The process is seldom reversible. For example of chemical adsorption is the hydrogen takes place on transition metals but not on gold or mercury. Generally some combination of physical and chemical adsorption is responsible for activated carbon adsorption in water and wastewater.

2.3   Activated Carbon

Activated carbon is the most important carbon materials used to adsorb organic solutes from aqueous solution, although the use of activated carbon fibers and activated cloths has been continuously growing in the recent years. These carbon materials are applied in varies system such as drinking water and wastewater treatment and also used in the food, beverage, pharmaceutical and also chemical industries. Furthermore, the activated carbon adsorption has been cited by the US Environmental Protection Agency as one of the best available environmental control technologies (Carlos, 2008).

Activated carbon is also called activated charcoal or activated coal is carbon produced from the carbonaceous source materials such as nutshells, peat, wood, coal and petroleum pitch. For all three variations of the name, "activated" is sometimes substituted by "active" (Uhrikova, 2007). Activated carbon does not bind well to certain chemicals such as alcohols, strong acids and bases, and most inorganic like sodium, lead and iron. However, the activated carbon can adsorb the iodine very well compare to the others. Activated carbon is produced by a process consisting of

pyrolysis of raw material followed by activation with oxidizing gases (Grassi et al, 2012).

The specific surface area of adsorbent affects the adsorption performance. The larger the specific surface area of AC, the better its performance in adsorption process (Gua and Lua, 2003). The optimum specific surface area of activated carbon is between 600 until 1200 m^2/g (Ng et. al, 2002). The adsorption capacity of adsorbent is influenced by its internal surface area and pore volume (Nurul Ain, 2007). Additionally, the effectiveness of activated carbon is depended on their surface chemistry, as well as their pore size distribution (Radovic, 2001). The surface chemistry is influenced by the chemical by its internal surface area and pore volume (Nurul Ain, 2007).

2.4   Types of Activated Carbon

Adsorption is a water treatment process that removes a soluble substance from the water. Adsorption is achieved by an active carbon which comes in two varieties which are Powder Activated Carbon (PAC) and Granular Activated Carbon (GAC), (Grassi et al, 2012). Activation carbon can be manufactured in powder and granular form from a large variety of raw materials and their highly developed porosity, large surface area and variable surface chemistry that make them very unique and versatile adsorbents (Carlos, 2008).

2.4.1 Powder Activated Carbon (PAC)

The powder activated carbon is made from the crushed or ground carbon particles. The particle size typically between 10 and 100μm in diameter .Powder activated carbon is normally used in processing units like, clarifiers, gravity filters and mix basins. Crushed or ground carbon particles are so finely powdered that most of them can easily pass through a designated mesh sieve or sieve. This is because it has small size will form large internal surface having small diffusion distance. The aim of PAC addition is often the removal of unpleasant tastes and odors or, in some cases, toxins produced by blue-green algae (cyanobacteria). In Europe and the Unites States PAC is also used to help control high levels of pesticides or other man made industrial micro pollutants in the source water (Gayle, 2008).

PAC can be added before coagulation, during chemical addition, or during the settling stage, prior to the sand filtration. It is removed from the water during the coagulation process and through filtration. One of the advantages of the PAC is that can be applied for the short period of time and when the problems occurs, then ceased when it is no longer required. With problems that may arise only periodically, for example algal metabolites, or accidental industrial chemical spills, that can be a great cost advantages (Gayle, 2008).

2.4.2   Granular Active Carbon (GAC)

While for the granular activated carbon, it forms smaller external surface because of their larger size as compared to powder activated carbon. The particle size is larger than that of the PAC, usually between o.4 and 2.5 mm.

Granulated carbons are mainly used for treating water. Their main function includes deodorization and separation of components of flow system. It also used to remove the micro pollutants such as pesticides, industrial chemicals and also taste and odors. It also sometimes used to removed natural organic material (NOM), such as humic and fulvic acid, which is present in all water bodies, and reacts with chlorine in the disinfection process to form potentially harmful disinfection by products (Gayle, 2008). The other function of the GAC is used as replacement for sand in conventional treatment filters as this is a low cost alternative to retrofitting GAC filters in an existing plant, where space constrains may not allow additional filters to be built.

Figure 2.1 Types of Activated carbon (Source: Kenneth, 2008):

2.5   Properties of the Activation Carbon

The properties of the activated carbon can be divided into two which are physical properties and chemical properties. Both physical properties and the chemical properties have their own characteristics.

2.5.1   The Physical Properties

The physical properties of the activated carbon are physical attraction of the contaminants to the pore walls of the filtration process. The important physical

properties are surface area, product density which is mesh size, abrasion resistance and ash content (Anthony et al, 2012). The amount and distribution of pores are important in determining how well contaminants are filtered. The contaminants are attracted differently depends to the size of the pore filter. Contaminants having large molecules are effectively removed by activated carbon filters. Particle size is an important parameter in specifying carbons for specific applications, which can be affecting such operating of activated carbon, is ash level, which reflects the purity of the carbon. (Robert et al, 2012). Conditions as pressure drop, filtration capabilities, backwash rate requirements and also the rate of adsorption of contaminants. While a smaller particle size will affects more pressure drop across a carbon bed, the rate of diffusion of an organic into the pore and its subsequent adsorption is will be increased.

2.5.2   The Chemical Properties

For the chemical properties of the activated carbon, the filter surface is always interacts chemically with organic molecules. Adsorption may also result by the electrical forces between the activated carbon surface and some contaminants. The activation process also determines the chemical properties of the adsorbing surface. The activation carbon materials that results from various activation processes will posses chemical properties that make them more or less attractive to various contaminants.

2.6 Function of Activated Carbon

Activated carbon or carbon adsorption process is used for removing various organic substances like oils, radioactive compounds, petroleum hydrocarbons, poly aromatic hydrocarbons and various halogenated compounds like chlorine, fluorine, bromine and iodine. (Richardson et al, 2002). Apart from organic compounds it also removes inorganic compounds like arsenic, cadmium, chromium, zinc, lead, mercury, copper and others. As carbon adsorption method is effective in removing pollutants, it is used in following industrial process for water treatment such as ground water purification, the de-chlorination of process water, water purification and also waste water treatment. (Kandasamy et al, 2012).

Activated carbon is an excellent adsorbent because it has a strong affinity for binding organic substances, even at low concentration. Activated carbon also has a vast network of pores of varying size to accept both large and small contaminants molecules and these pores also give activated carbon has a very large surface area. The larger percentage of the total surface area is believed to be of the planar surface type with the attached functional groups (Snoeyink and Weber, 1967). The majority of the adsorption on the surfaces considered because of the relative weak physical or Van der Waals forces (Van der Plas, 1968). On the other hand, the sides of these planar surfaces are attached with many functional groups such as organic carboxyl, phenol and also carbonyl group (Mattson and Mark, 1971) and inorganic oxygen complexes (Snoeyink and Weber, 1967).

The highly porous nature of the carbon provides a large surface area for contaminants to collect. The adsorption takes place because of the attractive force

between the molecules. Molecules at the surface of a solid attract other molecules. Hence, water contaminants get adsorbed to the surface of carbon. As the attraction of the carbon surface for contaminants is higher than the attractive forces that keep them dissolved in solution, water contaminants gets attracted. Activated carbon through adsorption also removes chemical like chlorine that combines with carbon to form chloride ions. This reaction helps not only in removing contaminants but also removes objectionable tastes and odors from drinking water.

Others industrial application involves use of activated carbon are in the metal finishing field. It is very widely employed for purification of electroplating solutions. For example, it is a main purification technique for removing organic impurities from bright nickel plating solutions. A variety of organic chemicals are added to plating solutions for improving their deposit qualities and for enhancing properties like brightness, smoothness and ductility. This is because of the passage of direct current and electrolytic reactions of anodic oxidation and cathodes reduction, organic additives generate unwanted break down products in solution. Activated carbon treatment removes such impurities and restores plating performance to the desired level. While in the medical application, the activated carbon is used to treat poisoning and overdoses following oral ingestion.

2.7   Properties of Acrylic Acid

Acrylic acid is also known as propenoic acid which has a colorless liquid with an irritating acrid odor at room temperature and pressure. Its odor threshold is

low (0.20-3.14 mg/m3). It is miscible in water and most organic solvents. This corrosive chemical is miscible in the water, alcohol, esters and polymerizes readily in the presence of oxygen forming acrylic acid. Acrylic acid is the simplest unsaturated carboxylic acid which has double bond and carboxyl group.

2.7.1 Chemical Properties of Acrylic Acid

Acrylic acid will undergo the typical reactions of a carboxylic acid, and reactions of the double bond similar to those of the acrylate esters. Acrylic acid is released during the use of an acrylate based grouting agent for sealing of constructions or stabilization of the ground. The high reactivity of these compounds stems from the by carbonyl group, behaves as an electrophile which is the favors the addition of large variety of nucleophiles and active hydrogen compounds to the vinyl group. Moreover, the carbon-carbon double bond undergoes radical-initiated addition reactions, Diels-Alder reactions with dienes, and polymerization reactions.

Acrylic acids polymerized very easily. The polymerization is catalyzed by heat, light, and peroxides and inhibited by stabilizers, such as monomethyle ether of hydroquinone or hydroquinone itself. These phenolic inhibiters are effective only in the presence of oxygen. The highly exothermic, spontaneous polymerization of acrylic acid is extremely violent.

2.7.2 Physical Properties of Acrylic Acid

Acrylic acid is biodegrable and there are no indications of a bioaccumulation potential. Acrylic acid is also susceptible to degradation by anaerobic microbes.

Acrylic acid is essentially non volatile. Under normal environment conditions, which is the pH value are 5.59, the acrylic acid is predominantly present in dissociated anionic form and highly mobile in the soil. It can be assumed that the adsorption behavior of the anionic form of acrylic acid depends primarily on the inorganic fraction of different soils.

Table 2.1 Specification of acrylic acid

Specification	Details
Molecular formula	$C_3H_4O_2$
Molecular weight	72.06 g/mol
Appearance	clear, colorless liquid
Boiling point	14 °C, 287 K, 57 °F
Melting point	141 °C, 414 K, 286 °F
Critical Temperature	342°C (647.6°F)
Density	1.051 g/mL
Solubility in water	Miscible
Acidity (pK_a)	4.35
Main hazards	Corrosive, Dangerous for the environment
Flash point	68 °C (154 °F)
Volatility	Not available.
Odor Threshold	0.092 ppm
Taste	Not available
Critical pressure, MPa	5.06
Heat of vaporization at 101.3 kPa	45.6 kJ/mol
Heat of combustion	1376 kJ/mol
Heat of melting at 13°C	11.1 kJ/mol

Table 2.1 Continue

Specification	Details
Heat of neutralization	58.2 kJ/mol
Heat of polymerization	77.5 kJ/mol
Henry's law constant	3.2×10^{-7} atm $\times$ m3/mol

(Source:Gong,2007)

2.8   Function of Acrylic Acid

The worldwide production of acrylic acid in 1994 was estimated to be approximately 2 million tonnes. Acrylic acid is used primarily as a starting material in the production of acrylic esters; as a monomer for polyacrylic acid and salts, as a comonomer with acrylamide for polymers used as flocculants, with ethylene for ion exchange resin polymers, with methyl ester for polymers.

Acrylic acid is used in a number of industrial applications. The primary use of acrylic acid, accounting for approximately 67 percent of all use, is in the production of acrylic esters and resins, which are used primarily in coatings and adhesives.   The fastest growing use of acrylic acid is in the production of superabsorbent polymers. It is also used in oil treatment chemicals, detergent intermediates, water treatment chemicals, and water absorbent polyacrylic acid polymers (Mannsville 1992).

Apart from that, according to Gong, (2007) acrylic acid is also can be used as painting, chemical fibers, adhesives, paper, oil additives and also detergent. It also can be used as a carboxylic acid to produce acrylic esters, acryl amide, N-substituted acryl amides and acryloyl chloride by common methods. Acrylic acid readily

undergoes addition reactions with a wide variety of organic and inorganic compounds. This makes the acrylic acid a very useful feed stock for the production of many low molecular compounds. For instance, acrylic acid can be used to produce derivatives of propionic acid with water, alcohols, amines, halogens and chlorinated hydrocarbons. It can also be used with other substances to produce unsaturated fatty acids, heterocyclic compounds and Diels-Alder addition products.

CHAPTER 3

METHODOLOGY

3.1   Introduction

This chapter of this study will focus mainly on the method used to in order conduct the study. This methodology will focus on the mathematical model based on the mass balance in the element of fixed bed adsorption of the acrylic acid removal. While for the validation of the simulation will be carried out by using experimental data from the previous work. It is to compare the simulation data and result of the experimental data from the different parameters such ad adsorption time and the concentration of the adsorbate which is acrylic acid. There are many software that can be used to develop the new mathematical model such Mat Lab, FAST 2.0 software and ASPEN ADSORPTION. However, in this researched only focused on the Mat lab software.

3.2   Methodology flow chart

This methodology flow chart is represents the main steps of the process that needed to be done in order to complete this study.
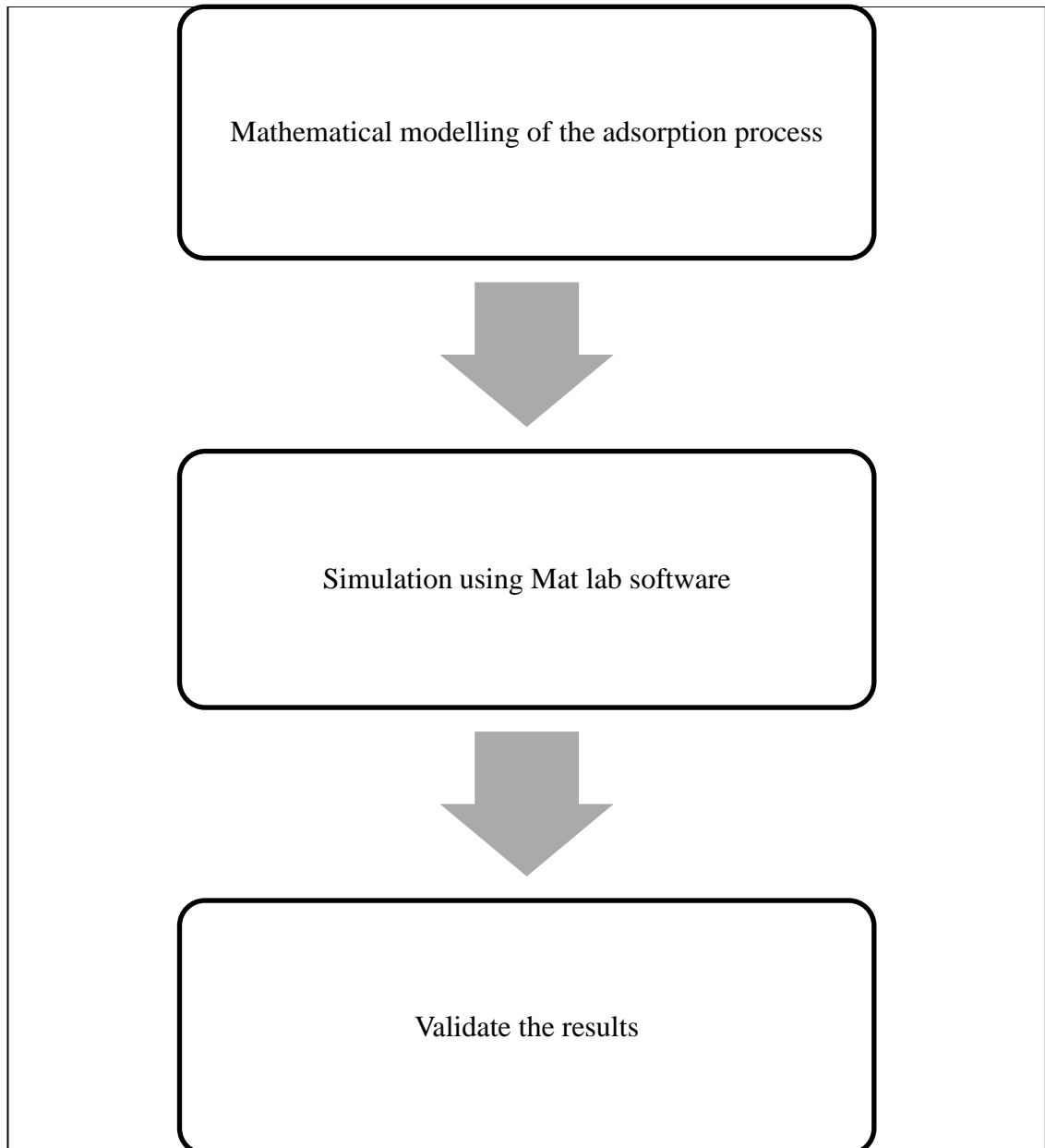
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┌─────────────────────────────────────────────────────────┐
│        ╭─────────────────────────────────────────╮       │
│        │                                         │       │
│        │  Mathematical modelling of the adsorption process │
│        │                                         │       │
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│                          ⬇                                │
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│        │                                         │       │
│        │       Simulation using Mat lab software  │       │
│        │                                         │       │
│        ╰─────────────────────────────────────────╯       │
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│        │                                         │       │
│        │            Validate the results          │       │
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Figure 3.1 Methodology flow chart

3.2.1 Mathematical Modeling

The mathematical modeling is created based on the mass balance (diffusion) of the continuous fixed bed adsorption. A mathematical model for the fixed bed column is proposed by incorporation for an important parameter, external mass transfer, resistance, internal mass transfer resistance and non-linear multi component isotherm. The proposed model can be extensively used for understanding the dynamics of fixed bed adsorption column. (Sulaymon, 2011).

The mathematical models are based on the following assumptions:

i) The system is operating under isothermal conditions. There is no temperature change during a running of simulation.

ii) The equilibrium of adsorption is described by Langmuir isotherm.

iii) Mass transfer across the boundary layer surrounding the adsorbent particles is characterized by the external film mass transfer coefficient, k_f.

iv) The linear velocity of the bulk phase varies along the fixed bed column.

v) The adsorbent particles are spherical and homogenous in size and density.

vi) The liquid density is constant.

Based on the above assumptions, the net rate of the accumulation is:

$$-D_L \frac{d^2 C_b}{dz^2} + V \frac{dC_b}{dz} + C_b \frac{dV}{dz} + \frac{dC_b}{dt} + \rho_p \left(\frac{1-\varepsilon}{\varepsilon}\right) \frac{dq_p}{dt} = 0$$
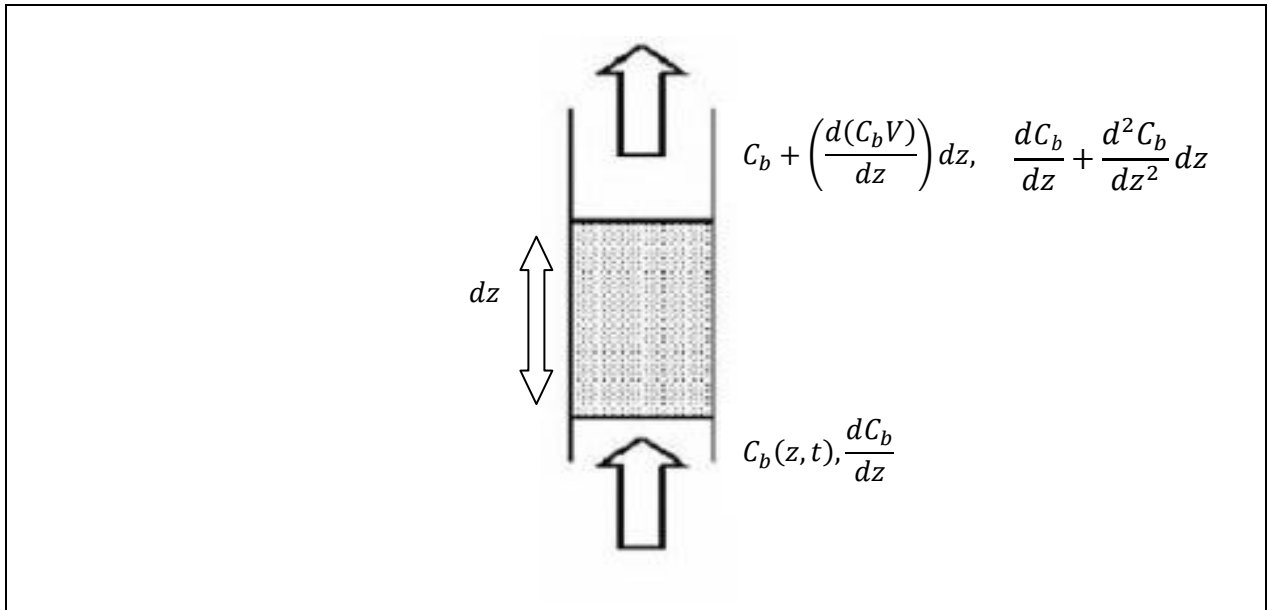
Figure 3.2 Mass balances in element of fixed bed

The initial condition is considered:

$$C_b = C_{bo} \qquad\qquad z = 0, t = 0$$

$$C_b = 0 \qquad\qquad 0 < z \leq L, t = 0$$

The counter conditions at both ends of the column:

$$D_L \frac{dC_b}{dz} = -V_o(C_{bo} - C_b), \qquad\qquad z = 0, t > 0$$

$$\frac{dC_b}{dz} = 0 \qquad\qquad z = L, t \geq 0$$

Total mass balance:

$$\rho_1 \frac{dV}{dz} = -(1 - \varepsilon)\rho_s \frac{dq_p}{dt}$$

Velocity boundary conditions:

$$V = V_o \qquad\qquad z = 0, t > 0$$

$$\frac{dV}{dt} = 0 \qquad\qquad z = L, t \geq 0$$

The inter phase mass transfer rate:

$$\rho_s \frac{dq_p}{dt} = \frac{3k_f}{a_p} + (C_b - C_s)$$

The macroscopic conservation equation:

$$\varepsilon_p \frac{dc}{dt} + (1 - \varepsilon_p)\rho_p \frac{dq}{dt} = D_p \left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{dc}{dr} \right)$$

Assuming instantaneous equation:

$$\frac{dq}{dt} = \frac{dc}{dt}\frac{dq}{dc} = 0$$

Rearranging equation:

$$\frac{dc}{dt} = \frac{1}{[1 + \rho_p \left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{dq}{dc}]} D_p \left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{dc}{dr} \right)$$

The initial condition:

$$c = 0, \; q = 0 \qquad\qquad 0 < r < a_p, t = 0$$

The symmetry condition at the center of the particles and continuity condition on the external surface of the adsorbent bed:

$$\frac{dc}{dr} = 0 \qquad\qquad r = 0, t > 0$$

$$k_f + (C_b - C_s) = D_p \left(\frac{dc}{dr}\right) \qquad\qquad r = a_p, t > 0$$

The adsorption isotherm is nonlinear, and it described by Langmuir isotherm:

$$q = \frac{q_m bc}{1 + bc}$$

3.2.2 Simulation Using Mat Lab Software

Based on the mathematical model of the fixed bed adsorption, the simulation of develop the mathematical model by using Mat lab is created. The equation is modified by using different parameters and variables such as the concentration of the adsorbate and the time used to adsorbing the adsorbate until no residual acrylic acid left in the wastewater. The simulation is run by using the ordinary differential equation (ODE).

3.2.3. Concentration of Acrylic Acid and Initial Concentration

The first mathematical model is based on the concentration removal of acrylic acid versus the initial concentration of acrylic acid. The manipulating variable is the initial concentration. On this condition, the time contact between the adsorption

processes is constant. Then, the graph is plotted with the Mat lab software and using Excel.

3.2.4 Concentration Removal and Time Contact

The second mathematical model is based on the concentration removal of acrylic acid versus the contact to remove the acrylic acid. The manipulating variable is the time contact of adsorption process. On this condition, the initial concentration of the acrylic acid is constant. The graph of concentration removal percentage versus time contact is plotted with the Mat lab software and Excel.

3.2.5 Validate the results

After the simulation is run, the results are analyzed and then will compare the results with the experimental data. The different is analyzed with the different parameters and variable of the data. The error between both previous experimental data and the simulation that has been run in the Mat Lab software is calculated by using the function in the Mat Lab software which is sum square error (SSE).

CHAPTER 4

RESULT AND DISCUSSIONS

4.1   Comparison between Results with Mat Lab and Data Experiment

Fixed bed column experiments are performed in order to generate the data for obtaining the breakthrough curves. The breakthrough time and the shape of the breakthrough curve are very important characteristics for the determination of dynamic response of the adsorption column.

The results of removal acrylic acid between acid removals are comparing between Mat lab software and experimental data by several parameters and variables.

4.2   Effect on Concentration of Acrylic Acid Removal versus Time

Initial concentration: 6.56 ppm

Table 4.1 Percentage of adsorption removal under time contact

Time, min	Final Concentration, ppm	Percentage of acrylic acid removal, %
15	5.86	10.67
30	1.142	82.60
45	0.151	97.70
75	0.0634	99.00
90	0.0000	100.00
176	0.0000	100.00
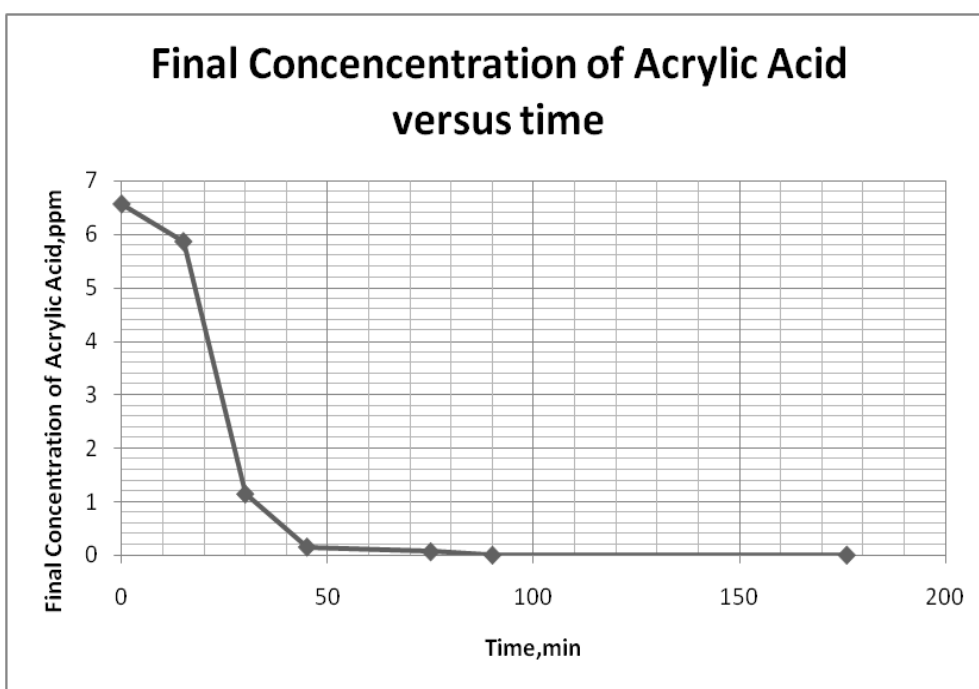
Figure 4.1 Final concentration of acrylic acid removal versus time

The Figure 4.1 is represents the final concentration of acrylic acid removal versus adsorption time from the previous experimental data. The data is validate with the

theory of the adsorption which is the final concentration of the acrylic acid removal from the waste water is rapidly decrease from the time range of zero minute until thirdly minutes. After the thirdly minutes, the final concentration of the acrylic acid removal is slowly decreases and then become constant until no residual of acrylic acid remaining in the waste water.
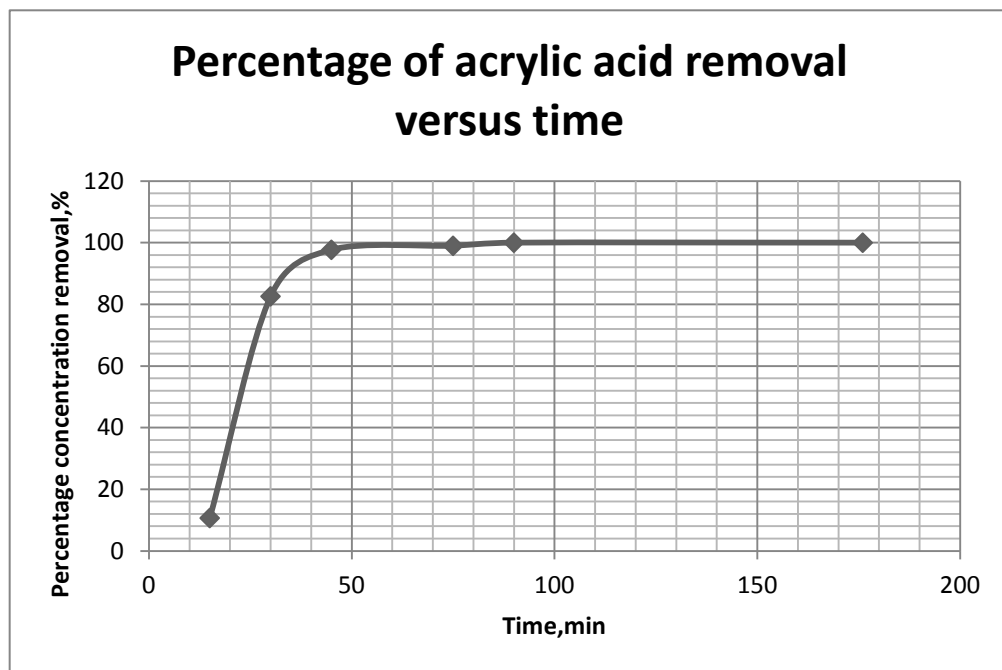
Figure 4.2 Percentage of acrylic acid removal versus time

The Figure 4.2 is represents the percentage concentration of acrylic acid removal versus adsorption time from the previous experimental data. This graph is the reverse of the graph of final concentration of acrylic acid removal in the waste water versus adsorption time. The data is validate with the theory of the adsorption which is the percentage concentration of the acrylic acid removal from the waste water is rapidly

increases from the time range of zero minute until thirdly minutes. After the thirdly minutes, the percentage concentration of the acrylic acid removal is slowly increases and then become constant until no residual of percentage acrylic acid remaining in the waste water.
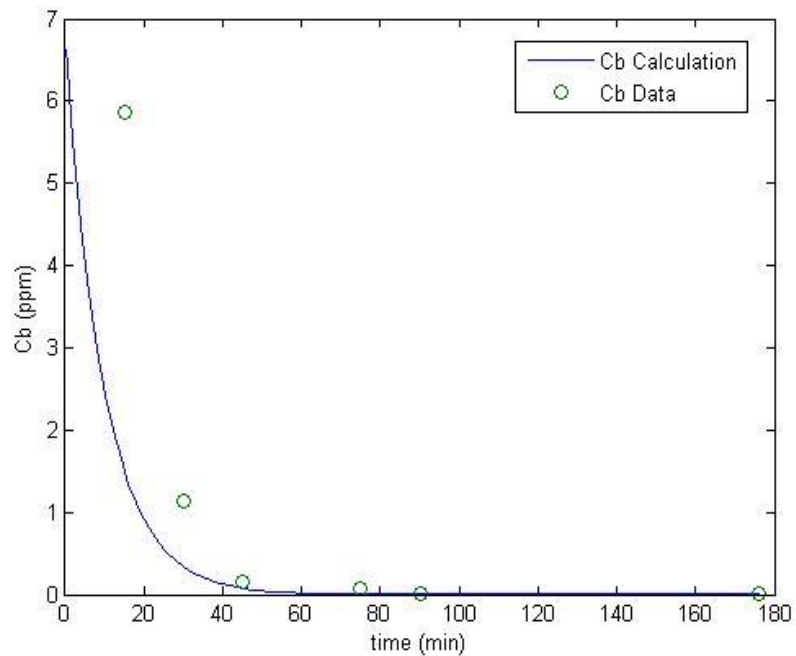
Figure 4.3 Final concentration of acrylic acid for simulation and previous experiment data

The C_b in the Figure 4.3 represent the final concentration of the acrylic acid removal for both simulation that had run in the Mat Lab software and the previous experimental data. The error is calculated by using the function of sum square error (SSE) in the Mat Lab software which is 19.5954. There is percent error between these two data which is 0.5792%. This simulation of the mathematical model of the adsorption

process is acceptable because the error is quite low. This is because of the simulation parameters error between the kinetics studies which is the value of kc and real column reaction in the continuous fixed bed adsorption. This occurs because of all the simulation, the constant parameters were derived from the kinetics adsorption.
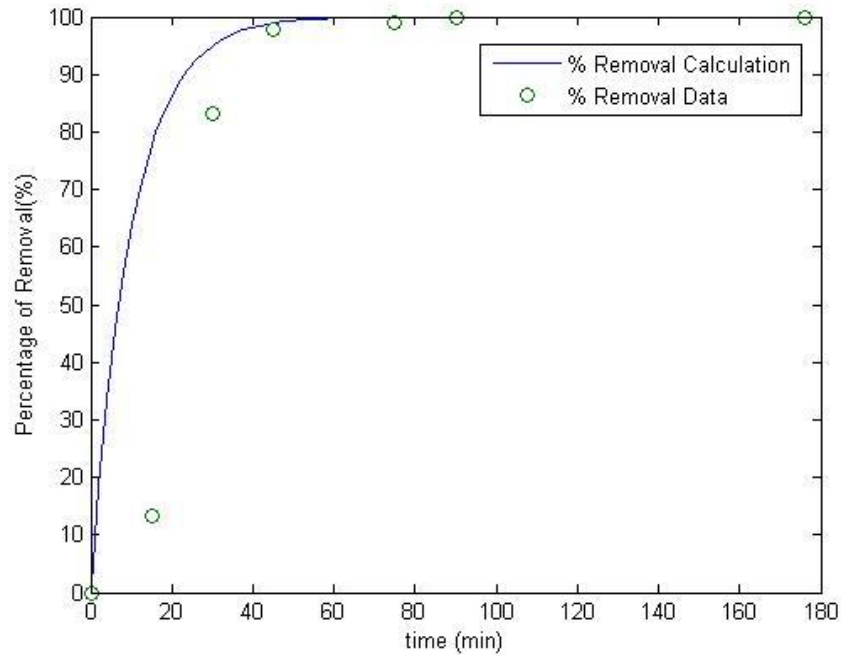
Figure 4.4 Percentage of acrylic acid removal for simulation and previous experiment data

The percentage of removal in the Figure 4.4 represents the percentage of the acrylic acid removal for both simulation that had run in the Mal Lab software and the previous experimental data. The error is calculated by using the function of sum square error (SSE) in the Mat Lab software which is 19.5954. There is percent error between these two data which is 0.5792%.

From the Figure 4.4, the concentration percentage acrylic acid removal is increase as the time increase. According to Senthilkumaar et al, 2009, said that the concentration of the percentage removal is increasing with the increasing of the time contact. During the adsorption of the acrylic acid, the initial of acrylic acid molecules reach to the boundary layer. During adsorption of acrylic acid, the initial of the acrylic acid molecules reach the boundary layer and then acrylic acid have to diffuse into the adsorbent surface. Finally, acrylic acid has to diffuse into the porous structure of the adsorbent. Hence, this phenomenon will take a relatively longer contact time.

The performance of packed bed is described through the concept of the breakthrough curve. Both, the time until the sorbed species are detected in the column effluent (breakthrough point) at a given concentration, and the shape of the concentration–time profile or breakthrough curve, are very important characteristics for operation, dynamic response and process design of a biosorption column because they directly affect the feasibility and economics of the sorption phenomena.

4.3 **Effect on Concentration of Acrylic Acid versus Initial Concentration**

Time constant: 2 hour

Table 4.2 Percentage of adsorption removal under initial concentration

Initial Concentration, ppm	Final Concentration, ppm	Percentage of acrylic acid removal, %
6	5.86	72.6
10	1.644	86.4

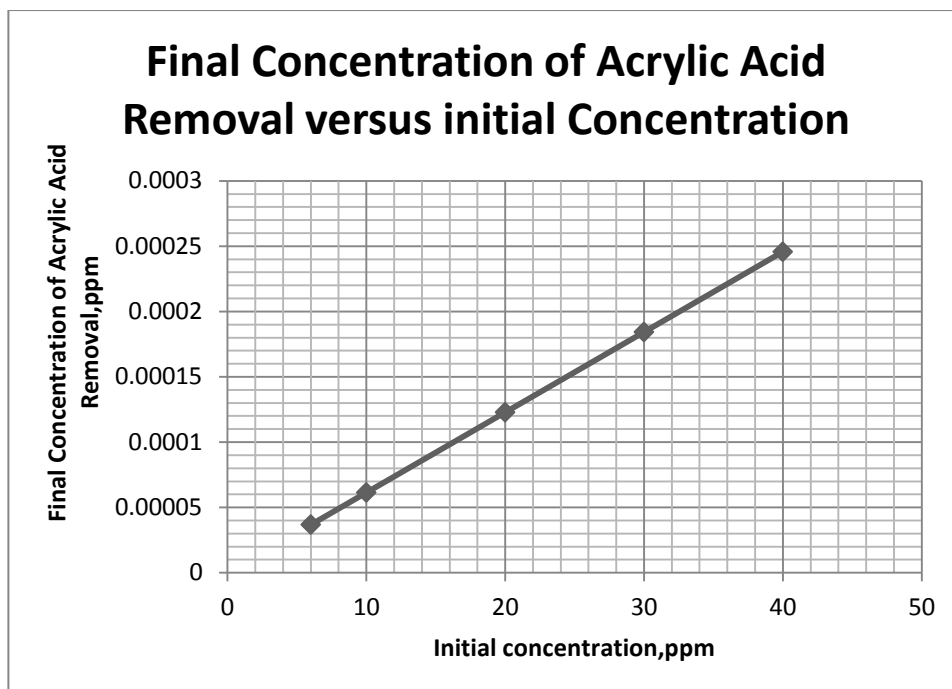| Initial Concentration, ppm	Final Concentration, ppm	Percentage of acrylic acid removal, %
20	1.364	80.35
30	3.93	83.63
40	4.91	87.7
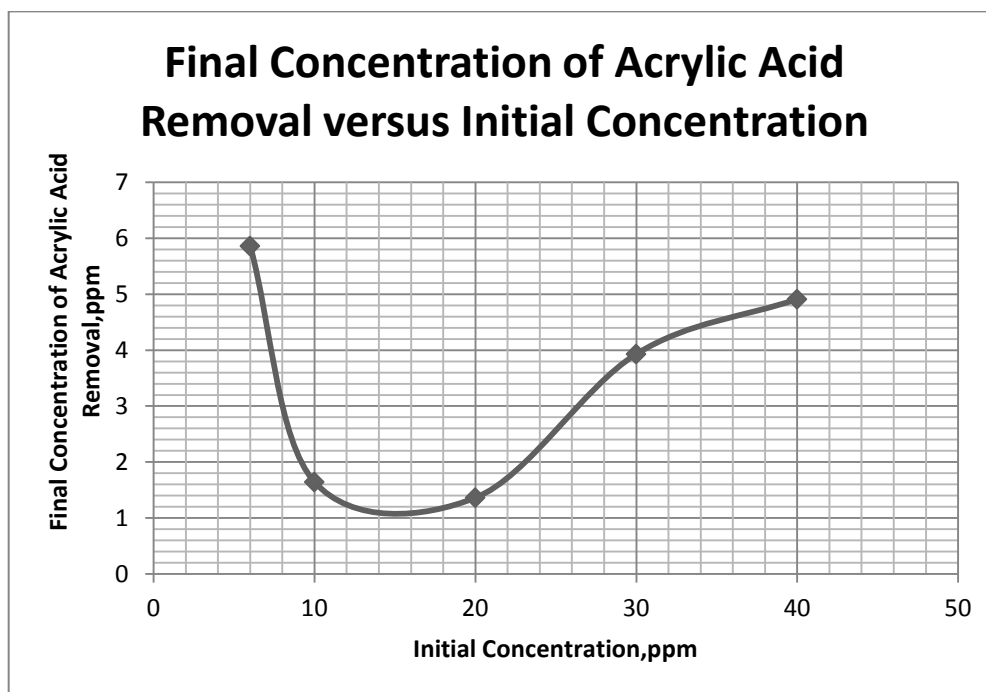
Figure 4.5 Final concentration of acrylic acid removal versus initial concentration

The Figure 4.5 is represents the value of the final concentration of the acrylic acid removal in the waste water versus the initial concentration used of the acrylic acid based on the previous experimental data that had been done by senior UMP. Based on the observation, the data in the graph is not validated with the theory of the adsorption process. The data trend should be linearly increasing as the initial concentration of the

acrylic acid increasing; the value of the final concentration of the acrylic acid removal from waste water should be increasing as well. This is because the value of the acrylic acid residual that has been adsorbing in the continuous fixed bed column has a limit. When the continuous fixed bed column reaches the equilibrium state, the value that the adsorbent which is the granular activated carbon can adsorbing the adsorbate which is the acrylic acid is constant.

Table 4.3 The final concentration and initial concentration based on the software

Initial Concentration, ppm	Final Concentration, ppm
6	3.68653E-05
10	6.14421E-05
20	0.000122884
30	0.000184326
40	0.000245768

The value data show in the Table 4.3 is run by the simulation by using same initial concentration of the acrylic acid. However, the value of the final concentration of the acrylic acid removal from the waste water is not same compare to the previous experimental data. This is because the value of the final concentration of the acrylic acid removal is depends on the value of the initial concentration of the acrylic acid.

Figure 4.6 Final concentration of acrylic acid removal versus initial concentration

The Figure 4.6 represents the final concentration of the acrylic acid removal from the waste water by using the simulation. The final concentration of the acrylic acid removals increases as the initial concentration of acrylic used is increases. This trend of the graph is valid with the theory of the adsorption process. This is because the value of the acrylic acid residual that has been adsorbing in the continuous fixed bed column has a limit. When the continuous fixed bed column reaches the equilibrium state, the value that the adsorbent which is the granular activated carbon can adsorbing the adsorbate which is the acrylic acid is constant.
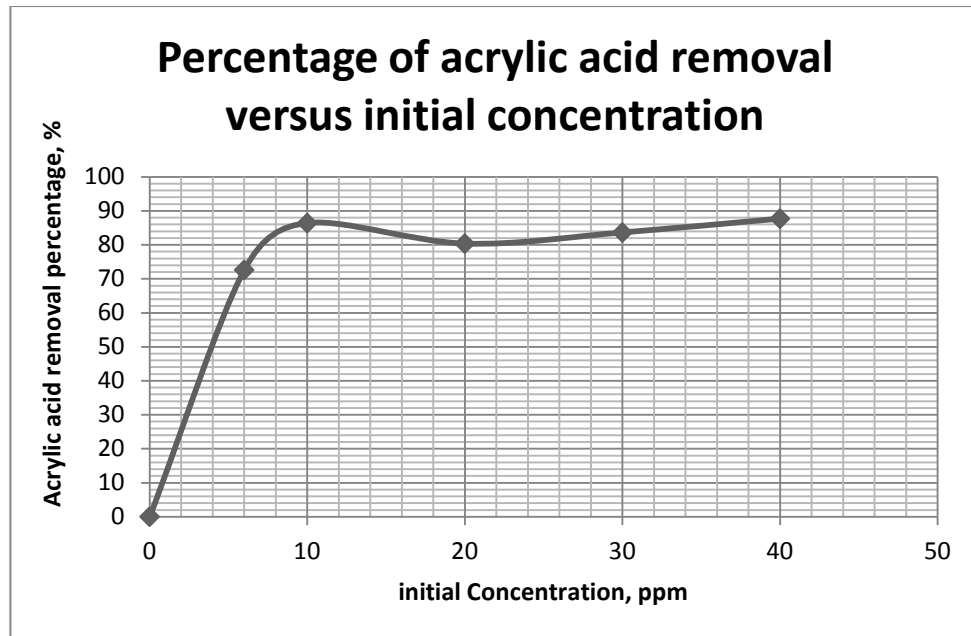
Figure 4.7 Percentage of acrylic acid removal versus initial concentration

As expected, the breakpoint time for a higher acrylic acid concentration was earlier than that for a lower influent dye concentration as the binding sites became more quickly saturated in the system at higher dye concentrations. Higher inlet of acrylic acid concentrations caused a faster breakthrough as expected (Senthilkumaar et al, 2005).

In the adsorption of the acrylic acid, a change in initial concentration affects the operating characteristics of the fixed-bed adsorption column. From the graph above, the initial concentration is perpendicular to the concentration of acrylic acid removal. As the initial concentration is increase, the concentration of acrylic acid removal is also increase. This is because of the higher the acrylic acid, the stronger the driving forces of the concentration gradient, thus the higher the adsorption capacity (Weng et al, 2009).

Figure 4.7 shows that the first initial concentration of acrylic acid which is 6 part per million (ppm) can remove 72.6 percentage of the acrylic acid removal. The initial concentration of acrylic acid is rapidly increase because of the relatively slower transport due to a decrease in diffusion coefficient and also decreased mass transfer coefficient at low acrylic acid concentration (Gupta et al, 2010).

Percent adsorption decreased with increase in initial acrylic acid concentration. However, the actual amount of acrylic acid adsorbed per unit mass of carbon increased with increase in acrylic acid concentration. When the initial concentration is 40 ppm, the percentage of acrylic acid removal is relatively constant which 87.7 percents is.

It is observed that the adsorbent get saturated faster at higher concentrations of adsorbate due to the higher rate of adsorbent exhaustion at higher acrylic acid concentration. For a low initial acrylic acid concentration, breakthrough occurs very late and surface of the adsorbents is saturated with acrylic acid at a relatively longer time. This fact is probably associated with the availability of adsorption sites around or inside the adsorbent particles that are able to capture the acrylic acid at lesser retention time.

The driving force for adsorption is the concentration difference between the solute on the sorbent and the solute in the solution. A high concentration difference provides a high driving force for the adsorption process and this may explain why higher adsorption capacities were achieved in the column fed with a higher acrylic acid concentration. The relatively low acrylic acid retention for adsorbent can be attributed to the difference in the surface morphology.(Aksu and Gonen, 2004).

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

As a conclusion from the research, the findings and the mathematical modeling that have been done and the results obtain will help the researcher to improve the kinetics and equilibrium studies on the acrylic acid removal from the wastewater by using granular activated carbon. The data showed that the prepared activated carbon has considerable potential for the removal of acrylic acid from wastewater treatment. For the validation of the simulation is carried out to compare the simulation data with the experiment data. This research is expected to improve the understanding of adsorption process of acrylic acid using activated carbon.

5.2 Recommendations

Some recommendations have been made to improve the results for future references:

1) The mathematical model of the adsorption process can be run by other software such as Fast Adsorption software.

2) The other variables parameters of the adsorption process can be consider such as effect on the flow rate, pH and bed length.

3) Make the same research but change the adsorbent with the powdered activation carbon (PAC).
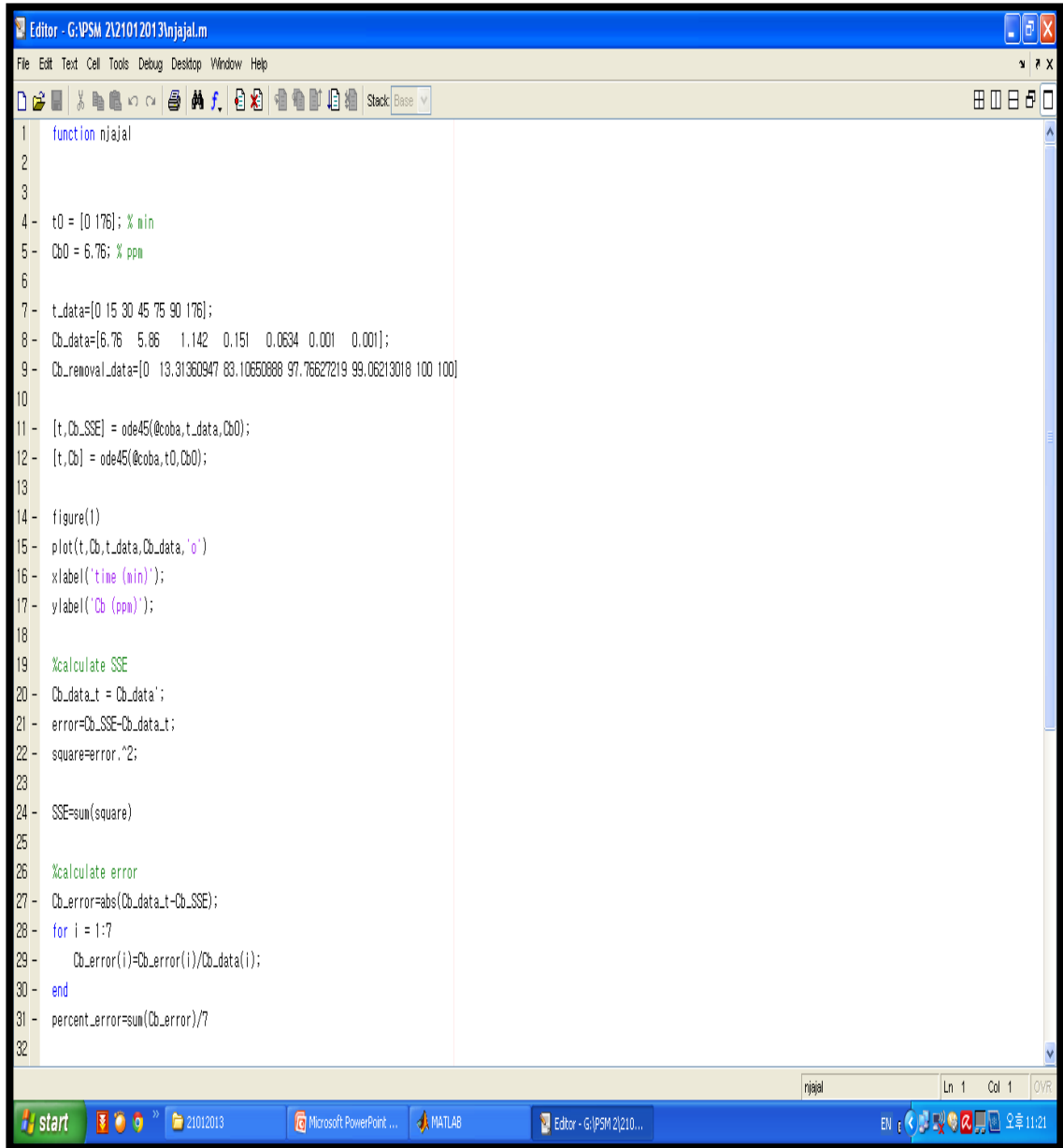
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S.Senthikumaar,S.K. Krishna, P. Kaalamani, S. V. Subburamaan, N. Gamonapathi Subramaniam.(2009). *Adsorption of Organophosphorous Pesticide From Aqeuous Solution Using Waste Jute Fiber* .

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APPENDICES

APPENDIX A

Figure A.1 Coding simulation from Mat Lab software

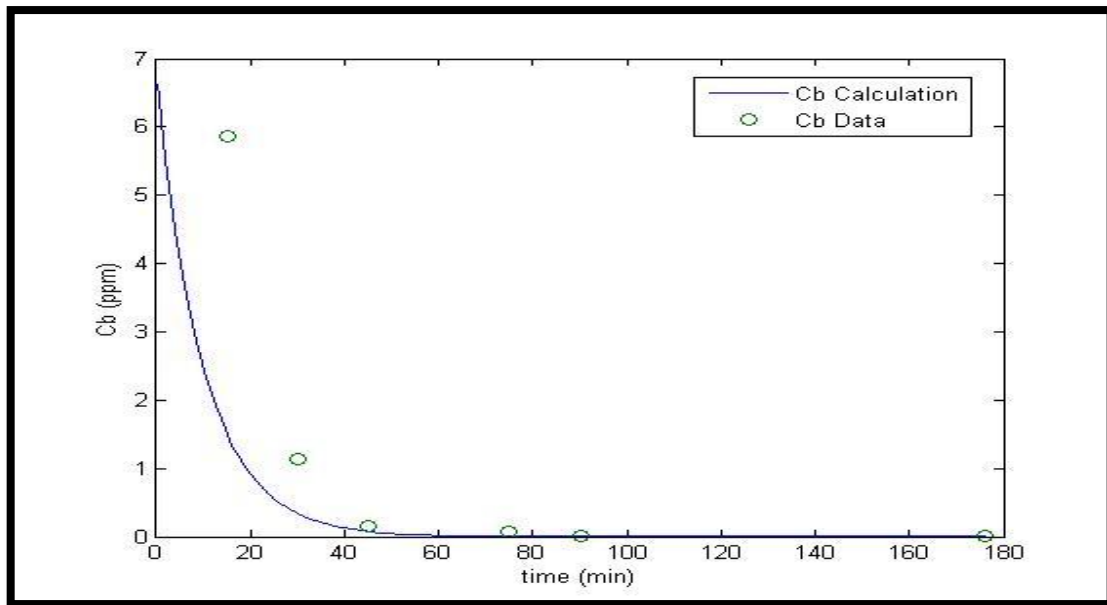**Figure A.2** Coding simulation from Mat Lab software (continue)

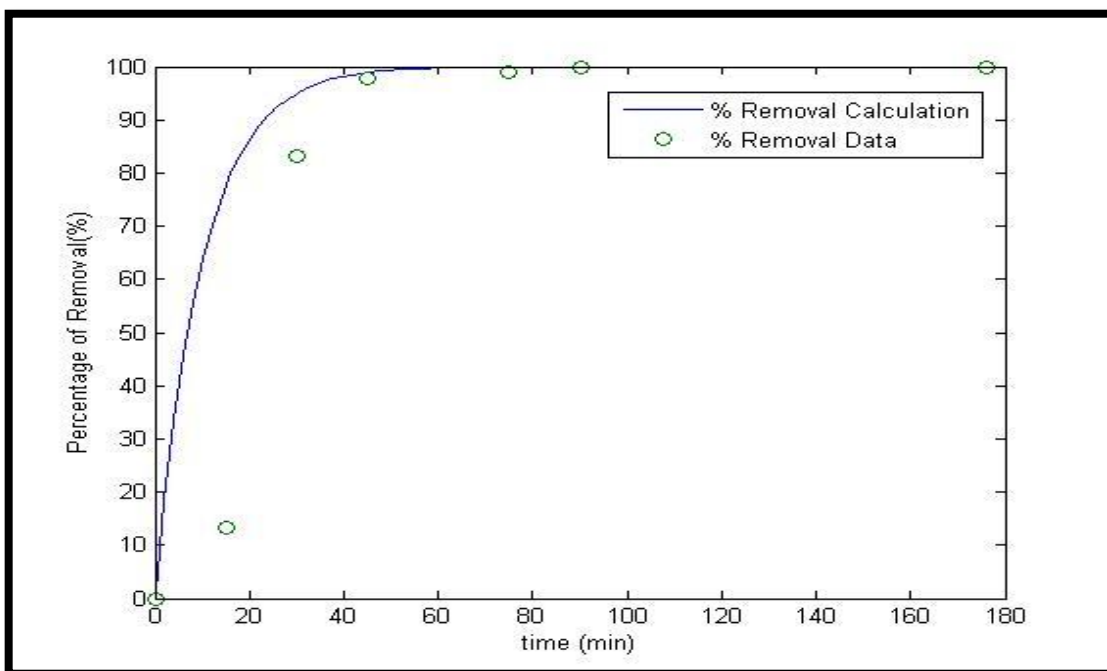**Figure A.3** Graph from Mat Lab software (concentration versus time)

Figure A.4 Graph from simulation Mat Lab software (percentage of concentration versus time)
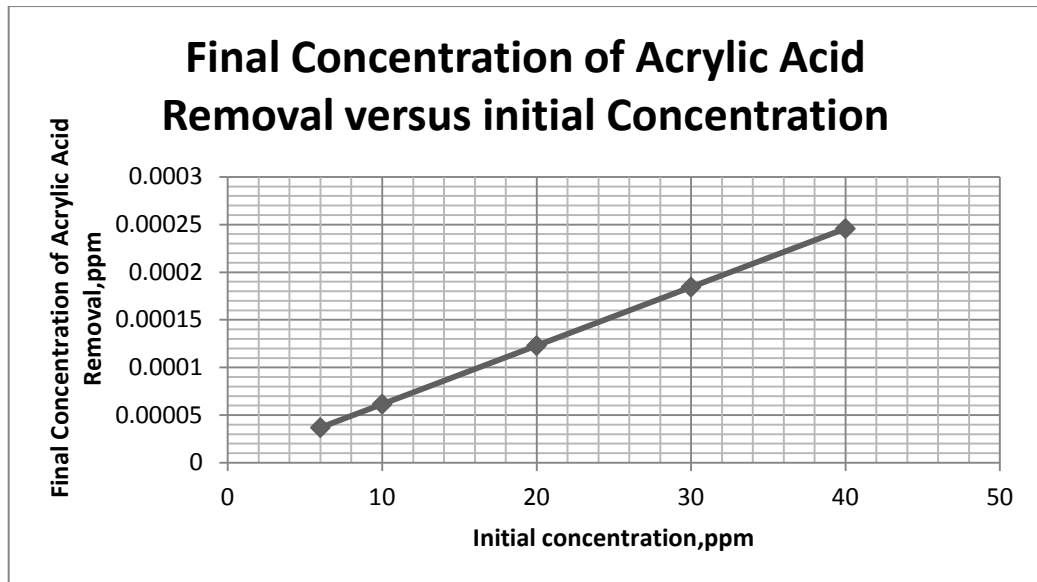
Figure A.5 Graph of simulation using Excel (concentration versus initial concentration)