

WASTEWATER TREATMENT BY CONTINUOUS STIRRED TANK
REACTOR (CSTR)

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ABSTRACT

The adsorption has been used for the industrial wastewater treatment, the batch and continuous studies were done. The aim of this study is to develop a new adsorption reactor to continuous removal of the contaminants which is the Continuous Stirred Tank Reactor (CSTR). The adsorbent used was the powdered activated carbon. By the batch studies, the equilibrium and kinetic parameters have been evaluated. Langmuir isotherm was been represented for equilibrium data and the 'unified approach model' which recently developed was been used to represent the kinetic data. The CSTR performance was studied and found that the CSTR operates as an ideal CSTR. Effect of initial concentration, contact time and adsorbent dosing rate on the dye removal efficiency in CSTR unit has been investigated.

RAWATAN SISA AIR OLEH TANGKI REAKTOR PENGACAU BERTERUSAN (CSTR)

ABSTRAK

Penjerapan telah digunakan untuk rawatan sisa air industri, kajian kelompok dan berterusan telah dilakukan. Tujuan kajian ini adalah untuk membangunkan reaktor penjerapan baru kepada penyingkiran berterusan bahan cemar iaitu Tanki Reaktor Pengacau Berterusan (CSTR). Adsorben yang digunakan adalah serbuk karbon aktif. Mengikut kajian kelompok, parameter keseimbangan dan parameter kinetik telah dinilai. Langmuir isoterma digunakan untuk data keseimbangan dan 'model pendekatan bersatu' yang baru dibangunkan untuk mewakili data kinetik. Prestasi CSTR telah dikaji dan didapati bahawa CSTR beroperasi sebagai CSTR yang ideal. Kesan kepekatan awal, masa interaksi dan kadar dos adsorben pada kecekapan penyingkiran pewarna dalam unit CSTR telah dikenalpasti.

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NOMENCLATURE

AC	Activated carbon
C_{AL}	Industrial authority limit, kg/m^3
C_i	Initial concentration, kg/m^3
C_e	Equilibrium concentration, kg/m^3
CSTR	Continuous stirred tank reactor
CV	Crystal violet
k_1	Adsorption rate constant, $\text{m}^3/\text{kg}\cdot\text{min}$
k_2	Desorption rate constant, min^{-1}
K	Langmuir empirical constant, m^3/kg
q	Amount adsorbed, kg/kg
q_e	Amount of heavy metal ion adsorbed at equilibrium, kg/kg
q_{\max}	Maximum capacity adsorption, kg/kg
q_t	Amount adsorbed at time t, kg/kg
q_{∞}	Maximum adsorption capacity for Langmuir model, kg/kg
R	Percentage removal, %
t	Time, min
u	Volumetric flow rate, $\text{m}^3/\text{min}^{-1}$
V	Reactor volume, m^3
w_a	Adsorbent dosage, kg/m^3

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Wastewater is the main factor of the water pollution. Therefore, the wastewater treatment is a mostly important process to reduce the water pollution. In the wastewater, it's containing a lot of harmful contaminants such as the lead, cadmium, manganese, zinc and etc (Rafatullah et al, 2009). Those heavy metals are very common found in the wastewater. As known, those contaminants are very dangers when the human or living species consume even contact with it. Those contaminants will affect the human health and kill the aquatic living in a given quantities.

In order to remove those contaminants from wastewater, adsorption process is carried out by industries before discharge the wastewater into the rivers. Adsorption is the effective way and widely use for contaminants removal from industrial wastewater (Barrear-Diaz et al, 2005). Adsorbent is used for adsorption process;

those adsorbents are normally in liquid or solid form to let the gas or liquid solute accumulates on its' surface.

Adsorption process has two types of removal techniques, which are batch process and continuous process. In the batch process, the adsorbents could be utilized up to its' maximum capacity. But it is not suitable for industrial uses because the industries continuously and largely producing wastewater, it need larger area to place the big reservoirs for storing the wastewater before treatment. It is costly and the process is needed a lot times to run. Therefore, the industrial wastewater treatment mostly using the continuous process. The fixed bed adsorption column is completely developed. The adsorbents beds are kept in a column for the wastewater to flow through it. But the bed is saturated with the adsorbate after operated and finally exhausted. The adsorbent has to be replaced when the bed is exhausted. Besides that, highly resistance and pressure drops in the operation due to the small size of adsorbent.

As sorption processes are mostly run in fixed-bed columns or batch reactors, literature dealing with the kinetics of sorption processes in CSTR is comparatively rare. According Datta, Croes and Rinker (1983), their studies give time domain solutions for the transient response of a CSTR for different cases of feed disturbances. From Loureiro, Costa, and Rodrigues (1988), their studies used a pore diffusion approach to fit effective diffusion coefficients to CSTR kinetic experiments. A more detailed discussion of the particularities of CSTR sorption processes is given by Chatterjee and Tien (1991). The CSTR that is used in these researches is not a perfect CSTR. Because on those CSTR the aqueous phase is fed

to the reactor continuously and a fixed bed of adsorbent is used. But for a reactor to be a true CSTR type adsorption unit both adsorbent and adsorbate must be fed to the reactor continuously. But in this study work a CSTR system is developed where both the adsorbate and adsorbent are fed to the reactor continuously. Therefore, the CSTR for wastewater treatment is needed to develop.

1.2 PROBLEM STATEMENT

From Regional Environment Awareness Cameron Highlands, it states that may be a lot of water on earth, but actually the fresh water are very insufficient for the humans demand. Around 3% of the water on earth is locked away in icecaps and glaciers or deep underground. For the remaining 97% of the water on earth is salt or undrinkable. For the human uses, actually only 0.003% of the water is available. Generally, there are main source of water pollution which is wastewater treatment plant. The government is strictly monitoring with the water quality in the area of wastewater treatment plant in order to reduce the water pollution.

Therefore, the industrial wastewater treatment is needed to control the water quality of the wastewaters. The removal of contaminants from wastewater is the important method in order to obtain the clean and safe water for human activities. The study of using adsorption of crystal violet dye using activated carbon is needed.

1.3 RESEARCH OBJECTIVES

The research Objectives of this study are

- 1.3.1 To develop a continuous stirred tank reactor (CSTR) system for industrial wastewater treatment.
- 1.3.2 To determine and optimize the performance of the CSTR.
- 1.3.3 To analyze the effects of initial concentration, residence time and adsorbent dosing rate on the dye removal efficiency in the CSTR unit.

1.4 SCOPE OF STUDY

The scope of study is to analyze the adsorption batch studies toward the process. Besides that, the effect of various parameters (adsorbent dosage, initial concentration and contact time) toward the adsorption of crystal violet dye is also one of the scopes for this study. By using the activated carbon as the adsorbent and the stock solution of crystal violet as the adsorbate to run the experiment of the study. The equipments will be used in this study are UV-Vis spectrophotometer, orbital shaker, and so on.

1.5 SIGNIFICANCE OF STUDY

This study is about to remove crystal violet that is one of the contaminant which cause an environmental pollution. These crystal violet cannot be destroyed as they are non-biodegradable. It can cause dangerous because it can spread out by food, water and air thus may expose a significant danger to human health (Kazemipour et al, 2008). The pollution will happen continuously as long as no immediate/effective action being taken. The study to remove these contaminants needs to be carried out. Adsorption is the alternative method to remove the contaminants instead of the conventional method such as ion exchange, reverse osmosis etc and it is such an economical method. Those adsorbents can be prepared and produced from agricultural waste such coconut shell, palm oil shell and etc. It means it can reduce agricultural waste and lower the cost to manage the waste.

CHAPTER 2

LITERATURE REVIEW

2.1 WASTEWATER

Wastewater defines as any water that has been adversely affected in quality by human activities influence. Wastewater is liquid waste discharged by domestic residences, commercial properties, industry, agriculture, which often contains some contaminants that result from the mixing of wastewater from different sources. Wastewaters are usually classified as industrial wastewater or domestic wastewater. Those contaminants in wastewater are suspended solid, biodegradable organics, pathogens, heavy metals and etc (Peavy et al, 1985). Wastewater contaminants will give the impacts on the environmental, human health and living activities. Environmental problem such pollution, will damage the aquatic living activities. Human health will be affected if they contact or consume that water that being polluted (Kazemipour et al, 2008). The contaminants containing in wastewater like dyes, lead, cadmium, manganese and etc (Rafatullah et al, 2009). These contaminants are non-biodegradable and easier to spread out by food, water, air and

etc. Several serious health effects including mutations, cancer, organ damage and death are caused by crystal violet dyes if in large quantities. The pollution and the human health problems will happen continuously as long as no effective action being taken and the human health will be worried.

According to research of the Department of Environment, the groundwater quality status was determined based on the National Guidelines For Raw Drinking Water Quality from the Ministry of Health (Revised December 2000) as the benchmark.

Table 2.1 Malaysia: National Guidelines for Raw Drinking Water Quality (Revised December 2000)

Parameter	Symbol	Benchmark (mg/l)
Sulphate	SO ₄	250
Hardness	CaCO ₃	500
Nitrate	NO ₃	10
Coliform	-	Must not be detected in any 100 ml sample
Manganese	Mn	0.1
Chromium	Cr	0.05
Zinc	Zn	3
Arsenic	As	0.01
Selenium	Se	0.01
Chloride	Cl	250
Phenolics	-	0.002
TDS	-	1000
Iron	Fe	0.3
Copper	Cu	1.0
Lead	Pb	0.01
Cadmium	Cd	0.003
Mercury	Hg	0.001

(Source: Ministry of Health, Malaysia)

2.2 DYE REMOVAL BY ADSORPTION PROCESS

Dye wastewater, which are discharge from the dyestuff manufacturing, dyeing, printing and textile industries (Lin et al, 2011). Most of the dyes used in industries are stable to light and oxidation as resistant to aerobic digestion. Several methods have been developed to removing of colour and dye such as coagulation, chemical oxidation, membrane separation, adsorption and so on. The best potential for all treatment is adsorption.

The adsorption process is a common and widely used in industries wastewater treatment. Adsorption process using the solid adsorbents is widely used to remove soluble substances from waters. The choosing an effective adsorbent is needed in order to run the adsorption process. There are two main types of adsorbent is used for adsorption, which are the low cost adsorbent and activated carbon.

2.2.1 Low Cost Adsorbent

Low cost adsorbent is generally refer to the natural materials and the wastes of industries that can used as adsorbent, which are directly used as adsorbent or just treat with the minor process as adsorbent. The low cost adsorbents are classified into two main types of adsorbent, which are natural materials and biosorbents.

Natural materials generally used as low cost adsorbents are the one existing in nature and used as such or with minor treatment. For natural materials, clays and zeolites are widely used as adsorbent for adsorption process. Among natural

materials, clays is occupied an outstanding position of their low cost, available in abundance and having high sorption properties. The price of clay is considered around 20 times cheaper than the activated carbon. The adsorption capabilities result from a net negative charge on the structure of minerals (McKay et al, 1985). This negative charge gives clays the capability to adsorb positively charge species. Their sorption properties also come from their high surface area and high porosity (Alkan et al, 2004). When clay minerals are used for industrial application, the swelling factor should be taken into account since it may cause remarkable pressure drop due to their different structural characteristics and ion-exchange mechanism (Babel et al, 2003).

Zeolites are a naturally occurring crystalline aluminosilicates consisting of a framework of tetrahedral molecules, linked with each other by shared oxygen atoms (Keane, 1998). Due to their low cost and available in abundance, the price of zeolite is very cheap depending on the quality of zeolite. However, low permeability of zeolites requires an artificial support when used in column operations (Babel et al, 2003).

2.2.2 Activated Carbon

The commercial activated carbons are usually derived from natural materials such as wood, coconut shell, lignite or coal, but almost any carbonaceous material may be used as precursor for the preparation of carbon adsorbents (Rozada et al., 2003). Therefore the commercial activated carbon is relatively high cost when compare to the using natural material or waste of industries as adsorbent. However,

an effective and widely way for water and wastewater treatment is been found, which is activated carbon adsorption due to the specific surface area and porosity.

Activated carbon is classified into two main forms, which are the powdered activated and granular activated carbon (Gupta et al, 2009). The fixed bed adsorption column for wastewater treatment is commonly using the granular activated carbon due to the size of the granular activated carbon which is most suitable and easy to be packed into the bed column. But for the batch process of wastewater treatment is using different type of activated carbon, which is powdered activated carbon. This is because of the surface area of the powdered activated carbon is larger than granular form, so it is most effective to used for batch process.

Small amount of adsorbent used can adsorb large quantities of adsorbate. The regeneration methods of activated carbon are used such as thermal, chemical and oxidation electrochemical (Chiang et al, 1997). The most common and widely used for regeneration methods is thermal regeneration. By using the regeneration, adsorbents can use again and again. Therefore, it make the activated carbon adsorption is become more economically. Some advantages of adsorption process for controlling water pollution, which are less space needed, lower capital investment, and easy for operation (Namasivayam et al, 1993).

Among all the adsorbent materials used, the most popular for the removal of chemical pollutants from wastewater is activated carbon (Babel et al, 2003; Ramakrishna et al, 1997). The effectiveness of adsorption on commercial activated carbons (CAC) for removal of a wide variety of dyes from wastewaters has made it

an ideal alternative to other expensive treatment options (Ramakrishna et al, 1997). Due to their great capacity to adsorb dyes, CAC are the most effective adsorbents. Due to their structural characteristics and their porous sizes which gives them a large surface area, and their chemical nature which can be easily modified by chemical treatment in order to increase their properties.

2.3 ADSORPTION TECHNIQUES

There are two types of removal techniques for adsorption process, which are batch process and continuous process.

2.3.1 Batch Process

In the batch process, the adsorbents could be utilized up to its' maximum capacity. However, it is not suitable for industrial uses because the industries continuously and largely producing wastewater, it need larger area to place the big reservoirs for storing the wastewater before treatment. It means a larger land is needed, therefore this process costly and a lot times is needed to complete this process. Therefore, the industries mostly using the continuous process for their wastewater treatment.

2.3.2 Continuous Process

Due to the imperfection of batch process, the continuous process is widely used for the industries wastewater treatment. For the continuous process, it has two types of system which are the fixed bed adsorption column and CSTR type adsorption unit.

2.3.2.1 Fixed Bed Adsorption Column

The fixed bed adsorption column is completely developed. The adsorbents beds are kept in a column for the wastewater to flow through it (Walker et al, 1997). But the bed is easier being saturated with the adsorbate particles after operated. Finally the bed is completely exhausted after certain time of process. The adsorbent has to be replaced when the bed is exhausted. The regeneration for the adsorption bed is needed when the bed is saturated. But the regenerate process of adsorbent is quite difficult and costly. Besides that, highly resistance and pressure drops in the operation due to the small size of adsorbent. Due to the inherent disadvantages of fixed bed adsorption column, the developing of the continuous stirred tank reactor (CSTR) type adsorption unit is needed.

2.3.2.2 Continuous Stirred Tank Reactor (CSTR) Type Adsorption Unit

As adsorption processes are mostly run in fixed-bed columns or batch reactors, studies dealing with the adsorption processes in CSTR are relatively less. According Datta, Croes and Rinker (1983), their studies give the time domain

solutions for the transient response of a CSTR for different cases of feed disturbances. From Loureiro, Costa, and Rodrigues (1988), their studies used a pore diffusion approach to fit effective diffusion coefficients to CSTR kinetic experiments. A more detailed discussion of the particularities of CSTR sorption processes is given by Chatterjee and Tien (1991). The CSTR that is used in these researches is not a perfect CSTR. Because on those CSTR the aqueous phase is fed to the reactor continuously and a fixed bed of adsorbent is used. But for a reactor to be a true CSTR type adsorption unit both adsorbent and adsorbate must be fed to the reactor continuously. But in this study work a CSTR system is developed where both the adsorbate and adsorbent are continuously fed to the reactor. Therefore, the CSTR for wastewater treatment is needed to develop.

CHAPTER 3

METHODOLOGY

3.1 MATERIALS

- i. Crystal violet
- ii. Powdered activated carbon
- iii. 0.1 M HCL
- iv. 0.1 M NaOH