REMOVAL OF ACETAMINOPHEN FROM AQUEOUS SOLUTION BY USING ACTIVATED CARBON DERIVED FROM SPENT TEA LEAVES

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Specially thanks to

my family,

my friends,

and

to all that involve in this master project….

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ABSTRACT

This study is about the removal of acetaminophen from aqueous solution by using activated carbon derived from spent tea leaves. Activated carbon was prepared by using phosphoric acid as chemical activating agents. The characteristics such as functional group, surface areas, pore volume, and morphology of activated carbon treated with H_3PO_4 (ACH) were identified by using Fourier Transform Infrared Spectroscopy (FTIR), Brunauer-Emmett- Teller (BET) and Field Emission Scanning Electron Microscopy (FESEM). The total surface areas and pore volume of ACH were 1,202.836m^2/g and 0.720cm^3/g, respectively. The effect of contact time, initial concentration, adsorbent dosage, pH and temperature were studied during the adsorption process. The highest removal percentage, 99.87% was achieved in the condition of initial concentration, adsorbent dosage; pH and temperature were 10 mg/L, 0.5g, pH 3 and ±25 ℃, respectively. To describe the equilibrium isotherm of adsorption, the experimental data were fitted into Langmuir and Freundlich isotherm models. The equilibrium data was followed to the Langmuir isotherm with the maximum capacity of 57.16 mg/g. Pseudo-first order, pseudo-second order and intraparticle diffusion kinetic models were used to analyze the kinetic equilibrium of adsorption process. The adsorption process of acetaminophen was followed Pseudo-second order kinetic. Negative values of ΔG^o (-1.1323 to -0.5071 kJ mol^{-1}), ΔH^o (-10.5754 kJ mol^{-1}) and ΔS^o (-31.0786 J/mol.K) indicated that the adsorption process of acetaminophen was feasible, spontaneous and exothermic in the condition of experiment. Based on the result, it can be concluded that activated carbon derived from spent tea leaves can be employed as low-cost activated carbon and remove acetaminophen from aqueous solution effectively.

ABSTRAK

Kajian ini tentang penjerapan acetaminophen daripada larutan akues dengan menggunakan karbon teraktif yang diperolehi daripada daun the buangan. Karbon teraktif telah disediakan dengan menggunakan asid forforik sebagai ejen penaktifan. Ciri-ciri seperti kumpulan berfungsi, luas permukaan, keliangan dan morfologi di karbon teraktif dengan H_3PO_4 (ACH) telah dikenal pasti dengan menggunakan Fourier Transform Infrared Spectroscopy (FTIR), Brunauer-Emmett Teller (BET), dan Field Emission Scanning Electron Microscopy (FESEM). Jumlah luas permukaan dan keliangan ACH adalah 1,202.836m^2/g dan 0.720cm^3/g. Kesan terhadap masa sentuhan, kepekatan awal, dos penjerapan, pH dan suhu telah dikaji semasa proses penjerapan. Penyingkiran acetaminophen yang tertinggi adalah 99,87% dan keadaan ini dicapai semasa dalam situasi kepekatan awal, dos penjerap, pH dan suhu adalah 10 mg/L, 0.5g, pH 3 dan ±25 ℃ masing-masing. Data eksperimen telah dianalisi dengan menggunakan model isotherm penjerapan: Langmuir dan Freundlich. Data eksperimen menunjukkan dengan baik oleh isoterma Langmuir dengan kapasiti maksimum 57.16 mg/g. Model kinetik pseudo-tertib pertama, pseudo-tertib kedua dan penyebaran intrapartikal telah digunakan untuk analisis keseimbangan kinetik proses penjerapan. Kadar penjerapan didapati mematuhi kinetik pseudo-tertib kedua. Nilai negatif piawai ΔG^o (-1.1323 hingga -0.5071 kJ/mol^{-1}), ΔH^o (-10.5754 kJ mol^{-1}) dan ΔS^o (-31.0786 J/mol.k) menunjukkan bahawa penjerapan acetaminophen boleh dilaksanakan dengan spontan dan eksortermik. Kesuluruhannya, keputusan menunjukkan bahawa karbon teraktif daripada daun teh buangan boleh digunakan sebagai karbon teraktif alternatif berkos rendah dan berkesan untuk penyingkiran acetaminophen daripada larutan akueus.

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LIST OF ABBREVIATIONS

AC0	-	Activated Carbon treated without treated with chemical
ACH	-	Activated Carbon treated with Phosphoric Acid
ACZ	-	Activated Carbon treated with Zinc Chloride
ACK	-	Activated Carbon treated with Potassium Carbonate
ACN	-	Activated Carbon treated with Sodium Hydroxide
AOPs	-	Advanced Oxidation Processes
BET	-	Brunauer-Emmett-Teller
CAS	-	Credential Assembly Service
CO_2	-	Carbon Dioxide
FESEM	-	Field Emission Scanning Electron Microscopy
FTIR	-	Fourier Transform Infra-Red
H_3PO_4	-	Phosphoric Acid
H_2SO_4	-	Sulfuric Acid
HCl	-	Hydrochloric Acid
HNO_3	-	Nitric Acid
IUPAC	-	International Union of Pure and Applied Chemistry
K_2CO_3	-	Potassium Carbonate
KOH	-	Potassium Hydroxide
NaOH	-	Sodium Hydroxide
NH_4Cl	-	Ammonium Cloride
NSAID	-	Nonsteroidal Anti-Inflammatory Drugs
STL	-	Spent Tea Leaves
UV	-	Ultra Violet
WHO	-	World Health Organization
$ZnCl_2$	-	Zinc Chloride

LIST OF SYMBOLS

Ce	-	Equilibrium concentration
Cm^3/g	-	Centimeter cubed per gram
Co	-	Initial concentration
g	-	Gram
g/mol	-	Gram per mol
hr (s)	-	Hour (s)
µg/L	-	Microgram per litre
µm	-	Micro Meter
g/mol	-	Gram/mole
g/cm^3	-	Gram per cubic centimetre
J	-	Joule
K	-	Kelvin
kJ	-	Kilo Joule
k1	-	Adsorption rate constant of first order adsorption
k2	-	Adsorption rate constant of second order adsorption
K_F	-	Freundlich constant
kJ/mol	-	Kilo Joule per mol
K_L	-	Langmuir constants related to the rate of adsorption
kp	-	Intraparticle diffusion rate constant
kV	-	Kilovolt
L	-	Liter
M	-	Molar
m^2/g	-	Meter square per gram
mg	-	Milligram
mg/g	-	Milligram per gram

mL	- Mililitre
mg/L	- Milligram per liter
min	- Minute
mm	- Milimetre
ng/L	- Nanograms/litre
nm	- Nanometre
q_e	- Amount of adsorbed on adsorbent at equilibrium
q_m	- Maximum adsorption capacity
q_t	- Amount of adsorbed on adsorbent at any time
R	- Universal gas constant
R_L	- Separation factor
ΔG^o	- Gibbs energy changes
ΔH^o	- Enthalpy change
ΔS^o	- Entropy change
°C	- Degree celcius
%	- Percentage
$<$	- Less than
$>$	- Greater than

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CHAPTER 1

INTRODUCTION

1.1 Background Study

Pharmaceutical compounds have been detected in surface and groundwater in recent years and this issue have attracted attention of the general public because these waters are used as potable water sources (Kolpin *et al.* 2002; Kim *et al.* 2007; Al-Odaini *et al.* 2011). Generally, pharmaceuticals compound and their metabolites were found in the range of micrograms/litre to nanograms/litre in surface water and groundwater (Daughton *et al.* 1999; Ternes *et al.* 2002; Huber *et al.* 2003; Huber *et al.* 2005). Although such concentrations have not revealed to cause any adverse health impacts towards human but they have shown to alter biological function of organisms. For example, the presence of antibiotics and hormones in the aquatic environment has led to the development of antibiotics resistant bacteria and feminization of fishes, respectively (Thorpe *et al.* 2003; Bound *et al.* 2004).

The discharge of domestic wastewater effluent is the prominent culprit for the presence of pharmaceutical compounds in the surface and groundwater, thus denoting that current wastewater treatment systems are not designed to remove pharmaceutical compounds from the wastewater (Ternes 1998; Carballa *et al.* 2004; Joss *et al.* 2005; Nikolaou *et al.* 2007; Vieno *et al.* 2007; Benitez *et al.* 2009).

Although, advanced treatment processes has shown higher efficiency rate than conventional treatments to eliminate pharmaceutical compounds, but these treatments required higher operation cost and consume more energy. Thus, this treatments are no longer attractive to apply in small scale due to cost inefficiency (Babel *et al.* 2003). Hence, many researches focus on finding other efficient alternative method to eliminate pharmaceutical compounds.

Adsorption has been proposed in recent years due to its low energy cost, environmental friendly, low energy consumption and high efficiency (Chen *et al.* 2011; Yakout *et al.* 2013; Xi *et al.* 2014; Tran *et al.* 2015). Activated carbons are widely applied as adsorbent in the adsorption process. However, the commercial activated carbons are derived from petroleum residual, coal, wood, peat and lignite which are non-renewable source and the cost is expensive. Thus, researches have been conducted by using the low cost materials such as inexpensive and renewable agriculture waste and lignocellulosic materials as activated carbon.

Tea is considered as second beverage after water in the world. However, once the tea leaves are brewed, it has no more profitable value and usually disposed as solid waste. The tea consumption have increased in recent years, in the other hand it means that the tea wastes have been disposed also increased (Cai *et al.* 2015; Tzeng *et al.* 2015). The increasing knowledge of the need for waste reduction and environmental protection has prompt for the possibility to reuse this waste. Thus, reuse of spent tea leaves as low-cost activated carbon not only reduce the quantity of solid waste, it also cost effective, environmental friendly as well as to replace the commercial activated carbon.

1.2 Problem Statement

In this study, the focused pharmaceutical compound is acetaminophen or known as paracetamol. It is the most popular over-the-counter (OTC) pain reliever to reduce headache, muscle ashes, arthritis, backache, toothaches, colds and fevers. The side effects of acetaminophen are includes hypersensitivity reactions and serious skin reaction and the most serious effect is liver failure due to the overdose.

The conventional wastewater treatment such as activated sludge and biodegradation are unable to eliminate pharmaceutical compounds effectively. There is residual found in the effluent discharge, surface and groundwater after the conventional wastewater treatment, even though the pharmaceutical compounds are detected in low concentration. Pharmaceutical compounds are not regulated as environmental pollutants and no listed in the WHO guidelines for the drinking water quality and legislation for the standard discharge limit for the wastewater and water treatment plants. Nevertheless, the drinking water should be free of pharmaceutical compounds to minimize the unpredictable health risks.

In order to achieve free pharmaceutical compounds in water source, adsorption has superior advantage over the other method in removing the pharmaceuticals compound with which is more environmental friendly, cost effective and high efficiency. Since the consumption of tea is the second beverage after the water in the world, the demand of tea consumption had increased in the recent years. However after consumption, the spent tea leaves are facing the problem of disposal. Thus, utilization of spent tea leaves is desirable. Using the agriculture waste as the low cost activated carbon has attracted the focus of the researches not only less cost, but also for environmental purpose to reduce the quantity of solid waste.

Previously, the studies on removal of pharmaceutical compounds using the low cost activated carbon such as agriculture waste are very limited. Many studies have focus on the adsorption of heavy metal, dyes and endocrine compounds by using the commercially activated carbon and low-cost activated carbon derived from pineapple peels, jackfruit peels, coconut shell and many others. Thus, this study exhibits the use of agriculture waste such as spent tea leaves as low-cost activated carbon as new trend which is cheaper and more environmental friendly.

1.3 Objectives

The objectives of this study were listed as follow:

(i) To synthesis and characterize activated carbon derived from spent tea leaves

(ii) To determine the effect of parameter, such as contact time, initial concentration, adsorbent dosage, pH, and temperature in acetaminophen removal

(iii) To analyze isotherm, kinetic, thermodynamic of the adsorption of acetaminophen onto activated carbon.

1.4 Research Scope

The goal of this research was to analyze the removal acetaminophen by using activated carbon derived from spent tea leaves as low-cost activated carbon. To achieve the goal, following tasks are carried out:

i. Preparation of activated carbon

Activated carbon was derived from spent tea leaves by using chemical activation method. Screening test was done among chemicals such as H_3PO_4, $ZnCl_2$, NaOH and K_2CO_3 to choose the potential removal chemical agents.

ii. Characterization of activated carbon:

The characteristic of activated carbon such as functional group, surface area, pore size, and surface morphology were identified by using Fourier Transform Infrared (FTIR) spectroscopy, Brunauer-Emmett-Teller (BET) and Field Emission Scanning Electron Microscopy (FESEM).

iii. Preparation of acetaminophen solution:

The sample used in this work prepared by dissolving the acetaminophen in distilled water to produce stock solution.

iv. Investigating the effect of the parameters:

Various parameters such as contact time (5-180 min), initial concentration of acetaminophen (10-100mg/L), adsorbent dosage (0.1-1.0g), pH (pH3- pH11) and temperature (30-50 ℃) were conducted to observe during the adsorption study.

v. Model Fitting:

The adsorption of acetaminophen by activated carbon derived from spent tea leaves was evaluated by using the models: equilibrium isothermal, kinetic and thermodynamics. For the equilibrium study, Langmuir and Freundlich isotherm models were applied. The Pseudo first-order, Pseudo second-order and intrapartice diffusion were applied for the kinetic study. The thermodynamics parameters of the adsorption of the adsorption of acetaminophen including the Gibbs free energy (ΔG), enthalpy (ΔH), entropy (ΔS) were calculated by using Van’t Hoff equation.

1.5 Research Significance

Pharmaceutical compounds have been detected in the surface and groundwater in recent years has attracted attention of the general public because these waters are used as potable water sources. However, these pollutants are not included in the legislation and WHO guidelines for drinking water quality. Although, the concentration detected are expected to be low, but there is no reliable information showed that there is no effect to human health in the long term. The acetaminophen is the most popular over-the-counter (OTC) pain reliever used in the worldwide. Fent *et al.* (2006) and Ziylan *et al.* (2011) had reported the most serious side effect of acetaminophen is liver failure if overdose.

The current wastewater treatments are unable to eliminate pharmaceutical compounds effectively to ensure the water is free of pharmaceutical compounds in the water source. Several techniques such as ozonation, photolysis, activated carbon, adsorption and many others have been developed to eliminate pharmaceutical compounds in treatment process. Among these techniques, adsorption has advantage over the other methods in eliminating pharmaceutical compounds which is environmental friendly and less costly.

Adsorption by using agriculture waste, industrial waste/by-product as the low cost activated carbon becomes part of the subject research interest. Findings ways to dispose the waste with minimal impact of the environmental is one the greatest challenge. Spent tea leaves were considered as waste after brewed, thus utilize the spent tea leaves as the low-cost activated carbon not only reduce the quantity of waste, it also bring tremendous environmental and economic benefits as well as limit the harmful effect by converting waste to wealth.

The used of spent tea leaves as low-cost activated carbon had been reported to remove heavy metals, phenols, and dyes (Amarasinghe *et al.* 2007; Ahmaruzzaman *et al.* 2010; Auta *et al.* 2011; Duran *et al.* 2011; Akar *et al.* 2013). However, there are limited studies on the removal of acetaminophen by using spent tea leaves as low-cost activated carbon. Thus, this study may provide an endeavor in promoting alternative technique for acetaminophen removal.

1.6 Thesis Outlines

This thesis contains five chapters. In Chapter 1 is about background study, problem statement, objectives, research scope and significance of this study. Chapter 2 is about reviews the literature those related to pharmaceutical compounds, adsorption process and activated carbon. Chapter 3 presents to the experimental setup, synthesis and characterization of the raw material and activated carbon derived from the spent tea leaves. The results and discussion are presented in Chapter 4. Finally, chapter 5 summarizes the finding of this research and provides the recommendation for the further studies.

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