REMOVAL OF ASPIRIN IN AQUEOUS USING ACTIVATED CARBON DERIVED FROM SPENT TEA LEAVES

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Specially dedicated to

my parents,

my siblings,

my beloved,

my best friends,

and

to all that involved in writing this thesis

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ABSTRACT

Aspirin is one of the most consumed drugs which can be found in aquatic environment. Even though the concentration is in trace amount, it may bring adverse impacts to human and environments. This study was conducted to i) synthesize and characterize activated carbon derived from spent tea leaves (AC-STL); ii) determine the effects of various parameters on the removal of aspirin by batch adsorption; iii) determine the adsorption isotherm, kinetic and thermodynamic behavior of the adsorption. Several types of adsorbent were synthesized such as raw spent tea leaves, untreated AC-STL, H_3PO_4 treated AC-STL, $ZnCl_2$ treated AC-STL and K_2CO_3 treated AC-STL. In a screening test for the best adsorbent to remove aspirin in aqueous, H_3PO_4 treated activated carbon derived from spent tea leaves (H_3PO_4-AC-STL) have the highest removal efficiency, thus it was used for further studies. H_3PO_4-AC-STL was characterized in terms of surface morphology, porosity and functional group using Field Emission Scanning Electron Microscopy, Micromeritics instrument and Fourier Transform Infrared Spectroscopy respectively. Batch study was conducted for H_3PO_4-AC-STL. The adsorption capacity was found to be dependent on reaction time, initial aspirin concentration, adsorbent dosage, pH and temperature. The highest removal efficiency observed was 94.28% after 60 minutes when the initial concentration was 100 mg/L, 0.5 g of adsorbent used, pH 3 and at a temperature of 30 ℃. The experimental data for adsorption of aspirin were well fitted into Freundlich isotherm model and obeyed pseudo-second order kinetics model. The adsorption of aspirin onto H_3PO_4-AC-STL was exothermic in nature ($\Delta H°$ = -13.808 kJ/mol) and have a negative entropy change, $\Delta S°$ (-41.444 J/mol). A negative Gibbs free energy, $\Delta G°$ was obtained indicating feasibility and spontaneity of the adsorption process. In conclusion, H_3PO_4-AC-STL could be employed as a low cost alternative to commercial activated in removal of aspirin in aqueous.

ABSTRAK

Aspirin merupakan salah satu ubat yang paling kerap diguna, di mana ia boleh didapati di persekitaran akuatik. Walaupun kepekatan aspirin di persekitaran akuatik adalah surih, tetapi ia mungkin membawa impak negatif kepada manusia dan persekitaran. Kajian telah dijalankan untuk i) sintesis dan mencirikan karbon teraktif sisa daun teh (AC-STL); ii) menyiasat beberapa kesan parameters bagi penyingkiran larutan aspirin dalam ujian berkelompok; iii) menyiasat tingkah laku isotherma, kinetik dan thermodinamik bagi penjerapan larutan aspirin. Beberapa bahan penjerap telah disintesis seperti sisa daun teh, karbon teraktif yang tidak dirawat, karbon teraktif yang dirawat dengan asid fosforik, karbon teraktif yang dirawat dengan zinc klorida dan karbon teraktif yang dirawat dengan potassium karbonat. Didapati karbon teraktif yang dirawat dengan asid fosforik (H_3PO_4-AC-STL) mempunyai kecekapan penyingkiran larutan aspirin yang tertinggi, maka ia dikaji dengan lebih lanjut. H_3PO_4-AC-STL telah dicirikan berdasarkan morfologi permukaan, keliangan, dan kumpulan berfungsi. Kapasiti penjerapan didapati bergantung kepada masa sentuhan, kepekatan awal aspirin, dos penjerap, pH dan suhu. Kecekapan penyingkiran tertinggi yand direkod ialah 94.28% selepas 60 minit ujian penjerapan berkelompok dengan menggunakan kepekatan awal aspirin = 100mg/L, dos penjerap = 0.5g, pH larutan = 3 serta pada suhu 30 ℃. Data eksperimen untuk penjerapan aspirin dalam larutan yang diperolehi, dapat dipadankan dalam model isoterma Freundlich dan memetuhi model kinetik pseudo-tertib kedua. Penjerapan aspirin dalam larutan bersifat eksotermik ($\Delta H°$ = -13.808 kJ/mol) dan mempunyai nilai negatif bagi perubahan entropi, $\Delta S°$ (-41.444 J/mol). Nilai negatif piawai tenaga bebas Gibbs, $\Delta G°$ menunjukkan kespontanan proses penjerapan aspirin dalam larutan oleh H_3PO_4-AC-STL. Kesimpulannya, H_3PO_4-AC-STL boleh digunakan sebagai bahan penjerap alternatif berkos rendah bagi menggantikan karbon teraktif komersial dalam penyingkiran aspirin dalam larutan.

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LIST OF ABBREVIATIONS

AC	-	Activated Carbon
BET	-	Brunauer-Emmett-Teller
CO_2	-	Carbon Dioxide
FTIR	-	Fourier Transform Infra-Red
H_2O	-	Water
H_3PO_4	-	Phosphoric Acid
HCl	-	Hydrochloric Acid
H_2SO_4	-	Sulfuric Acid
KOH	-	Potassium Hydroxide
K_2CO_3	-	Potassium Carbonate
KCH_3COO	-	Potassium Acetate
N_2	-	Nitrogen Gas
NaOH	-	Sodium Hydroxide
NaCl	-	Sodium Chloride
NSAIDs	-	Non-steroidal anti-inflammatory drugs
UV	-	Ultra Violet
STL	-	Spent Tea Leaves
$ZnCl_2$	-	Zinc Chloride

LIST OF SYMBOLS

C_e	-	Equilibrium concentration
C_0	-	Initial concentration
g	-	Gram
g/mol	-	Gram per mol
hr (s)	-	Hour (s)
μm	-	Micro Meter
J	-	Joule
K	-	Kelvin
K_{eq}	-	Equilibrium constant
k_1	-	Adsorption rate constant of first order adsorption
k_2	-	Adsorption rate constant of second order adsorption
K_F	-	Freundlich constant
kg	-	Kilogram
kJ	-	Kilo Joule
kJ/mol	-	Kilo Joule per mol
K_L	-	Langmuir constants related to the rate of adsorption
k_{int}	-	Intraparticle diffusion rate constant
L	-	Liter
M	-	Molar
m^2/g	-	Meter square per gram
mg	-	Milligram
mg/g	-	Milligram per gram
mg/L	-	Milligram per liter
min	-	Minute
mg/g	-	Miligram per gram

mg/L	-	Miligram per Liter
mm	-	Millimeter
n	-	Freundlich constant
nm	-	Nanometer
℃	-	Degree celcius
q_e	-	Amount of adsorbent at equilibrium
q_t	-	Equilibrium rate constant
q_{max}	-	Maximum adsorption capacity
R	-	Universal gas constant
R^3	-	Correlation coefficient
T	-	Absolute solution temperature
t	-	Time
$t^{0.5}$	-	Half-life time
V	-	Volume
W	-	Weight of adsorbent
wt%	-	Weight percent
$\Delta G°$	-	Gibbs Free Energy
$\Delta H°$	-	Enthalpy
$\Delta S°$	-	Entropy

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CHAPTER 1

INTRODUCTION

1.1 Background Study

Pharmaceutical compounds are widely consumed by humans to prevent or treat diseases, however some pharmaceuticals may bring adverse effects to human or environment. Many studies reported that pharmaceutical compounds and its metabolites are commonly detected in wastewater, sewage, surface water, ground water and even drinking water with concentration range from nano-gram/liter (ng/L) to micro-gram/liter (μg/L) (Ternes 1998; Hirsch *et al.* 1999; Kim *et al.* 2007; Zwiener 2007; Benotti *et al.* 2008; Mompelat *et al.* 2009; Sim *et al.* 2010).

Pharmaceutical compounds in aquatic environment are mostly come from sewage from residential, medical facilities and pharmaceutical manufacturers. Pharmaceuticals compounds are consumed, adsorbed and excreted to sewage sewers either in its parent compound or in a more polar and soluble forms of metabolites or conjugates(Kummerer 2001; Heberer 2002, 2002; Radjenović *et al.* 2009; Sim *et al.* 2010). This become an emerging issue to the world as the presence of pharmaceutical compounds are not known for its effect to human and environment even though the concentration found are low. In addition, current legislation and law does not set a standard concentration limit for pharmaceutical compounds thus, it leads to current water and wastewater treatments are not meant to remove pharmaceutical compounds (World Health Organization 2011).

Many researchers seek different removal methods from conventional to advanced water and wastewater treatment. Among the methods, adsorption was claimed to be one of the most effective treatment and widely used in other industries. This is because adsorption is advantageous in operational perspective such as capabilities to treat large volume and different pollutants at a time, simplicity of its design and operation, lower energy required and adsorbent can be regenerated for reuse (Crittenden *et al.* 2012).

However commercial activated carbon is expensive. Hence, researchers around the world are looking for more economical and environmental friendly replacement for the precursor of commercial adsorbent. One of the replacements is agricultural waste which is abundant and can be obtained easily. Example of agricultural waste are rice husk (Vadivelan & Kumar 2005), durian peel (Lazim *et al.* 2015), hazelnut shell, almond shell, walnut, poplar, saw dust (Ahmad *et al.* 2009), jackfruit peel (Hameed 2009), tea waste (Amarasinghe & Williams 2007; Uddin *et al.* 2009) and many more were studied for its efficiency in adsorption.

Most of this adsorbent were studied in lab-scale and used synthetic effluent where the aqueous solution was mixed with pollutant of interest. This is to prevent the complexity of the real effluents in optimizing the removal process. In addition, using synthetic effluent can prevent imprecise results which may lead to improper design of treatment system.

1.2 Problem Statement

Current commercial activated carbon is expensive, thus researchers around the world are searching for cheaper raw material to reduce the cost. Many cheap natural material or waste/ by-products of industries or synthetically prepared were investigated. Spent tea leaves and tea wastes are one of the potential sources for precursor of activated carbon. This is because tea is the most consumed beverage after water (Awasom 2011). According to Euromonitor, Worldbank in 2014, Malaysia was ranked 21st in the world for the average tea consumption of about 0.5 kg per capita per year. On top of that, tea leaves are biodegradable, non-toxic and commonly found in every household.

In previous studies tea waste or spent tea leaves were modified either physically or chemically to increase the efficiency of pollutants removal. For examples, some studies modified the tea waste or spent tea leaves by impregnated magnetic nanoparticle onto the surface, physically activated the carbon in high temperature, bases treated and others (Nasuha & Hameed 2011; Panneerselvam *et al.* 2011; Peng *et al.* 2013; Weng *et al.* 2014). However, most of these studies were not meant for removal of pharmaceutical compounds.

Previous studies used tea waste as adsorbent to remove dyes and heavy metals but only a few studies reported the efficiencies of tea waste to adsorb pharmaceutical compounds (Tee & Khan 1988; Amarasinghe & Williams 2007; Uddin *et al.* 2009; Nasuha *et al.* 2010; Dutta *et al.* 2015). High removal rate and adsorptive capacities can be found in Seedher and Sidhu (2007) study using spent tea leaves as biosorbent to remove several pharmaceutical compounds. Based on Dutta *et al.* (2015) study on removal of acetaminophen using microwave activated carbon derived from tea waste, the removal rate is high and the adsorption capacities was found to be about 200mg/g. Thus, there is a possibility of using tea waste or spent tea leaves for the removal of pharmaceutical compounds.

In addition, few activated carbons were derived from spent tea leaves using chemical activation, but none of this adsorbent were employed for the removal of pharmaceutical compound (Auta & Hameed 2011; Duran *et al.* 2011; Gundogdu *et al.* 2012; Gurten *et al.* 2012; Akar *et al.* 2013; Gundogdu *et al.* 2013). There is one study conducted by Ahmaruzzaman and Gayatri (2010), they did the removal of p-nitrophenol using phosphoric acid treated activated carbon derived from spent tea leaves. The reported results indicate a high removal efficiency (>95%) and adsorptive capacities.

In this study, the focused pharmaceutical compound is aspirin or known as acetylsalicylic acid (ASA) which is can be easily obtained as it is over-the-counter medication. ASA was known for its teratogenicity in rats and was categorized as potentially harmful pharmaceutical compounds towards aquatic. In human, ASA can cause skin, eye, and upper respiratory tract irritation (i.e asthma) upon direct contact and gastrointestinal bleeding if chronic ingested. However, studies on removal of aspirin using adsorption were limited to biosorbent, commercial activated or nanocomposite polymers generated using microwave assisted polyol method (Beninati *et al.* 2008; Mphahlele *et al.* 2015; Rakić *et al.* 2015). Hence, present study was conducted to study the removal of aspirin using chemically activated spent tea leaves.

1.3 Objectives

The objectives of this study were as follows:

i. To synthesis and characterize activated carbon derived from spent tea leaves (AC-STL).

ii. To determine the effect of parameters such as, contact time, initial aspirin concentration, pH, temperature and adsorbent dosage.
iii. To determine the adsorption isotherm, kinetic and thermodynamic behavior of aspirin onto the AC-STL.

1.4 Research Scope

The aim of this study was to evaluate the adsorption capacities of AC-STL to remove aspirin in aqueous solution. In order to achieve the aim, following tasks were carried out:

i. Chemical activation of spent tea leaves prior carbonization using different chemical activating agents.
ii. Screening test to select the best chemical activating agent to produce activated carbon with best removal of aspirin in aqueous.
iii. Characterization of best aspirin removal AC-STL for its surface area and surface morphology using Brunauer-Emmett-Teller (BET) analysis and Field Emission Scanning Electron Microscopy (FESEM) and its functional group toward the adsorption of aspirin using Fourier Transform Infrared (FTIR) spectroscopy.
iv. Preparation of aspirin stock solution.
v. Investigation of the effect of various parameters such as, contact time (0-180 minutes), initial aspirin concentration (100-500 mg/L), adsorbent dosage (0.1-1.0g), pH (3-11) and temperature (30-50 ℃).
vi. Model fitting of experimental data using the adsorption isotherm models (i.e Freundlich and Langmuir Isotherms), kinetic models (i.e Pseudo-first and Pseudo-second order and intraparticle diffusion) and thermodynamic study (i.e Gibbs free energy (ΔG), enthalpy energy (ΔH) and entropy energy (ΔS)) for adsorption of aspirin onto the AC-STL.

1.5 Research Significance

As discussed in earlier sections, pharmaceutical compounds are one of the emerging issues of concern to human. The detection of these compounds may be low in concentration but it may possess the risk to human and environment. The release of these compounds into environment may causes adaptation in certain bacteria or viruses to be immune to available drugs. In addition, some pharmaceutical compounds were known to affect endocrine system of aquatic animals and causes changes in ecosystem.

In this study, one of the pharmaceutical compounds, acetylsalicylic acid or known as aspirin was investigated. Cleuvers (2004) reported aspirin as potentially harmful drugs to environment, using established method by European Unions. Hence, the study on removal of aspirin is important for future water and wastewater treatment design.

Other than that, the commercial activated carbons are costly, thus the usage of tea waste or spent tea leaves may be another potential replacement of precursor for activated carbon in water and wastewater treatment industry. In this study, AC-STL using chemical activation such as phosphoric acid (H_3PO_4), zinc chloride ($ZnCl_2$) and potassium carbonate (K_2CO_3) may provide a new possibility of advancement in this industry. Previous studies only reported the usage of tea waste or spent tea leaves activated carbon derived from physical and chemical activation for the removal of heavy metals, phenols and ionic dyes which are commonly used in textile industry (Gundogdu *et al.* 2012; Khosla *et al.* 2013; Wan *et al.* 2014). However, only a few studies that used tea waste or tea waste derived activated carbons for the removal of pharmaceuticals specifically aspirin (Beninati *et al.* 2008; Mphahlele *et al.* 2015;

Rakić *et al.* 2015). Consequently, this study may provide a better solution in removal of aspirin using the stated chemicals treated AC-STL.

1.6 Thesis Outline

This study comprised of five chapters:

Chapter 1 **:** Introduction for the background of study, problem statement, objectives of study, research scope and significance of this study.

Chapter 2 **:** Literature review of pharmaceutical compound specifically aspirin, current removal of pharmaceutical compounds, adsorption, effects of various parameters, isotherms model, kinetic model and thermodynamic.

Chapter 3 **:** Methodology to conduct this study which includes synthesis and characterization of AC-STL and procedure to study the effects of various parameters in adsorption of aspirin using AC-STL.

Chapter 4 **:** Result and discussion of the analyzed experimental result.

Chapter 5 **:** Conclusion of this study and recommendation for future study.

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