SYNTHESIS AND UTILIZATION OF β-CYCLODEXTRIN MODIFIED CHITOSAN FOR THE ADSORPTION OF ASPIRIN

MUHAMMAD ASYIQ BIN AZMAN

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Philosophy

School of Chemical and Energy Engineering
Faculty of Engineering
Universiti Teknologi Malaysia

AUGUST 2019

DEDICATION

To my beloved parents,

Azman Bin Mohd Shah

Rohayati Binti Mohd Salleh

To my supervisor,

Assoc. Prof. Dr. Norzita Nagdi

Also to all my friends,

Thank you for your love, support and guidance.

ACKNOWLEDGEMENT

In the name of Allah, the Most Gracious and the Most Merciful. Alhamdullilah, all praises to Allah for giving me the strength, patience and knowledge in completing this thesis.

A deepest appreciation to my supervisor, Assoc. Prof. Dr. Norzita Ngadi for her guidance and support throughout the completion of this thesis. I would like to express a special gratitude to my parents for their loves, supports and blessings. Last but not least, thanks to all my friends for their support during my study.

To those who indirectly contributed in this research, your kindness means a lot to me. Thank you very much. May Allah S.W.T. bless and reward them for their kindness and generosity.

ABSTRACT

Chitosan is a very versatile substance in terms of its usage. It has a number of uses ranging from agricultural to medicinal usage. In adsorption study, chitosan is a very promising material as it can be used to adsorb a variety of waste such as dyes, metal ions and pharmaceutical. This particular ability can be attributed to the presence of amino and hydroxyl group in its molecules. However, these reactive groups tend to form hydrogen bond with each other and greatly reduces the adsorption efficiency of chitosan. A lot of research have been done in order to improve the adsorption efficiency of chitosan. One of the methods used is by modifying the surface of chitosan with another chemical. In this study, chitosan was modified with β-cyclodextrin by using impregnation method. The response for this study was the removal of aspirin in an aqueous solution. This study was conducted to synthesize and characterize chitosan modified with β-cyclodextrin, to determine the adsorption performance of the adsorbent for aspirin removal and analyze the adsorption mechanism of the adsorbent for aspirin removal. Chitosan was modified without using any harmful and hazardous chemical. The β-cyclodextrin was initially dissolved in distilled water before being mixed with the chitosan. After 30 minutes of mixing, the resulting solid was filtered and dried at 60 °C before being subjected to adsorption study. The characterization of the adsorbents was conducted using Fourier transform infrared spectroscopy, point of zero charge, carbon, hydrogen, nitrogen and sulphur analysis, Field emission scanning electron microscopy and Brunauer-Emmett-Teller analysis. The adsorption kinetics were studied using the pseudo-first and pseudo-second order kinetic model and Elovich equation. The adsorption isotherm was studied using the Freundlich, Langmuir, Temkin and Dubinin-Radushkevich isotherm model. The adsorption thermodynamics was determined by studying the changes in enthalpy, changes in standard entropy and Gibbs free energy. The result shows an improvement in adsorption capacity when chitosan was modified with β-cyclodextrin. The maximum adsorption capacity of chitosan was 236.97 mg/g while the maximum adsorption capacity for β-cyclodextrin modified chitosan was 359.87 mg/g which is an increase of 51%. The best condition for the removal of aspirin is 10 minutes of contact time, pH 3, 30 ºC temperature, 500 mg/L initial concentration of aspirin and 0.05 g of adsorbent. The results of the model fitting showed that the adsorption of aspirin onto the adsorbent occurs via physical adsorption.

ABSTRAK

Kitosan adalah bahan serba boleh dari segi kegunaannya. Ia mempunyai beberapa kegunaan merangkumi bidang pertanian hingga perubatan. Dalam kajian penjerapan, kitosan adalah bahan yang sangat berpotensi kerana ia boleh digunakan untuk menjerap pelbagai sisa seperti pencelup, ion logam dan farmaseutikal. Keupayaan ini boleh dikaitkan dengan kehadiran kumpulan amino dan hidroksil dalam molekul kitosan. Akan tetapi, kumpulan-kumpulan ini cenderung untuk membuat ikatan hidrogen antara satu sama lain dan menurunkan kecekapan penjerapan kitosan. Terdapat banyak penyelidikan yang telah dilakukan untuk meningkatkan kecekapan penjerapan kitosan. Salah satu kaedah yang digunakan adalah dengan mengubahsuai permukaan kitosan dengan bahan kimia lain. Dalam kajian ini, kitosan telah diubah suai dengan β-siklodekstrin dengan menggunakan kaedah rendaman. Respon untuk kajian ini adalah penyingkiran aspirin dari larutan air. Kajian ini dijalankan untuk mensintesis dan mencirikan kitosan yang diubahsuai dengan β-siklodekstrin, untuk menentukan prestasi penjerap untuk penyingkiran aspirin dan menganalisis mekanisme penjerapan penjerap untuk penyingkiran aspirin. Kitosan diubahsuai tanpa menggunakan bahan kimia yang berbahaya. β-siklodekstrin pada awalnya dilarutkan dalam air suling sebelum dicampur dengan kitosan. Selepas 30 minit percampuran, pepejal yang terhasil ditapis dan dikeringkan pada suhu 60 °C sebelum digunakan dalam kajian penjerapan. Pencirian penjerap dilakukan dengan menggunakan spektroskopi transformasi inframerah Fourier, titik cas sifar, analisis karbon, hidrogen, nitrogen dan sulfur, imbasan pancaran lapang elektron mikroskop dan analisis Brunauer-Emmett-Teller. Kinetik penjerapan telah dikaji menggunakan model kinetik pseudo tertib-pertama, pseudo tertib-kedua dan persamaan Elovich. Isoterma penjerapan telah dikaji menggunakan model isoterma Freundlich, Langmuir, Temkin dan Dubinin-Radushkevich. Termodinamik penjerapan ditentukan dengan mengkaji perubahan entalpi, perubahan entropi standard dan tenaga bebas Gibbs. Keputusan kajian menunjukkan peningkatan kapasiti penjerapan apabila kitosan diubah suai dengan β-siklodekstrin. Kapasiti penjerapan maksimum kitosan ialah 236.97 mg/g manakala kapasiti penjerapan maksimum untuk kitosan yang diubahsuai dengan β-siklodekstrin adalah 359.87 mg/g yang merupakan peningkatan sebanyak 51%. Keadaan terbaik untuk penyingkiran aspirin adalah 10 minit masa sentuhan, pH 3, suhu 30 ºC, 500 mg/L konsentrasi awal aspirin dan 0.05 g penjerap. Keputusan dari penyesuaian model menunjukkan penjerapan berlaku melalui penjerapan fizikal.

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LIST OF ABBREVIATIONS

AOPs	-	Advanced Oxidation Processes
BET	-	Brunauer-Emmett-Teller
BPA	-	Bisphenol A
CAS	-	Chemical Abstracts Service
CBC	-	Chitosan modified with β-Cyclodextrin
CBZ	-	Carbamazepine
CDCM	-	β-Cyclodextrin–chitosan modified Fe_3O_4 nanoparticles
CHNS	-	Carbon, Hydrogen, Nitrogen and Sulphur
CM-β-CD	-	Carboxymethyl-β-cyclodextrin
COD	-	Chemical Oxygen Demand
Cr(VI)	-	Hexavalent chromium
Cs/WCG	-	Chitosan/Waste Coffee-Ground
Cu(II)	-	Copper ion
DMAP	-	4-Dimethylaminopyridine
DMF	-	Dimethylformamide
D-R	-	Dubinin-Radushkevic
EDC	-	Carbodiimide hydrochloride
EDTA	-	Ethylenediaminetetraacetic acid
Fe(II)	-	Ferrous ions
Fe/N-CNT/β-Cyclodextrin	-	Incorporated zero valent iron (Fe) onto the N-CNT/β-Cyclodextrin
Fe_3O_4/β-CD/GO	-	Magnetic β-cyclodextrin-graphene oxide
FESEM	-	Field Emission Scanning Electron Microscopy
FTIR	-	Fourier Transform Infrared
H_2O_2	-	Hydrogen peroxide
HPMC-βCD	-	β-cyclodextrin hydroxypropyl methylcellulose
LC-MS	-	Liquid Chromatography coupled to Mass Spectrometry
LC-MS2	-	Liquid Chromatography coupled to Tandem Mass Spectrometry

MAO	-	Magnetic amidoxime
MB	-	Methylene blue
MCM-41	-	Mobil Composition of Matter No. 41
MDL	-	Minimum Detection Limit
MS2	-	Tandem Mass Spectrometry
NaOH	-	Sodium hydroxide
N-CNT/β-Cyclodextrin	-	Nitrogen doped carbon nanotube-β-Cyclodextrin composite
NH_4Cl	-	Ammonium chloride
NHS	-	Hydroxyl succinimide
NSAIDs	-	Nonsteroidal Anti-Inflammatory Drugs
O_3	-	Ozone
OFAT	-	One-Factor-at-A-Time
PbO_2	-	Nickel doped lead dioxide
PCC	-	Phosphonium-enhanced chitosan
pHpzc	-	Point of Zero Charge
SIL	-	sildenafil citrate
THF/DMF	-	Tetrahydrofuran/dimethylformamide
THPS	-	Tetrakis(hydroxymethyl)phosphonium sulfate
TOC	-	Total Organic Carbon
UV-Vis	-	Ultraviolet visible
WHO	-	World Health Organization
WWTP	-	Wastewater Treatment Plant

LIST OF SYMBOLS

ΔH	-	Changes in enthalpy
ΔS	-	Changes in standard entrop
ΔG	-	Gibbs free energy
mg/g	-	Milligram per gram
%	-	Percentage
ºC	-	Degree celcius
mg/L	-	Milligram per litre
g	-	Gram
ng/L	-	Nanogram per litre
g/mol	-	Gram per mole
g/cm^3	-	Gram per centimetre cube
mm Hg	-	Millimetre mercury
mL	-	Millilitre
mg/kg/day	-	Milligram per kilogram per day
mg/day	-	Milligram per day
K_{ow}	-	Octanol-partition coefficient
K_d	-	Dissociation coefficient
kJ/mol	-	Kilojoule per mole
mmol/g	-	Millimole per gram
g/g	-	Gram per gram
min	-	Minute
L/mg	-	Litre per milligram
J/mol K	-	Joule per mole kelvin
K	-	Kelvin
mol^2/kJ	-	Mole square per kilojoule
R^2	-	Coefficient of determination
χ^2	-	Chi-squared

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

The detection of pharmaceutical compounds in surface and groundwater have made the topic of pharmaceutical waste a highly discussed issues. This is because of the fact that these compound might be bioactive in the environment [1]. Due to the advancement of analysis technology, pharmaceutical compounds have been detected in small amount ranging from micrograms/litre to nanograms/litre [2-4]. This is a very concerning phenomenon as it will affect the quality of natural water, thus affecting the ecosystem and might impact human drinking water supplies [5, 6]. Although there is a lack of knowledge on the adverse effect of these compounds on human health, the effect of the pharmaceutical compounds on the environment can be clearly seen. The presence of antibiotics in aquatic environment has given rise to the antibiotic-resistance bacteria [7]. Besides that, the feminization of fishes, where male fishes turn into female, has been observed due to the presence of hormones in the fishes' habitat [8].

Aspirin is one of the most widely known and used pharmaceutical compounds in the world. In many countries, aspirin usage and consumption is rated the highest among all of the pharmaceutical compounds [9-12]. This can be attributed to the fact that aspirin is easily acquired as an over-the-counter medication mainly used to treat pain and fever. Aspirin may cause allergic reaction when absorbed through the skin [12]. At higher dose such as in the case of overdose, it can lead to gastrointestinal bleeding [13].

Hospital wastes, pharmaceutical industry wastes and human excretion are the major culprit of the presence of pharmaceutical compounds in surface and groundwater [14-18]. This is worrisome as it indicates that the current wastewater treatment is not capable of treating these compounds. Advanced treatment such as photo-catalytic degradation and membrane filtration have shown promising resulst in eliminating pharmaceutical compounds as they have higher efficiency compared to conventional treatment. However, these advanced treatments have their own drawbacks that limit their usage as they are complex and have high operating cost [19].

In recent years, the popularity of adsorption have been increasing due to their high efficiency, low cost, practicality and environmentally friendly[20, 21]. Activated carbon is the most well-known adsorbent being used today. However, despite all of its advantages, commercial activated carbon is derived from non-renewable sources such as coal [22-24]. This has prompted researchers to find adsorbents that are less expensive, abundant and derived from renewable material such as chitosan [25], clay [26], fly ash [27], agriculture waste[28], and biowaste [29].

Chitosan is seen as a very promising adsorbent because of its versatility in adsorbing different types of adsorbate such as dye [30], heavy metal [31], crude oil [32] and pharmaceuticals [33]. Besides that, chitosan also boosts a lot of other useful attributes such as biocompatibility, biodegradability and non-toxicity. These intriguing characters have led researchers to find ways to further improve the adsorption efficiency of chitosan. One of the ways is by functionalizing the surface of chitosan with another chemical or substance. The most common ways to do this are by crosslinking and grafting. Some of the modification that has been done to chitosan are with pandan extract [34], β-cyclodextrin [35], epichlorohydrin-triphosphate [36] and graphene oxide [37].

1.2 Problem Statement

Chitosan is a multifunctional substance. It has a number of uses and is utilized in a lot of different areas such as agriculture and medical. In terms of wastewater treatment, a lot of research have been done on the use of chitosan as an adsorbent for a number of different wastes. The vast usage of chitosan in different field can be attributed to its favourable characteristics such as renewability, biocompatibility, biodegradability and non-toxicity. Moreover, chitin, the raw material for producing chitosan, is the second most abundant biopolymer making the usage of chitosan sustainable in the long run.

Unfortunately, chitosan also has some poor characteristics that poses a challenge in its application, especially for wastewater treatment. Due to the presence of amino and hydroxyl groups in chitosan, the linear chains of chitosan tend to form hydrogen bond with each other thus becoming crystallized. This, in turn, makes chitosan insoluble in water, alkaline solution and most organic solvent. Besides that, since the amino and hydroxyl groups are the reactive component of chitosan, the rigid crystallized structure limits the accessibility and interaction between these groups and the adsorbate molecule in the wastewater.

These limitations prompted researchers to find ways to overcome the drawbacks of chitosan. The most investigated way is by modification of the chitosan itself. This can be done by a lot of different modification methods such as crosslinking and grafting. The reactive groups on the chitosan provided a good site for these modifications to take place.

Although modifications of chitosan shows some promising improvement, it should still be noted that the modification involved the usage of harmful chemicals such as 4-Dimethylaminopyridine (DMAP) and formaldehyde, complex and time-consuming processes. For this reason, there is a necessity for a more simple method of modification that also uses less harmful chemicals. This study does not use any harmful chemicals and the process to synthesis the adsorbent was very simple. It only involves the usage of distilled water as the solvent for preparing the β-cyclodextrin solution before impregnating chitosan in the solution for a short period of time.

β-cyclodextrin is a compound derived from starch with the sugar molecule bonded together in a ring. Since it is a product of the enzymatic conversion of starch,

(b) Characterization of adsorbent: The characteristic of the adsorbent such as functional group, surface morphology and surface area were identified by using Fourier Transform Infrared (FTIR) spectroscopy, point of zero charge (pH_{pzc}), CHNS analysis, Field Emission Scanning Electron Microscopy (FESEM) and Brunauer-Emmett-Teller (BET) surface area analysis.

(c) Investigate the effect of adsorption parameters: Various parameters such as contact time (0.5-2.0 hours), pH (pH3- pH11), temperature (30-90ºC) initial concentration of aspirin (100-500mg/L) and adsorbent dosage (0.05-0.6g) were conducted during the adsorption study

(d) Investigate the adsorption kinetics, isotherms and thermodynamics: The adsorption kinetics was studied using pseudo-first order and pseudo-second order kinetic model and Elovich equation. The adsorption isotherm was studied using Freundlich, Langmuir, Temkin and Dubinin-Radushkevich isotherm model. The adsorption thermodynamics was determined by studying the changes in enthalpy (ΔH), changes in standard entropy (ΔS) and Gibbs free energy (ΔG).

(e) Regeneration: The adsorbent was regenerated by washing with distilled water and dried at 60 °C in a convection oven for one hour. Seven regeneration cycles were done in order to investigate the regenerative ability of the adsorbent.

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