การดูดซับยาต้านการอักเสบจากสารละลายน้ำโดยใช้เศษยางรถยนต์เหลือทิ้งดัดแปรด้วยไคโตซาน

นางสาววริญธร ผาสุพันธ์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาเคมี ภาควิชาเคมี
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2559

ADSORPTION OF ANTI-INFLAMMATORY DRUGS FROM AQUEOUS SOLUTION USING CHITOSAN-MODIFIED WASTE TIRE CRUMB RUBBER

Miss Warintorn Phasuphan

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Chemistry
Department of Chemistry
Faculty of Science
Chulalongkorn University
Academic Year 2016

Thesis Title	ADSORPTION OF ANTI-INFLAMMATORY DRUGS FROM AQUEOUS SOLUTION USING CHITOSAN-MODIFIED WASTE TIRE CRUMB RUBBER
By	Miss Warintorn Phasuphan
Field of Study	Chemistry
Thesis Advisor	Associate Professor Narong Praphairaksit, Ph.D.
Thesis Co-Advisor	Assistant Professor Apichat Imyim, Ph.D.

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

....Dean of the Faculty of Science

(Associate Professor Polkit Sangvanich, Ph.D.)

THESIS COMMITTEE

....Chairman

(Associate Professor Vudhichai Parasuk, Ph.D.)

....Thesis Advisor

(Associate Professor Narong Praphairaksit, Ph.D.)

....Thesis Co-Advisor

(Assistant Professor Apichat Imyim, Ph.D.)

....Examiner

(Assistant Professor Suchada Chuanuwatanakul, Ph.D.)

....External Examiner

(Junya Jettanasen, Ph.D.)

วริญธร ผาสุพันธ์ : การดูดซับยาต้านการอักเสบจากสารละลายน้ำโดยใช้เศษยางรถยนต์เหลือทิ้งดัดแปรด้วยไคโตซาน (ADSORPTION OF ANTI-INFLAMMATORY DRUGS FROM AQUEOUS SOLUTION USING CHITOSAN-MODIFIED WASTE TIRE CRUMB RUBBER) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร.ณรงค์ ประไพรักษ์สิทธิ์, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ผศ. ดร.อภิชาติ อิ่มยิ้ม, 86 หน้า.

ในงานวิจัยนี้เศษยางรถยนต์เหลือทิ้งที่ผ่านการดัดแปรด้วยไคโตซานถูกเตรียมขึ้นเพื่อใช้เป็นตัวดูดซับในการกำจัดยาต้านการอักเสบ ได้แก่ ไอบูโพรเฟน ไดโคลฟีแนค และนาพรอกเซน จากสารละลายน้ำ การพิสูจน์เอกลักษณ์ของตัวดูดซับที่เตรียมขึ้นนี้ทำได้โดยใช้เทคนิคฟูเรียร์ทรานสฟอร์มอินฟราเรดสเปกโทรสโกปี เทคนิคการวิเคราะห์หาองค์ประกอบธาตุ และเทคนิคการวิเคราะห์การเปลี่ยนแปลงน้ำหนักของสารโดยอาศัยสมบัติทางความร้อน จากนั้นศึกษาชนิดและปริมาณไคโตซานที่เหมาะสมสำหรับการเตรียมตัวดูดซับ การศึกษาพีเอชที่ทำให้ประจุรวมบนพื้นผิวของตัวดูดซับมีค่าเป็นศูนย์ (pH_{pzc}) ผ่านเทคนิคการไทเทรตมวล (mass titration method) พบว่า พื้นผิวตัวดูดซับจะเป็นศูนย์เมื่อสารละลายมีพีเอชเท่ากับ 6.01 อีกทั้งพบว่า พีเอชของสารละลายเป็นปัจจัยสำคัญที่ส่งผลกระทบต่อประสิทธิภาพการดูดซับยาต้านการอักเสบของตัวดูดซับนี้ โดยไอบูโพรเฟน ไดโคลฟีแนค และนาพรอกเซน จะถูกดูดซับได้ดีในช่วงพีเอช 4-9, 5-10 และ 3-10 ตามลำดับ ซึ่งพีเอชของสารละลายที่เหมาะสมสำหรับการกำจัดยาต้านการอักเสบทั้งสามชนิดดังกล่าวคือพีเอช 6 โดยไอบูโพรเฟน ไดโคลฟีแนค และนาพรอกเซน ถูกดูดซับไป 3.20, 10.94 และ 0.53 มิลลิกรัมต่อกรัมตามลำดับ ทั้งนี้กระบวนการการดูดซับของไอบูโพรเฟน และไดโคลฟีแนค จะเข้าสู่สมดุลเมื่อเวลาผ่านไป 1 ชั่วโมง ในขณะที่การดูดซับนาพรอกเซนจะเข้าสู่สมดุลเมื่อเวลาผ่านไป 2 ชั่วโมง และในการศึกษาจลนพลศาสตร์การดูดซับยาต้านการอักเสบทั้งสามชนิดด้วยเศษยางรถยนต์เหลือทิ้งที่ผ่านการดัดแปรด้วยไคโตซานเป็นไปตามแบบจำลอง second-order ส่วนการศึกษาไอโซเทอมของการดูดซับยาต้านการอักเสบทั้งสามชนิดบนตัวดูดซับที่เตรียมขึ้นเป็นไปตามไอโซเทอมการดูดซับแบบฟรุนดลิช (Freundlich isotherm) มากกว่าไอโซเทอมการดูดซับแบบแลงเมียร์ (Langmuir isotherm) สุดท้ายตัวดูดซับที่ดัดแปรด้วยไคโตซานดังกล่าวถูกนำไปใช้สำหรับการกำจัดยาต้านการอักเสบในน้ำตัวอย่างจริงจากสระน้ำจุฬาลงกรณ์มหาวิทยาลัย น้ำจากคลองประปา และน้ำประปาซึ่งให้ผลเป็นที่น่าพอใจ ด้วยเหตุทั้งหมดที่กล่าวมานี้เศษยางรถยนต์เหลือทิ้งที่ผ่านการดัดแปรด้วยไคโตซานจึงเป็นตัวดูดซับชนิดใหม่ที่ราคาไม่สูงแต่ให้ประสิทธิภาพสูงในการกำจัดยาต้านการอักเสบ

ภาควิชา เคมี ลายมือชื่อนิสิต ....
สาขาวิชา เคมี ลายมือชื่อ อ.ที่ปรึกษาหลัก ....
ปีการศึกษา 2559 ลายมือชื่อ อ.ที่ปรึกษาร่วม ....

5772141723 : MAJOR CHEMISTRY

KEYWORDS: ANTI-INFLAMMATORY DRUG / IBUPROFEN / DICLOFENAC / NAPROXEN / TIRE / CHITOSAN / ADSORPTION

WARINTORN PHASUPHAN: ADSORPTION OF ANTI-INFLAMMATORY DRUGS FROM AQUEOUS SOLUTION USING CHITOSAN-MODIFIED WASTE TIRE CRUMB RUBBER. ADVISOR: ASSOC. PROF. NARONG PRAPHAIRAKSIT, Ph.D., CO-ADVISOR: ASST. PROF. APICHAT IMYIM, Ph.D., 86 pp.

In this research, waste tire crumb rubber was modified by polymeric chitosan to be used as a novel modified adsorbent for the removal of anti-inflammatory drugs including ibuprofen, diclofenac, and naproxen from aqueous solution. The chitosan-modified adsorbent was characterized by infrared spectroscopy, elemental analysis, and thermogravimetric analysis. The appropriated types and amount of chitosan were determined. The pH_{pzc}, investigated by mass titration method, was 6.01. The efficiency of anti-inflammatory drug adsorption using the adsorbent strongly depended on the solution pH. Ibuprofen, diclofenac, and naproxen were greatly adsorbed over pH ranges of 4-9, 5-10, and 3-10, respectively. The optimal solution pH for all three anti-inflammatory drugs removal is 6, at which the adsorption amounts of ibuprofen, diclofenac, and naproxen were 3.20, 10.94, and 0.53 mg/g, respectively. The adsorption equilibria of ibuprofen and diclofenac were reached in one hour while naproxen adsorption took two hours. The adsorption processes of all drugs followed the second-order kinetic model. The adsorption isotherm of these drugs onto the modified adsorbent was fitted with Freundlich isotherm model better than Langmuir isotherm model. Finally, the chitosan-modified adsorbent was applied to remove the anti-inflammatory drugs from real water samples, i.e., Chulalongkorn University's pond, canal water (untreated water), and tap water with satisfactory results. Therefore, the chitosan-modified waste tire crumb rubber adsorbent was the novel adsorbent which has the potential to be an economical and effective adsorbent for the removal of anti-inflammatory drugs.

Department:	Chemistry	Student's Signature	....
Field of Study:	Chemistry	Advisor's Signature	....
Academic Year:	2016	Co-Advisor's Signature	....

ACKNOWLEDGEMENTS

I would like to appreciate everyone who is helpfulness, supportive, and suggestive for my research skill improvement. I am deeply grateful to my thesis advisor, Associate Professor Dr. Narong Praphairaksit and my co-advisor, Assistant Professor Dr. Apichat Imyim, for their invaluable assistance, suggestion, kindness, and their patience in proofreading throughout this research. Moreover, I also sincerely thank to my committee members: Associate Professor Dr. Vudhichai Parasuk, Assistant Professor Dr. Suchada Chuanuwatanakul, and Dr. Junya Jettanasen for their invaluable advices and comments to improve the thesis quality.

I would like to extend my sincere appreciation to Assistant Professor Dr. Fuangfah Unob for her kindness and encouragement. Furthermore, I would also like to thank Assistant Professor Dr. Puttaruksa Varanusupakul for her kindness to provide and teach me how to use high performance liquid chromatograph (HPLC). Moreover, this research achievement cannot be completed without encouragement, friendship, suggestion, and support from all members of the Environmental Analysis Research Unit (EARU), 1234 Laboratory, and ChemCU#79.

And indispensable, I really appreciate my parents and my family not only for their encouragement, support, understanding, and care throughout the period of this research but also for their unconditional love that I always receive.

CONTENTS

Page

Page

LIST OF FIGURES

Page

LIST OF TABLES

Page

LIST OF ABBREVIATION

g	Gram
mg	Milligram
L	Liter
mL	Milliliter
M	Molar
mg/L	Milligram per liter
mg/mL	Milligram per milliliter
mg/g	Milligram per gram
w/w	Weight by weight
w/v	Weight by volume
v/v	Volume by volume
nm	Nanometer
rpm	Revolutions per minute
min	Minute
DI	Deionized water
%	Percent
^{o}C	Degree celsius

CHAPTER I

INTRODUCTION

1.1 Statement of the problem

Non-steroidal anti-inflammatory drugs (NSAID) such as ibuprofen, diclofenac and naproxen have been widely used to treat pain, sore throat as well as various inflammation. As a consequence, an excess amount of these drugs are excreted through human and animal excretory systems into the environment. Furthermore, these substances can also be introduced into the sewerage or garbage via mishandling or disposal of expired drugs, which will eventually make their way to contaminate natural resources such as groundwater and underground water. The contaminated water has various impacts on humans and aquatic animals which use or live therein, such as, altered behavior and reproduction, delayed development in fish and delayed metamorphosis in frogs. A prolonged accumulation of these substances in human body can lead to a malfunction of the endocrine system and the abnormal development of human immune system [1]. Although there is currently no explicit criteria for determining the minimum contaminant level (MCL) of anti-inflammatory drugs in water, many researchers are aware of the risks that arise from the accumulation of these drugs in human and animal body, as mentioned above. From this reason, the researchers are trying to study and develop the efficient yet inexpensive methods for the removal of anti-inflammatory drugs contaminated in water resources.

Generally, there are several common methods for the anti-inflammatory drugs removal, for example, biological degradation [2], catalytic wet oxidation [3], flocculation-coagulation and sedimentation [4], ozonation [4, 5], air stripping, ion exchange, solvent extraction [6], sedimentation, membrane separation including adsorption. Each of these methods has its own advantages and disadvantages. The most interesting method which is widely used for the anti-inflammatory drugs removal of contaminated water is adsorption because this method does not generate any substances that present toxicity in water [7, 8]. Moreover, this method is relatively simple with no requirements of skilled operators, inexpensive yet especially effective to the removal of anti-inflammatory drugs [9].

Many previous researches have been conducted in an attempt to find ideal materials that can be used as the adsorbent for anti-inflammatory drugs adsorption from contaminated water, such as, layered double hydroxides (LDHs) [9], granular activated carbon [10, 11], polyaniline [12], carbon blacks [13] and clay-micelle complex [14]. Although being somewhat effective, most adsorbents previously mentioned all suffer common drawbacks in that they are either expensive or their syntheses are relatively complicated. Therefore, the objective of this research is to develop a novel adsorbent which can be simply prepared, inexpensive and effective to remove the anti-inflammatory drugs from water resources.

Waste tire crumb rubber is an abundant and seemingly useless material. A massive amount of this material is generated each year and this is typically disposed of by landfill or incineration, eventually leading to the increased environmental pollution [15]. In an attempt to alleviate this problem, waste tire crumb rubber has been adopted as an alternate adsorbent for the removal of various contaminants from wastewater. The tire rubber molecules are normally comprised of both polar and non-polar parts and thus they are expected to interact with both polar and non-polar substances. However, their adsorption efficiency toward these substances remain far less than ideal.

Chitosan, a chitin derivative produced from shrimps, crabs and other crustacean shells, has also been used as an adsorbent for a variety of substances. Being a polysaccharide structurally, the amino groups on chitosan can be protonated under acidic conditions which generates positive charges on its molecular structure. A strong adsorption process toward negatively charged species can thus be driven by their electrostatic interaction. Anti-inflammatory drugs, such as ibuprofen, diclofenac and naproxen, all commonly contain carboxylic groups which can dissociate into carboxylate ions and present negative charges on their structures. Hence, these species as well as other anti-inflammatory drugs with carboxyl functional group should literally be adsorbed by the protonated amino groups on chitosan structure. A modification of waste tire crumb rubber with chitosan assembled thereon could therefore be a potential adsorbent for the removal of these anti-inflammatory drugs.

Accordingly, the objective of this study was to prepare a low-cost, simple, and effective adsorbent from waste tire crumb rubber modified with chitosan for the removal of anti-inflammatory drugs including ibuprofen, diclofenac and naproxen in aqueous solution. The optimum conditions for the preparation and adsorption process such as amount of chitosan, solution pH, adsorption time and adsorption isotherm were investigated.

1.2 Scope of the research

- To prepare chitosan-modified waste tire crumb rubber and use it as an adsorbent to remove anti-inflammatory drugs in aqueous solution.
- To characterize the adsorbent by the following techniques; elemental analysis (EA), Fourier transform infrared spectroscopy (FT-IR) and thermogravimetric analysis (TGA).
- To study parameters affecting the adsorption efficiency of anti-inflammatory drugs by this chitosan-modified waste tire crumb rubber adsorbent, including the loading amount of chitosan, pH of solution, contact time, and adsorption isotherm.
- To evaluate the efficiency of the developed adsorbent for the removal of anti-inflammatory drugs from real wastewater samples.

1.3 Benefits of this research

The novel adsorbent, chitosan-modified waste tire crumb rubber, was prepared and used as an effective adsorbent for the removal of anti-inflammatory drugs, including ibuprofen, diclofenac, and naproxen from aqueous solution to mitigate this threatening environmental issue.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Anti-inflammatory drugs

2.1.1 Properties of anti-inflammatory drugs

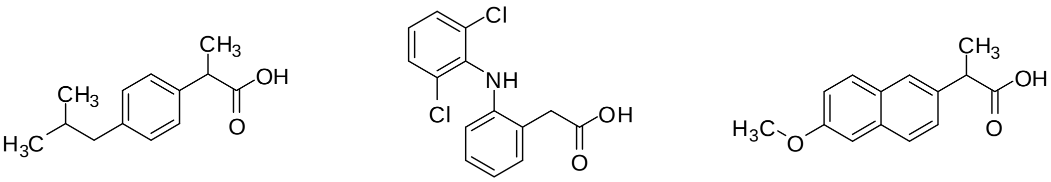
Ibuprofen, diclofenac, and naproxen are common anti-inflammatory drugs used for treating pain and inflammation caused by various conditions such as toothache, headache, and back pain etc. Some key physical and chemical properties of these drugs are presented in Table 2.1.

Table 2.1 Properties of anti-inflammatory drugs

Chemical name	Ibuprofen	Diclofenac	Naproxen
Molecular formula	$C_{13}H_{18}O_2$	$C_{14}H_{11}Cl_2NO_2$	$C_{14}H_{14}O_3$
Molecular weight	206.3 $g{\cdot}mol^{-1}$	296.2 $g{\cdot}mol^{-1}$	230.3 $g{\cdot}mol^{-1}$
Appearance	Crystalline stable solid	Crystals	White crystalline powder
Melting point	75-77 ^{o}C	156-158 ^{o}C	155 ^{o}C
Water solubility (at 25 ^{o}C)	21 $mg{\cdot}L^{-1}$	2.37 $mg{\cdot}L^{-1}$	15.9 $mg{\cdot}L^{-1}$
pKa	4.35 [16-19]	4.70 [16-18, 20]	4.27 [16, 19]
λmax	222 nm	276 nm	230 nm

The molecular structures of these anti-inflammatory drug compose of both polar and non-polar moieties. The non-polar moiety is represented by aromatic rings and hydrocarbon chains while the polar moiety mainly consists of carboxylic

(-COOH) functional group. These carboxyl functional groups can be deprotonated to generate negatively charged carboxylate ions and thus possess acidic properties.



Ibuprofen Diclofenac Naproxen

Figure 2.1 Molecular structures of the anti-inflammatory drugs

The anti-inflammatory drugs exist in many species depending on their pKa and pH of the solution. When pH of solution is equal to pKa of the drugs, 50% of the carboxyl functional groups on the drugs are deprotonated to form carboxylate ions which consist of the negative charges. The percentage of carboxylate ions is decreased when pH of the solution is reduced (pH<pKa) as these ions are protonated and reverted to carboxyl groups. On the other hand, the percentage of carboxylate ions were increased when increasing the pH of solution (pH>pKa) due to the deprotonation. These molecules are fully deprotonated to carboxylate ions when pH of solution is 2 units above their pKa, and thus these anti-inflammatory drugs demonstrate the negative charges in the solution. Figure 2.2 shows the relationship between the percentage of the two forms in the solution under different pH conditions.

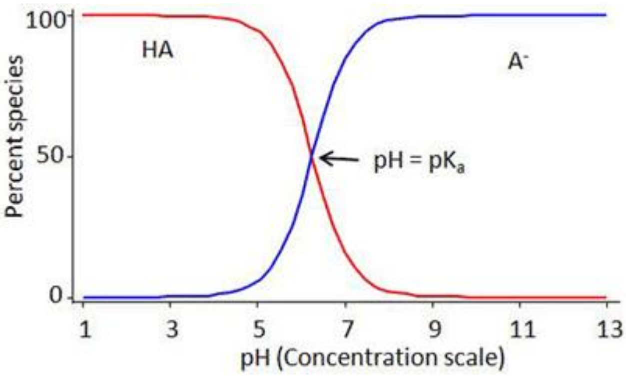


Figure 2.2 The percentage of acid-base species in the solution [21]

2.1.2 Usages of anti-inflammatory drugs

Anti-inflammatory drugs are used to reduce fever and treat pain or inflammation caused by many conditions in living organism. Ibuprofen, diclofenac, and naproxen are the three anti-inflammatory drugs of interest in this work.

Ibuprofen, (RS)-2-(4-(2-methylpropyl)phenyl)propanoic acid, is widely used to treat pain and inflammation such as migraine, headache, menstrual cramps, arthritis, and minor injury. However, a long term use or intake overdoses can result in adverse effect to the people who have the heart disease. Stomach and intestines can also be damaged with overdose of ibuprofen. Moreover, ibuprofen reportedly has been linked to endocrine disrupting activity in human and wildlife [22, 23] and its intermediates, obtained by biological treatment, are toxic to aquatic environment [24].

Diclofenac, 2-[2-(2,6-dichlorophenyl)aminophenyl] ethanoic acid, is the most commonly found contaminant in water among these three drugs. Diclofenac is widely used to relieve mild or moderate pain, as well as to treat rheumatoid arthritis, osteoarthritis, and migraine. This drug has a noticeable acute toxicity [25-27], and thus humans and animals with prolonged consumption or exposure may be adversely affected. For example, a debilitation of the fishes health, alterations of their gills, and inducing renal lesions have been observed [28].

Naproxen, (+)-(S)-2-(6-methoxynaphthalen-2-yl)propanoic acid, is used for treating pain in both humans and animals [29]. Bones and joints inflammation such as gout, cramps, tendinitis, bursitis, arthritis, and ankylosing spondylitis could be alleviated by this drug. Furthermore, its by-products generated by photo-degradation are more toxic than itself [30].

2.1.3 Contamination of the anti-inflammatory drugs

Due to growing consumption of anti-inflammatory drugs in humans and animals, the excess amount of these has become increasingly contaminated into the water resources. Not only through the excretion mechanism but the anti-inflammatory drugs can also be introduced into the environment via the improper disposal, wrong distribution, and industrial waste [31] as schematically shown in

Figure 2.3. These drugs are not easily decomposed and thus their prolonged contamination in water is most likely. In previous works, the anti-inflammatory drugs were reported as contaminants in surface water and ground water in many countries such as Austria, Brazil, Canada, Croatia, England, Germany, Greece, Italy, Spain, Switzerland, The Netherlands, and the U.S. [32, 33]. Moreover, trace level of these drugs were reportedly found in drinking water along with µg/L level in sewage influent and effluent [32, 34-37].

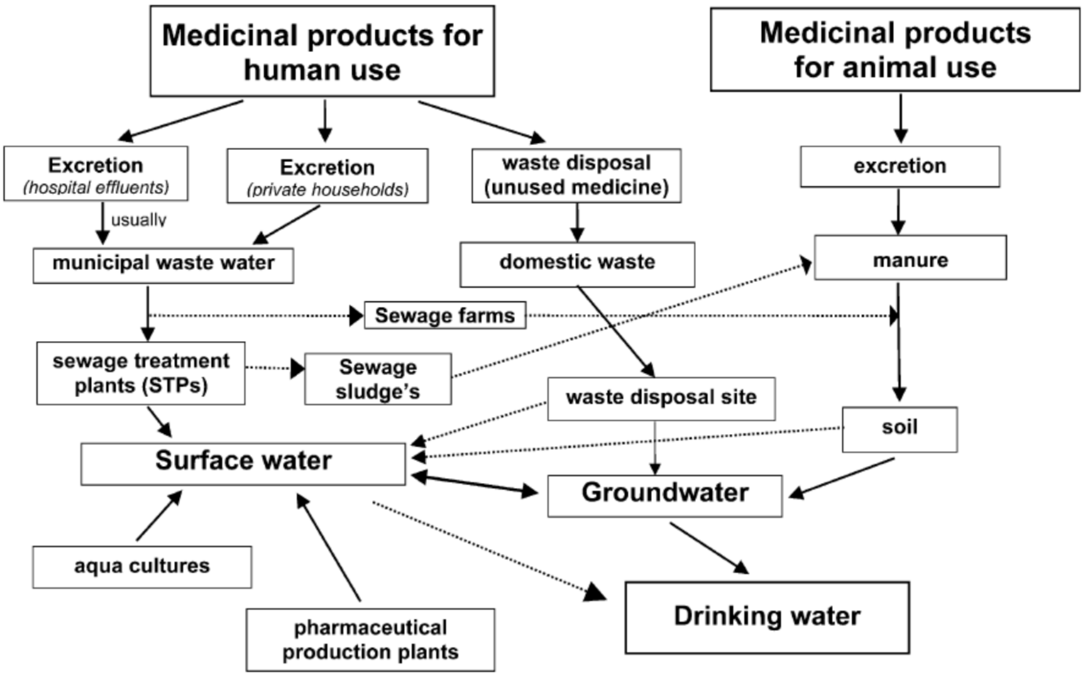


Figure 2.3 The contamination pathways of anti-inflammatory drugs into water resource [32]

2.1.4 Toxicity

Although the anti-inflammatory drugs are beneficial for the treatment or alleviation of diseases in humans and animals, overdosing or undue usage may have serious effects to the organism health. Furthermore, the prolonged consumption of contaminated water even with trace level of anti-inflammatory drugs might cause undesired health effects in humans and chronic toxicity in some aquatic organisms [38]. Many previous works reported that the anti-inflammatory drug residues in water resource have unsought effects to the ecotoxicology [27], the functions of target and non-target organism in various vertebrates and invertebrates [39, 40], the development of immune system and the functions of endocrine system in human [1], as well as the mutation to susceptible species [41]. In addition, It was related to the decrease of vulture population in India [42] and Pakistan [43]. Moreover, the combination of these drugs in contaminated water may produce synergistic effect on toxicity [44].

2.2 Methods for anti-inflammatory drugs removal

Due to the growing threat of contaminated anti-inflammatory drugs in aqueous solution, many removal methods have been researched and developed for wastewater treatment. Various methods for anti-inflammatory drugs removal have been established such as ozonation, membrane filtration, biodegradation, catalytic wet oxidation, coagulation-flocculation, and adsorption. The description of these methods are explained in the following subsection.

2.2.1 Ozonation method

Ozonation is a famous type of oxidation method for anti-inflammatory drugs removal. The advantages of this method is not only increasing the amount of oxygen in wastewater but it also does not directly add the chemical reagents to aqueous solution. This method is processed by generating and adding the ozone (O_3) into wastewater [45, 46]. Ozone molecules will easily react with the electron rich moiety such as activated aromatic rings, double bonds, and hetero-atoms then the highly reactive but non-selective free radicals of the contaminants are formed [7]. The contaminant molecules including the anti-inflammatory drugs are degraded by ozone and become less toxic molecules. Nevertheless, the ozonation method alone does not remove the anti-inflammatory drugs from aqueous solution, it must be combined with other techniques such as adsorption [5, 47], advanced oxidation processes (AOPs) [48-50], and filtration [51].

2.2.2 Membrane filtration method

Membrane filtration method is used for the removal of contaminants in wastewater via flowing the aqueous solution, which contain contaminated molecules or particles such as organic molecules, bacteria, heavy metals, gravel, etc., through a special membrane filter. The appropriate type of membrane filter is selected in acoordance with the contaminant properties. The membrane filtration method can be categorized into four types based upon the pore size of membrane filter used, which are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO).

Nowadays, the membrane filtration method is less popular when compared with other methods because it is usually expensive and less efficient in the removal of anti-inflammatory drugs in aqueous solution [52, 53].

2.2.3 Biodegradation method

Biodegradation method is utilized for organic contaminated wastewater treatment including hydrocarbons (such as oil), polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), heterocyclic compounds, radionuclides, metals, and pharmaceutical substances. These substances are energy sources of microbial growth. Both aerobic [54] and anaerobic [55] organisms were employed for mineralizing and/or degrading the contaminated pollutants into carbon dioxide (CO_2), water (H_2O), and inorganic ions, and thus the purification of wastewater was effected [56]. Nevertheless, a number of harmful byproducts were produced by this method [57]. Moreover, a large amount of pollutants were not effectively removed through this biodegradation method [58] and under the extreme treatment condition, the current method was not suitable for the living of microorganisms. The wastewater treatment processes which rely on the biodegradation method were operated in the form of activate sludge (AS), rotating biological contactor (RBC), oxidation ditch (OD), aerated lagoon (AL), trickling filter, stabilization pond, upflow anaerobic sludge blanket (UASB), and anaerobic filter (AF).

2.2.4 Chemical coagulation-flocculation method

The chemical coagulation process involves the addition of coagulant into the contaminated wastewater to destabilize fine suspension and colloidal particles in order to achieve the agglomeration of these substances. Various chemicals were used as the coagulant for wastewater treatment such as alum (aluminium sulphate), liquid alum (polyaluminium chloride, PAC), and iron salts such as ferric chloride and ferric sulphate [18]. The chemical coagulation is usually followed by the flocculation process which refers to the aggregation of neutralized particles to form the larger particle of flocs which settle faster. Finally, the settled flocs of contaminant were removed through the filtration procedure.

It was reported that the chemical coagulation-flocculation can only remove a small amount of pharmaceutical substances [4, 59]. Therefore, this method is not effective for the removal of pharmaceutical products from wastewater. However, it is widely used as a pre-treatment step for some processes such as ozonation, sand filtration, and activated carbon filtration.

2.2.5 Adsorption method

Adsorption is an alternate method which is relatively simple, inexpensive and effective for the removal of anti-inflammatory drugs [9]. The method is safe and does not generate disinfection by-products (DBP) [7, 8] which are more toxic in aqueous solution. The adsorption method relies on the interaction between the adsorbent surface and adsorbate which is the contaminants in water such as ions, atoms, and molecules. The adsorption process occurs through the accumulation of contaminants on the adsorbent surface to purify the water solution. This method can be operated in either batch or continuous modes [60]. The adsorption efficiency depends on the properties of the adsorbent surface which relate to the adsorbent material type. The materials used as adsorbent can be obtained from various sources, for instance, natural products, agricultural wastes, industrial wastes, synthetic materials, modification products, and commercial products, etc. To achieve the highest adsorption efficiency for contaminants removal in aqueous solution, the properties of the adsorbate is considered to match with the appropriate and effective adsorbent.

2.3 Adsorption

The adsorption process takes place when the contaminants or adsorbates in the solution are deposited on the adsorbent surface. This process is normally composes of three sequential steps as follows [61, 62];

I. External mass transfer diffusion: the transferring of adsorbates from bulk solution (boundary film) to the external surface of adsorbents by diffusion process.

II. Interparticular mass transfer diffusion: the adsorbates are transported from external adsorbent surface to the interparticular active sites.

III. Equilibrium adsorption: the adsorbates are uptaked on the active sites of the adsorbents through chemical or physical sorption.

The adsorption efficiency for the removal of contaminants in aqueous solution depends on various factors including the chemical and physical properties of both adsorbent and adsorbate, the adsorption conditions such as pH of solution, contact time, stirring rate, temperature, adsorbent concentration, and the initial concentration of solution also influenced the adsorption efficiency.

2.3.1 Adsorption types

The adsorption phenomenon relates to the interactions between adsorbent surface (solid phase) and adsorbate molecules in aqueous solution (liquid phase). These interactions are indicative of the strength of adsorption and species of the associated molecules. The adsorption is generally classified into physical adsorption (physisorption) and chemical adsorption (chemisorption).

2.3.1.1 Physical adsorption

Physical adsorption or physisorption is the adsorption mechanism which is generated by a weak interaction between adsorbent and adsorbate. The adsorbent surface is attracted by adsorbent atoms/molecules through intermolecular interactions, including Van der Waals and electrostatic interactions, and thus the multilayer adsorption may be occurred. Based on these mechanisms, a fast and reversible adsorption can be found [63]. The maximum adsorption capacity for this process is defined by the surface area and pore volume of adsorbent material [64].

2.3.1.2 Chemical adsorption

Chemical adsorption or chemisorption is described by the adsorption process which features the chemical bonding between the adsorbent surface and adsorbate atoms/molecules. The chemical bonding involves the sharing of electrons and binding of the functional groups to certain sites on the sorbent (covalent bonding), therefore this type of adsorption is only formed as monolayer and often irreversible process [63, 65].

2.3.2 Adsorption kinetics

The adsorption kinetics are key parameters that can be used to investigate the rate of analyte adsorbed onto the adsorbent surface in order to design the treatment processes. To describe the adsorption kinetic, first-order and second-order kinetic models are used to fit with the experimental results.

2.3.2.1 The first-order kinetic model

The first-order kinetic model is more appropriate for low contaminant concentration solution. This model can be represented be the equation below [62];

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{2.1}$$

Where q_t is the amount of adsorbate adsorbed or adsorption capacity of adsorbent at time t (mg/g)

q_e is the equilibrium adsorption capacity of the adsorbent (mg/g)

k_1 is the first-order rate constant

t is the time (t)

When integrating the equation (2.1) by applying the initial concentrations with varying q_t (q_t=0 to q_t=q_t) and t (t=0 to t=t), the equation (2.2) is obtained as follows [62, 66];

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{2.2}$$

The value of first-order rate constant, k_1, is the slope of linear line obtained from the plot of $\ln(q_e\text{-}q_t)$ against t (min). And the equilibrium adsorption capacity, q_e, is an intercept.

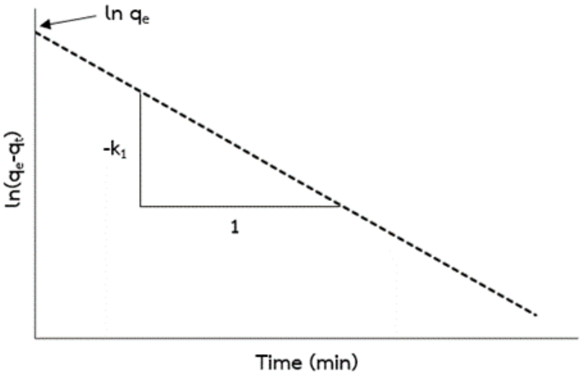


Figure 2.4 The plot of first-order kinetic model

2.3.2.2 The second-order kinetic model

The second-order kinetic model is used to predict the adsorption behavior over the whole range. The amount of adsorbate adsorbed on the adsorbent surface and equilibrium adsorption capacity is the factor that define the adsorption rate. This model can be represented by equation (2.3) [62].

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{2.3}$$

The integration of equation (2.3) by applying the initial concentrations with varying q_t (q_t=0 to q_t=q_t) and t (t=0 to t=t), the equation becomes (2.4) [62, 66].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{2.4}$$

The second-order rate constant value, k_2, is calculated from the intercept of the linear line when plotting the t/q_t versus t (min). The equilibrium adsorption capacity, q_e, is derived from the slope.

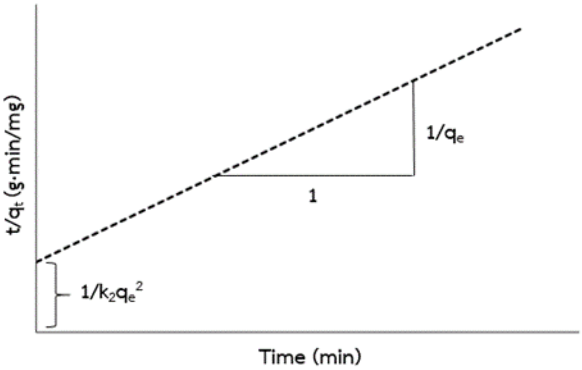


Figure 2.5 The plot of second-order kinetic model

2.3.3 Adsorption isotherms

An adsorbent can continuously adsorb contaminants in aqueous solution until the concentration of contaminants on the adsorbent surface become unchanged, i.e. the equilibrium state is reached. The investigation of the interactive behavior between the adsorbent and adsorbate at equilibrium under constant temperature is referred to as adsorption isotherm. The different initial concentrations are applied to obtain the isotherm parameters including the equilibrium concentration and the adsorption capacity. In order to study the adsorption isotherm, two widely used models; Langmuir and Freundlich; are fitted by the experimental data obtained.

2.3.3.1 Langmuir adsorption isotherm model

In 1916 Irving Langmuir developed this adsorption isotherm to describe the adsorption behavior. This isotherm is determined on the assumption that a monolayer adsorption with homogeneous surface has only one type of binding sites and energetically identical [67]. The adsorption capacity of the adsorbent is limited by the available number of active sites through the chemisorption (chemical adsorption).

This isotherm model is suitable for a wide variety of the experimental data. The Langmuir isotherm equations is expressed by the following [68, 69];

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \tag{2.5}$$

The equation (2.5) is rearranged to provide a simple linear equation as followed;

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \tag{2.6}$$

Where C_e is the concentration of the adsorbate at equilibrium (mg/L)

q_e is the adsorption capacity or the amount of adsorbate adsorbed at equilibrium (mg/g)

q_m is the maximum adsorption capacity of the adsorbent (mg/g)

K_L is the Langmuir isotherm constant (L/mg) which relates to the free energy of adsorption

The Langmuir isotherm curve is obtained by the plot of the equilibrium concentration of adsorbate, C_e, and the equilibrium adsorption capacity, q_e. The maximum adsorption capacity, q_m, and Langmuir isotherm constant, K_L, are calculated from the slope and the intercept of the linear plot of C_e against C_e/Q_e.

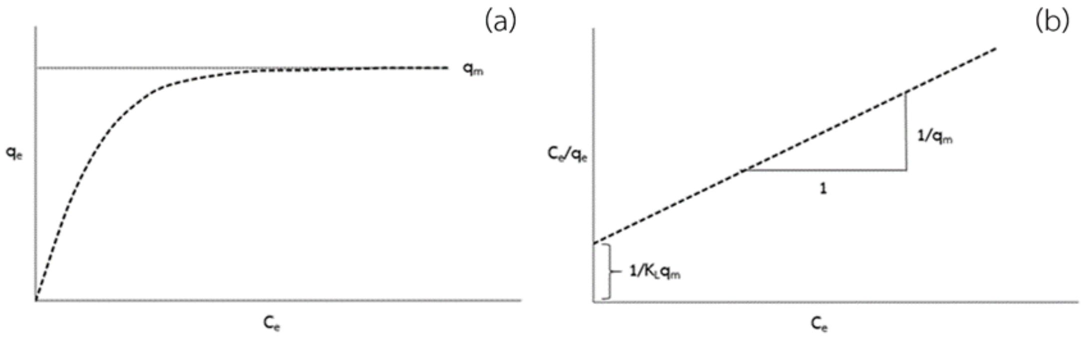


Figure 2.6 (a) Adsorption isotherm plot and (b) linearized equation plot of Langmuir adsorption isotherm

2.3.3.2 Freundlich adsorption isotherm model

Herbert F. Freundlich presented an empirical isotherm model based on the assumption about the occurrence of multilayer adsorption with various interaction types on the heterogeneous surfaces. The Freundlich isotherm model is represented in equation (2.7) [68, 69].

$$q_e = K_F C_e^{1/n} \tag{2.7}$$

The linear form of the Freundlich isotherm equation as shown in equation (2.8) is obtained by taking the logarithm into the above equation.

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{2.8}$$

Where	K_F	is	the Freundlich isotherm constant (mg/g)
	n	is	a dimensionless constant known as the heterogeneity factor
	q_e	is	the equilibrium adsorption capacity (mg/g)
and	C_e	is	the equilibrium concentration of the adsorbate (mg/L)

A plot between the equilibrium concentration of adsorbate, C_e, and the equilibrium adsorption capacity, q_e, provided the theoretical Freundlich isotherm curve. The Freundlich isotherm constant, K_F, and heterogeneity factor, n, which is related to the adsorption intensity are calculated from the intercept and slope of the linear plot between log C_e versus log q_e.

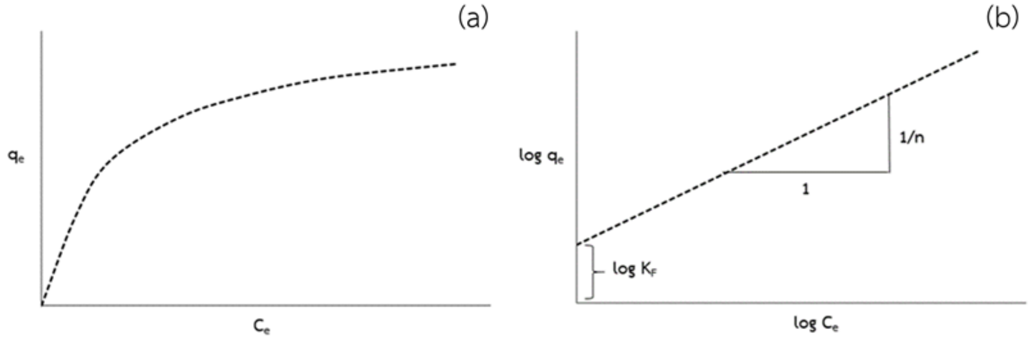


Figure 2.7 (a) Adsorption isotherm plot and (b) linearized equation plot of Freundlich adsorption isotherm

2.3.4 Types of adsorbent

The adsorbent is a key factor which determined the efficiency of adsorption process and thus the removal of contaminants. Therefore, the adsorbent must be appropriately chosen to efficiently and, more preferably, selectively attract the contaminant molecules of interest. Currently, the preferred adsorbent properties for the treatment of wastewater should be cost-effective materials, good kinetic properties, large number of active sites for contaminant which collectively would lead to high adsorption capacity and high adsorption efficiency. Three types of adsorbent based on their sources are described herein.

2.3.4.1 Natural adsorbent

Due to increasing environmental concerns about the enormous amount of waste being generated, many attentions have turned to the utilization of natural materials, especially those that are abundantly available and considered useless. Various naturally abundant materials which are environmental friendly, such as, coconut shell, zein, rice husk, chitosan, and cellulose etc. [70] have been employed as natural adsorbent for the treatment of contaminated water. Some of which and their applications are shown in Table 2.2.

Table 2.2 Typical applications of some natural adsorbents

Adsorbents	Typical applications	References
Bentonite, Calcite, Kaolinite, Zeolite	Removal of phosphorus	[71]
Pine bark	Persistent organic pollutants (POPs) removal,	[72]
	Removal of heavy metals	[73]
Bagasse, Paddy husk, Corn cob, Wheat bran, Peanut skin, Human hair	Removal of heavy metals	[74]
Milkweed (Asclepias) fiber, Cotton fiber	Adsorption of crude oil	[75]
Rice straw, Rice bran, Rice husk, Hyacinth roots, Neem bark, Saw dust of teakwood origin, Neem leaves, Coconut shell	Removal of chromium [Cr(VI)]	[76]

2.3.4.2 Commercial adsorbent

Commercial adsorbents can be classified into three classes in accordance with their properties, which are hydrophilic (polar compounds), hydrophobic (non-polar compounds) and polymer-based adsorbent (both polar and non-polar moiety). Some commercial adsorbents and their applications are presented in Table 2.3.

Table 2.3 The applications of some commercial adsorbents

Adsorbents	Typical applications	References
Clay, Activated alumina	Removal of naphthenic acid from petroleum oil	[77]
Activated carbons	Adsorption of fluoride	[78]
Mesoporous silica	Removal of ammonia and trimethylamine	[79]
Silica	Removal of basic dye	[80]
Alumina-carbon composite	Removal of methylene blue and alizarin red-S	[81]

2.3.4.3 Low-cost adsorbent

Low-cost adsorbent has recently emerged as an alternative yet promising material for the removal of contaminants. This adsorbent can be either natural, waste or by-product materials which are abundant and economically valueless. Using their availability as a criteria, these low-cost adsorbents can be divided into three groups, i.e.,

(a) Agricultural/industrial/domestic wastes or by-products such as bagasse fly ash, sludge, red mud, fly ash, slag etc.

(b) Natural materials such as pinewood, lignite, peat, wood, coal etc.

and (c) Synthesized products [82].

Typical applications of some low-cost adsorbents are revealed in Table 2.4.

Table 2.4 The applications of some low-cost adsorbents

Adsorbents	Typical applications	References
Fruit wastes, coconut shell, scrap tyres, bark and other tannin-rich materials, sawdust and other wood type materials, rice husk, petroleum wastes, fertilizer wastes, fly ash, sugar industry wastes blast furnace slag, chitosan and seafood processing wastes, seaweed and algae, peat moss, clays, red mud,zeolites, sediment and soil, ore minerals	Removal of organic pollutants such as industrial dyes, polycyclic aromatic hydrocarbons (PAHs), waste frying oil (WFO), phenolic compounds, pesticide, pyridine,	[83]
Activated tamarind seeds, activated neem leaves, sawdust, activated flyash	Removal of chromium [Cr(VI)]	[84]
Waste tire rubber ash	Removal of lead (Pb)	[85]
Waste tyre rubber	Removal of oil	[86]

Table 2.4 (cont.) The applications of some low-cost adsorbents

Adsorbents	Typical applications	References
Coir pith, orange peel, banana peel, rice husk, straw, date pit, oil palm fiber: activatedcarbon, durian shell: based activatedcarbon, guava (Psidiumguajava) leaf powder, almond shell,pomelo (Citrus grandis peel),broad bean peel,peanut hull, citrulluslanatus rind	Removal of congo red, aid violet, basic blue 9, acid yellow 36, basic blue 9, basic blue 9, malachite green, methylene blue, methylene blue, direct red 80, methylene blue, methylene blue, reactive dye, crystal violet,	[87]

Nevertheless, these low-cost adsorbents may not provide sufficient adsorption efficiency for the removal of the contaminants in aqueous solution. The modification of such materials are thus necessary in order to improve its adsorption performance. This modification process can be incorporated by providing the appropriate functional groups, compatible pore size and pore volume, and larger surface area to the adsorbent material. The modification process of low-cost adsorbent surface can also be applied in conjunction with the synthesis and preparation of novel adsorbents which have superior performance than the original materials [88]. Some modified adsorbents are presented in Table 2.5.

Table 2.5 Typical applications of some modified low-cost adsorbents.

Adsorbent	Typical applications	References
Modified bagasse fly ash	Removal of cadmium	[89]
Wood based modified adsorbent	Removal of copper, nickel, chromium, lead, zinc, cadmium	[90]
Surfactant modified banana trunk	Removal of benzene	[91]
Phytic acid modified wheat straw	Removal of cationic dye	[92]
Modified plantain peel	Removal of 2,6-dichlorophenol	[93]
Magnetically modified coffee silverskin	Removal of xenobiotics	[94]
Modified potato starch-magnetic nanoparticles (MPS-MNPs)	Removal of copper, lead, nickel	[95]
Ferric and ferrous modified natural common clays (Clay/$FeSO_4$, Clay/$FeCl_3$)	Removal of arsenate	[96]

2.4 Tire rubber

The use of rubber tires has immensely increased over the years due to the rapid growth of automobile industry. The key composition of rubber tires are synthetic rubber (SR), natural rubber (NR) and other chemicals in different percentages as shown in Figure 2.8. The different composition greatly affect the properties of these tires. Nowadays, the synthetic rubber are being used as the main component for tire manufactures as they provide tires with superior quality, better road adhesion, heat and oil resistant, than the natural rubber. The structures of synthetic rubber used in the tire production are styrene-butadiene rubber (SBR), butadiene rubber (BR), and butyl rubber (IIR) as shown in Figure 2.9. The different structures of synthetic rubber also provided different properties to these tires [97].

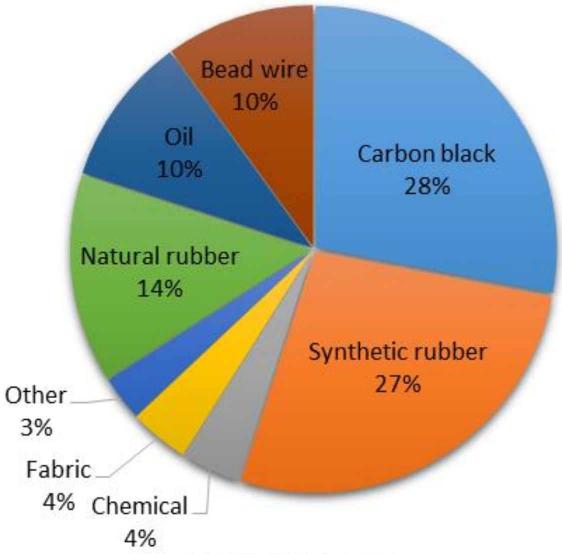
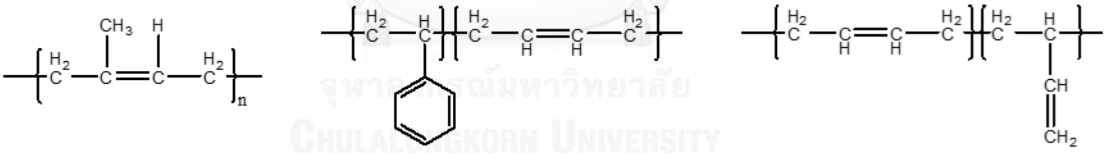


Figure 2.8 Typical tire rubber composition [98]



Natural rubber, NR Styrene-butadiene rubber, SBR Butadiene rubber, BR

Figure 2.9 The synthetic rubbers used for tire production

Moreover, the additives such as fabric, bead wire, carbon black, oil, kaolin, sulfer, and other chemicals are added into the tire production for the improvement of its properties. Nevertheless, the exceptionally high durability of these rubber tires also brings negative aspects as enormous amount of worn and used tires become waste which are extremely difficult to dispose of. Currently most of these tire rubber wastes are eliminated by landfill disposal or combustion, resulting in various other problems, such as wasted space, leachate leakage, and the environmental problems including air and water pollution [99].

As mentioned above, waste tire rubber has increasingly grown environmental concerns because a massive amount of these materials are being generated every day making its disposal especially troublesome [15]. Therefore, the reuse or recycle of these materials to maximize their utilization has been particularly of interest. This will not only reduce the waste residue but also reduce the manufacturing cost of some materials such as Portland cement [100] and in concrete pedestrian block [101].

2.5 Chitosan

Chitosan is a derivative of chitin which is vastly available in shrimp, mussels, crayfish and other crustacean shells. Chitosan is obtained by deacetylation process of chitin using alkaline substance such as sodium hydroxide to decrease the acetyl functional groups and increase glucosamine moieties of chitin. Chitosan is insoluble in water because their structure comprises low amount of polar moiety whereas the acid addition thereof provides better solubility of chitosan because the amino groups on chitosan are protonated by the hydrogen ions (H^+) from acid substance. The average deacetylation percentage (%DD) of chitosan is one of the parameters which determine their solubility. A higher percentage of deacetylation results in more solubility of chitosan in the solution. Moreover, the solution pH, the ionic concentration, the nature of acid, and the acetyl group distribution along the chain are also the factors defining the water solubility of chitosan. The properties of chitosan are displayed in Table 2.6.

Table 2.6 The physical, chemical and biological properties of chitosan [102, 103]

Physical properties	Chemical properties	Biological properties
● Yellow powder ● Semicrystalline natural polymer ● Soluble in acid aqueous medium ● pKa 6.5 of amino group	● Reactive amino groups ● Reactive hydroxyl group ● Transitional metal ions chelation	● Biocompatible ● Biodegradable ● Biological tolerance ● Safe and non-toxic ● Relates to mammalian and microbial cells aggressively;accelerates the osteoblast for bone formation, hemostatic, fungistatic, anticholesteremic. ● Hydrolyzed by lyzosyme

The structure of chitosan is a polysaccharide which has a pendant amino group (-NH_2), the charge of which depends on the solution pH as shown in Figure 2.10. Under acidic condition, the amino groups are protonated and presented the positive charge on their molecules as pseudonatural cationic polymer [102]. With its unique properties, chitosan has been used in many industrial applications in the form of powder, gel, solution, film, and fiber [104]. Various applications of chitosan are shown in Table 2.7.

Table 2.7 Various applications of chitosan [102]

Industry	Applications
Agriculture	Capsule of nutrients and fertilizers releasing into soil Frost protection by seed coating Growth stimulator of plant
Biopharmaceutics	Hemostatic Anticoagulant Bacteriostatic Antitumoral Immunologic
Cosmetics & toiletries	Acne and skin moisture treatment Hair softness improvement Hair static electricity reduction Oral care product such as chewing gum and toothpaste
Food & beverages	Preservative Cholesterol reducing by binding with lipids Additive for sauces Antibacterial and fungistatic Fruit coating
Water & waste treatment	Ecological polymer Removal of the contaminants such as heavy metals Flocculant to purify water Odors reducer

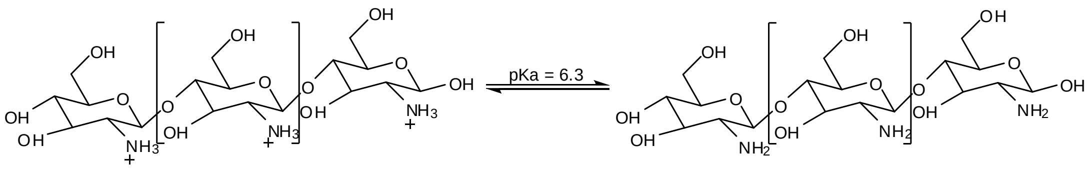


Figure 2.10 The chitosan structure

2.6 Literature review

There are several techniques that can be used for the removal of anti-inflammatory drugs but what stands out as a simple, cost-effective, and safe without the generation of any disinfection by-product is the adsorption. The anti-inflammatory drugs that are adsorbed onto the adsorbent surface lead to a simplified handling and thus the removal of these substances. Adsorbents with different types of binding sites can lead to various types of interactions and thus effective removal of particular contaminants [105].

2.6.1 Removal of anti-inflammatory drugs from wastewater

A variety of materials have been used as adsorbents for removing anti-inflammatory drugs from wastewater. To obtain the maximum adsorption efficiency, the adsorbent with high adsorption capacity is preferred. Several adsorbents for the removal of anti-inflammatory drugs, particularly ibuprofen, diclofenac, and naproxen, have been demonstrated. Some of these adsorbents are summarized below.

Jin and Row (2005) [106] prepared a molecular imprinted polymer (MIP) by using 4-vinylpyridine (4VPY) as a functional monomer. The prepared material was used for the removal of ibuprofen through adsorption process. The adsorption isotherm of the prepared molecular imprinted polymer was compared with blank polymer via the static method. It was indicated that both polymers were fitted well with Radke-Prausnitz isotherm over the others. In addition, the ibuprofen adsorption efficiency of the prepared molecular imprinted polymer was higher than the blank polymer.

Mestre et al. (2007) [107] studied the ibuprofen removal using prepared powdered activated carbons. Cork waste was used as the raw material for the preparation of two powdered activated carbons, CAC and CPAC. The chemical activation of cork waste with K_2CO_3 provided CAC adsorbent while CPAC was obtained by stream activation of CAC using N_2 (two step method). The different preparation procedures provided distinct chemical properties of surface with small different texture. The PZC of these prepared materials were investigated through Boehm's titration and the result showed that the PZC of CAC was lower than that of CPAC. This indicated that the surface of CAC was more acidic than CPAC. The temperature adjustment in the range of 25 to 40 ^{o}C had no significant influence to the adsorption efficiency of ibuprofen. The optimum solution pH to achieve the maximum adsorption efficiency of both prepared materials was in the range of 2 to 4; however, upon increasing the solution pH to 11, the adsorption efficiency of CAC and CPAC were continually decreased by 85% and 30%, respectively. The adsorption kinetics for ibuprofen of both adsorbents followed the pseudo-second-order kinetic model and the adsorption equilibrium was in compliance with the Langmuir adsorption isotherm model. Both adsorbents were suitable for ibuprofen removal, but CPAC had surpassing performances including wide range of appropriated solution pH, high adsorption rate, high adsorption capacity, and high adsorption efficiency. This improved performance can be attributed to the more developed supermicroporous structure in CPAC via the two-step method preparation.

Bajpai and Bhowmik (2010) [12] synthesized the polyaniline (PAn) for diclofenac removal from aqueous solution. The optimal solution pH for diclofenac adsorption was in a wide range of 5.5 to 10.5 and the pseudo-second-order kinetic model fitted well with the kinetic experimental data. Moreover, the rate determining step of this process was controlled by the intraparticle diffusion procedure. Furthermore, the diclofenac removal by this method was reportedly linked to the enhancement of a bacterial growth, *Escherichia coli.*, which beneficially assisted in the removal of harmful heavy metals as well.

Cuerda-Correa et al. (2010) [13] prepared carbon black for the application as a low-cost adsorbent for the removal of naproxen and ketoprofen from river water. The adsorption ability of the prepared carbon black was governed by temperature, ionic strength, and solution pH. The pH_{pzc} of the prepared carbon black was 4.9 and thus when the solution pH was raised above pH_{pzc}, the negative charge of adsorbent surface was demonstrated. Moreover, the dissociation of both drugs to generate negative charge occurred at the solution pH above 4.6. Accordingly, lower pH of solution is more favorable to conquer the highest adsorption efficiency. In addition, at low pH of solution, low temperature, and low ionic strength, the maximum adsorption efficiency of both drugs were obtained. Under the optimal condition, approximately 517 mg/g and 400 mg/g of naproxen and ketoprofen, respectively, were removed from water.

Hasan et al. (2012) [108] investigated the adsorption efficiency of naproxen and clofibric acid using metal-organic frameworks (MOFs), MIL-101 [porous chromium-benzenedicarboxylate (Cr-BDC)] and MIL-100-Fe [iron-benzenetricarboxylate (Fe-BTC)]. The adsorption process occurred through electrostatic interaction between the adsorbents and contaminants, hence, lower pH of solution was preferable. Both types of adsorbents provided fast adsorption rate and high adsorption capacity due to the large pore size and pore volume. The adsorption kinetics followed the pseudo-second-order kinetic model. Under the optimum condition, the experimental data of both adsorbents were best fitted with Langmuir adsorption isotherm.

Karaman et al. (2012) [14] prepared a clay-micelle complex from octadecyltrimethylammonium (ODTMA) and clay (montmorillonite). The prepared material which had positive charge, large surface area, and large hydrophobic moiety was used as the adsorbent for diclofenac removal from wastewater. Due to the large number of positive charges on the clay-micelle complex, anionic diclofenac could be adsorbed with a relatively high adsorption affinity. Therefore, diclofenac in trace level was also effectively removed by the prepared adsorbent. The equilibrium adsorption data was fitted with Langmuir isotherm model and the maximum adsorption capacity of diclofenac onto this clay-micelle complex was 153.8 $mg \cdot g^{-1}$.

Reza et al. (2014) [109] activated bamboo waste with $ZnCl_2$ followed by microwave heating to obtain the inexpensive adsorbent for the removal of ibuprofen and clofibric acid from aqueous solution. The maximum adsorption capacity of ibuprofen and clofibric acid onto the activated bamboo waste (ABW) calculated from Langmuir isotherm model were 278.55 mg/g and 229.35 mg/g, respectively. In the thermodynamic study, the Gibbs free energy was $-6.15\ kJ\cdot mol^{-1}$ for ibuprofen and $-5.56\ kJ\cdot mol^{-1}$ for clofibric acid which indicated that these adsorption processes were spontaneous, exothermic, and thermodynamically favorable. The adsorption kinetics followed pseudo-second-order kinetic model; moreover, the rate determining step of the adsorption processes was determined by the diffusion of the contaminants into micropore and mesopore. Finally, the reusable process of the prepared material was investigated via the desorption of used adsorbent with methanol. The result showed that methanol was a suitable desorbing agent for both ibuprofen and clofibric acid with the former being preferentially desorbed.

Khatem et al. (2015) [9] synthesized two novel materials, hydrotalcite (HT) which is layered double hydroxide (LDHs) and its calcined form (HT-C), for use as adsorbents in the diclofenac removal process. The hydrotalcite was prepared via a conventional co-precipitation method at constant pH, afterward the prepared hydrotalcite was calcined at 550 ^{o}C to obtain HT-C. The adsorption kinetics of both materials followed the pseudo-second-order kinetic model with fast adsorption rate. The Langmuir adsorption isotherm model was applicable for describing the interaction between diclofenac and both HT and HT-C. The maximum adsorption capacity of HT-C was $1.9\ mmol\cdot g^{-1}$ which was higher than that of HT. This improvement can be ascribed to the calcination process wherein the active sites on HT-C material were increased and thus the adsorption ability was also enhanced.

However, these adsorbents have not been widely used because of their high costs and complicated preparations. Simple and inexpensive but yet effective adsorbents are still needed.

2.6.2 Removal of contaminants in wastewater using tire crumb rubber

Tire crumb rubber is an abundant waste material which is relatively stable and non-degradable. It is normally considered as worthless and discarded. The structure of tire rubber consists of both polar and nonpolar parts, thereby it is capable of interacting with both polar and nonpolar molecules. In fact, waste tire crumb rubber has been reported to having been used as an adsorbent for the removal of a variety of contaminants from wastewater. Some of its applications were reviewed herein.

Knocke and Hemphill (1981) [110] prepared the vulcanized tire rubber as the adsorbent for the removal of inorganic mercury from waste solution. The solution pH was the most important factor that defined the adsorption efficiency. The optimum pH for the adsorption of mercury onto the vulcanized tire rubber was in the range of 5.5 to 6.0. The rate limiting step of the adsorption process was determined by the pores diffusion procedure. The adsorption efficiency of mercury by the tire rubber varied essentially by its species with the hydroxyl-mercury complexes being most preferably removed. Nonetheless, the mercury adsorption efficiency on the vulcanized tire rubber was compared with those of the sulfur-free tire rubber material and it was shown both materials provided comparable removal efficiency toward inorganic mercury.

Calisir et al. (2009) [111] investigated the adsorption process of Cu(II) ions from aqueous solution in batch system using tire crumb rubber. The adsorbent ability was mainly depended on the solution pH and the optimum condition for the removal of copper was demonstrated at pH 6.0. The adsorption mechanism was rationalized through the ion exchange process between zinc [Zn(II)] in the starting material and copper in the contaminated aqueous solution. Langmuir adsorption isotherm model was applied to describe the interactive behavior between tire adsorbent and copper under the optimum conditions; moreover, the maximum adsorption capacity of copper ions onto the tire crumb rubber was approximately 1.5152 $mg{\cdot}g^{-1}$.

Wu and Zhou (2009) [86] utilized the waste tire rubber (WTR) as a raw material for the adsorption of oil in pure toluene and diluted crude oil with toluene. WTR was modified with 4-*tert*-butylstyrene (tBS) through the graft copolymerization-blending method, where benzoyl peroxide (BPO) and divinylbenzene (DVB) were used as the initiator and crosslinking agent, respectively. The adsorption efficiency of WTR-*g*-tBS was defined by both DVB concentration and the feed ratio of WTR to tBS. When the DVB concentration and feed ratio of two monomers were 1%wt and 60/40, the maximum adsorption capacity of the prepared WTR-*g*-tBS obtained was roughly 24.0 $g{\cdot}g^{-1}$. The adsorption mechanism between WTR-*g*-tBS and oil was described by pseudo-first-order kinetic model and the oil adsorption rate in diluted crude oil was slower than that in the pure toluene.

Mousavi et al. (2010) [85] prepared a low-cost and effective adsorbent, waste tire rubber ash (WTRA), by burning the waste tire rubber at 500 $^{\circ}$C for 2 hours. This material was used for the depletion of lead (II) ions from aqueous solution. The optimal solution pH for the adsorption of lead (II) ions onto WTRA was around 6. The kinetics of the adsorption process was described by the pseudo-first-order kinetic model with fast adsorption rate. The equilibrium contact time was reached after 90 minutes. Moreover, the equilibrium experimental data was fitted for the Langmuir adsorption isotherm model with approximately 22.35 $mg{\cdot}g^{-1}$ of the maximum adsorption capacity. Thermodynamic results indicated that the adsorption of lead (II) ions onto WTRA was a spontaneous and endothermic process in which the adsorption efficiency was increased with the increasing adsorption temperature.

Gupta et al. (2011) [112] developed the porous carbonaceous adsorbent for the removal of pesticides which are methoxychlor, atrazine, and methyl parathion from wastewater. In the preparation process, the chemical and thermal treatments of waste tire rubber provided the inexpensive, effective, and efficient activated carbon adsorbent with favorable surface properties, high mesopore and macropore. In batch system, approximately 112.0 $mg{\cdot}g^{-1}$ of methoxychlor, 104.9 $mg{\cdot}g^{-1}$ of atrazine, and 88.9 $mg{\cdot}g^{-1}$ of methyl parathion were removed under the optimal condition which presented by 60 minutes of adsorption time with solution pH 2. The pseudo-first-order kinetic model was used for described the adsorption mechanism of the pesticide onto the developed activated carbon. While the interactive between these pesticides and the activated carbon was explained by the Langmuir isotherm model. The rate determining step was determined by the diffusion of pesticides into adsorbent pores (pores diffusion). In the thermodynamic study, the results indicated that these adsorption phenomenon were exothermic and spontaneous process. Moreover, 91% of methoxychlor, 82.1% of atrazine, and 71.78% of methyl parathion were adsorbed on the developed adsorbent when applied with column experimental system.

Gupta et al. (2013) [113] used the waste tire rubber as a precursor in the preparation of activated carbon adsorbent for chromium removal from wastewater. The activated carbon (AC) was prepared by the carbonization of waste tire rubber where the rubber was subjected to a chemical treatment with hydrogen peroxide followed by N_2 steam activation. The efficiency of chromium removal was largely dependent on the solution pH. The suitable solution pH for the removal of chromium was in the range of 4-6. A rapid adsorption was observed at the beginning and was equilibrated roughly after 1 hour. Under the optimal condition, the adsorption on this material followed Langmuir isotherm model and provided the maximum adsorption capacity of chromium around 12.08 $mg{\cdot}g^{-1}$.

According to these previous works, the waste tire rubber has demonstrated the adsorption capability towards both polar and nonpolar molecules. Hence, it was believed that the anti-inflammatory drugs which contain both polar and nonpolar moieties could be adsorbed on this material as well. The use of waste tire rubber as an adsorbent for this matter will not only eliminate harmful substances from water resources but also diminish these unwanted and understandably worthless materials from the environment.

2.6.3 Removal of the contaminants in wastewater using chitosan

Chitosan is widely used as either the adsorbent or adsorbent modifier for the treatment of wastewater for it is structurally comprised of somewhat reactive amino (-NH_2) functional groups. Under acidic conditions, these amino groups can be protonated which generate positive charges in the molecular structure. The surface modification of a given material by chitosan thereby leads to the incorporation of positively charged sites on its surface. Thus, under appropriate pH, strong adsorption processes can be driven by electrostatic interaction between this positively charged surface-bound chitosan and the adsorbates with negatively charged functional groups. Some of the previous works on this regard are illustrated herewith.

Pietrelli et al. (2015) [114] investigated the removal efficiency of a variety of dyes including acid (Telon B red), basic (Astrazon GTLN red), reactive (Remazol RR gran yellow), and direct (Scarlet red 23) dyes from textile wastewater through decolorization system using chitosan. The kinetics of adsorption was observed to comply with the pseudo-second-order kinetic model with dramatic adsorption in the first two hours before reaching equilibrium. The adsorption isotherm which described the related interaction of these processes was best fitted with the Langmuir adsorption isotherm model. The maximum adsorption capacity of acid, basic, reactive, and direct dyes were approximately 144.90, 58.82, 98.04, and 142.80 $mg{\cdot}g^{-1}$, respectively. It was clearly observed that acid and direct dyes were more favorably adsorbed by chitosan than the others probably due to their chemical characteristic including the types of functional groups on their surface. In addition, it was also reported that this chitosan can be reused effectively for at least three times by treating it with basic solution to regenerate the active sites on its surface.

Zhang et al. (2016) [115] synthesized a series of chitosan-based magnetic composite particles with core-brush topology, CS-MCP, as an efficient adsorbent for the removal of diclofenac and tetracycline hydrochloride from water. As for its preparation procedure, the chitosan was combined with Fe_3O_4 to produce magnetic core particles (MCP), and grafting co-polymerization was used to modify the MCP surfaces (core-brush topology) to obtain CS-MCP adsorbent. Various types of grafted polymer brushes including 2-methyl acryloyloxyethyltrimethyl ammonium chloride (DMC), acrylic acid (AA), and methylmethacrylate (MMA) were used to prepare CD-MCP, CA-MCP, and CM-MCP, respectively. CD-MCP was the best adsorbent which presented the highest adsorption capacity with the electrostatic interaction between the positive charges of brushes and the negative charges on the contaminant surface. The kinetic and isotherm experimental data of this adsorbent followed the pseudo-second-order kinetic model and the Langmuir adsorption isotherm model, respectively. Nevertheless, the active sites of this adsorbent were competitively adsorbed by hydroxide ions (OH^-) in solution and thus the adsorption performance was decreased.

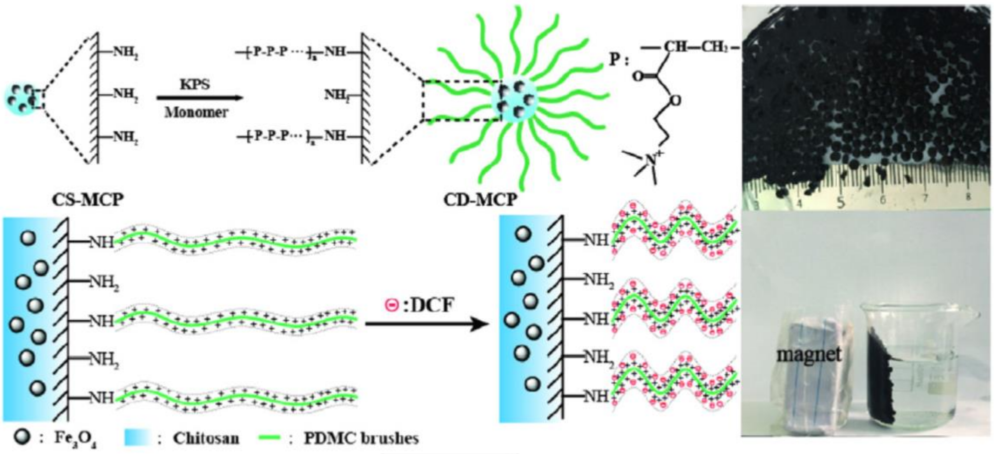


Figure 2.11 The adsorption of diclofenac using chitosan-based material [115]

Based on the above reviews, both dyes and diclofenac have carboxyl functional groups (-COOH) which can be deprotonated in basic solution to produce negative charges on their structures. Therefore, these compounds and any aquatic contaminants including the anti-inflammatory drugs with ionized carboxyl functional groups can potentially be adsorbed via electrostatic interaction with protonated amino groups on chitosan. Moreover, the adsorption process can also be driven by hydrogen bonding between amino groups of chitosan and carboxyl group of the drugs. Therefore, the incorporation of chitosan onto the waste tire crumb rubber should be an interesting and potentially promising modification to this low-cost adsorbent in order to achieve the enhancement on its adsorption efficiency for the anti-inflammatory drugs removal.

In this work, a simple and low-cost composite adsorbent was prepared by a surface modification of waste tire crumb rubber using adsorbed polymeric chitosan. Then, the adsorption efficiency of the prepared adsorbent was evaluated for the removal of three anti-inflammatory drugs; ibuprofen, diclofenac, and naproxen, from aqueous solution.

CHAPTER III
EXPERIMENTAL

3.1 Analytical instruments

Table 3.1 Instrument list.

Instruments	Model, Manufacturer
High-performance liquid chromatograph	Waters^{TM} 600 controller, Waters^{TM} 600 pump, Waters^{TM} 717 plus auto sampler, Waters^{TM} 996 photodiode array detector
Ultraviolet-visible spectrometer	Agilent HP8453
Elemental analyzer	Thermo Scientific^{TM} FLASH 2000
Fourier transformed infrared spectrometer	NICOLET 6700, Thermo Scientific
Multi-position hotplate stirrer	KIKA-WERKE
pH meter	UltraBASIC-10, Denver
Shaker	VELP$^{®}$ scientifica ROTAX 6.8 Overhead mixer
Sonicator	LEO ultrasonic
Stirrer	CREST
Thermogravimetric analyzer	NETZSCH TG209F3 TGA209F3A-0364-L
Oven	MEMMERT
Multi-position hotplate stirrer	KIKA-WERKE

The high-performance liquid chromatography coupled with ultraviolet-visible spectrometer (HPLC-UV) was used to measure the concentration of anti-inflammatory drugs; ibuprofen, diclofenac, naproxen, in aqueous solutions. The operating conditions for the determination of these compounds are shown in Table 3.2.

Table 3.2 Operating conditions of HPLC-UV for the determination of anti-inflammatory drugs.

Analytical column	ZORBAX Eclipse XDB-C18 column (4.6 × 150 mm i.d., 5 μm)
Column temperature	25±2 ^{o}C
Mobile phase A	0.1% formic acid in water
Mobile phase B	0.1% formic acid in acetronitrile
Gradient	15:85
Injection volume	10 μL
UV detection	227 nm
Flow rate	1.0 mL/min
Run time	7 minutes
Delay time	5 minutes
Wash solvent	90:10 (v/v) water:acetonitrile
Replicates	3

3.2 Chemicals

Table 3.3 shows the list of chemicals used in this work. Most of these chemicals were analytical reagent grade excepted acetonitrile that was HPLC grade.

Table 3.3 Chemicals list

Chemicals	Supplier	Grade
Acetic acid 100%	Merck	Analytical reagent
Acetonitrile	Merck	HPLC
Oligomer chitosan	Fluka	Analytical standard
Low MW chitosan	Fluka	Analytical standard, DD 95%
Moderate MW chitosan	Takeda	Analytical standard
High MW chitosan	Fluka	Analytical standard, DD ≥ 85%
Diclofenac sodium salt	Sigma-Aldrich	Analytical standard
Formic acid 98%	Fisher chemical	Analytical reagent
Hydrochloric acid 37%	Merck	Analytical reagent
Ibuprofen sodium salt	Sigma-Aldrich	Analytical standard, ≥ 98% (GC)
Naproxen sodium salt	Sigma-Aldrich	Analytical standard, 98.0-102.0%
Sodium hydroxide	Merck	Analytical reagent
Tire crumb rubber	Union Commercial Development Co. Ltd. (Samut Prakan, Thailand)	Average diameter of 295 μm, particle size distribution shown in Figure 3.1 [116]

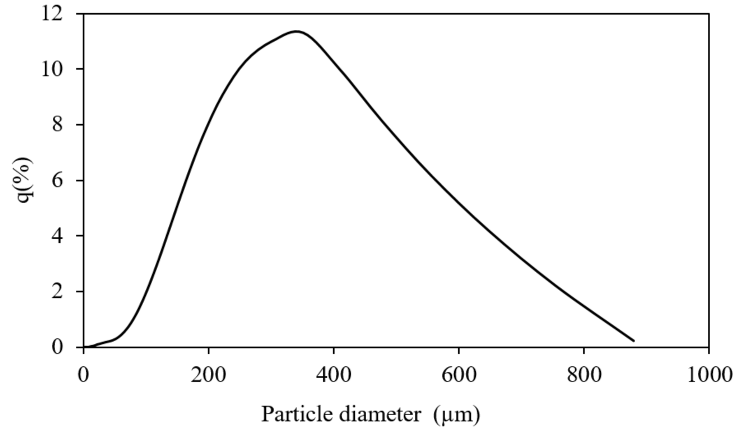


Figure 3.1 Particle size distribution of the waste tire crumb rubber characterized by particle size analyzer [116].

3.3 Preparation of chitosan-modified waste tire crumb rubber adsorbents

Chitosan-modified waste tire crumb rubber adsorbents were prepared by mixing the tire crumb with 2% (w/w) chitosan solution. First, a chitosan solution was prepared by dissolving chitosan powder in 5% acetic acid. Then varying amount of chitosan solution was added into this waste tire crumb rubber to obtain the final ratios of the waste tire crumb rubber: chitosan in the range of 10:0 to 10:10 [0-50%(w/w) of chitosan to the modified adsorbent]. The mixture was stirred for 1 hour at room temperature (25 ± 2°C). After that the mixture was dried overnight at 100°C in an oven to obtain the chitosan-modified waste tire crumb rubber adsorbent. The prepared adsorbent was kept in dry bottle until further use.

3.4 Preparation of solutions

Acetic acid solution

A 5% of acetic acid solution was prepared by dilution of glacial acetic acid with deionized water.

Chitosan solution

Chitosan solution was prepared by dissolving an appropriate amount of chitosan powder in a 5% acetic acid solution.

Diclofenac solution

Diclofenac solution was prepared in a concentration of 40 mg/L from diclofenac sodium salt. Diclofenac sodium salt was weighed exactly 21.5 mg and then dissolved in deionized water using a 500.0 mL volumetric flask. Diclofenac solution was kept in a glass bottle in a dry place.

Formic acid in acetonitrile

Formic acid (98%) was diluted to prepare the formic acid solution at a concentration of 0.1% with acetonitrile. This was used as a mobile phase B for the HPLC-UV analysis.

Formic acid solution

A 0.1% formic acid solution was prepared by diluting 98% formic acid with deionized water. The solution was sonicated for 1 hour before use as a mobile phase A in HPLC-UV technique.

Hydrochloric acid solution

Concentrated hydrochloric acid (37%) was diluted to prepare 1 M hydrochloric acid solution with deionized water.

Ibuprofen solution

A 30 mg/L ibuprofen solution was prepared from ibuprofen sodium salt by weighing exactly 16.7 mg of ibuprofen sodium salt then dissolving in deionized water using a 500.0 mL volumetric flask. Ibuprofen solution was kept in a glass bottle in a dry place until further use.

Naproxen solution

Naproxen sodium salt was weighed exactly 11.0 mg to prepare 10 mg/L of naproxen stock solution with a total volume of 250.0 mL. Then, it was dissolved and made up to the volume with deionized water. A 10 mg/L naproxen stock solution was diluted to 3 mg/L of naproxen solution with a total volume of 500.0 mL and kept in a glass bottle in a dry place until further use.

Sodium hydroxide solution

1 M sodium hydroxide solution was prepared by dissolving an appropriate amount of sodium hydroxide in deionized water.

3.5 Characterization of the adsorbent

Physical and chemical characterization of the waste tire crumb rubber and chitosan-modified waste tire crumb rubber adsorbent were performed using standard characterization techniques below.

3.5.1 Fourier transform infrared spectroscopy (FT-IR)

The functional groups or reactive sites of the chitosan-modified waste tire crumb rubber adsorbent were identified by using the attenuated total reflectance mode (ATR) of FT-IR spectrophotometer (PerkinElmer RXI Spectrophotometer, USA). The spectra were recorded from 600 to 4000 cm^{-1}.

3.5.2 Elemental analysis (EA)

Elemental analysis or EA almost always refers to CHN analysis. The percentage of elements including carbon (C), hydrogen (H), and nitrogen (N) in the chitosan-modified adsorbent and non-modified adsorbent were analyzed by the elemental analyzer (Thermo Scientific^{TM} FLASH 2000).

3.5.3 Themogravimetric analysis (TGA)

The thermal stability changes of modified and non-modified adsorbent were investigated using thermogravimetric measurement (NETZSCH TG209F3 TGA209F3A-0364-L). It was performed using a heating rate of 10 ^{o}C min^{-1} in the temperature range of 35-950^{o}C under ambient environment. The amount of chitosan in the modified waste tire crumb rubber adsorbent was calculated from the thermogram obtained.

3.5.4 The point of zero charge measurement

The pH of point of zero charge (pH$_{pzc}$) of the chitosan-modified waste tire crumb rubber adsorbent was determined by mass titration method (MT) [117].

First, the chitosan-modified tire crumb rubber adsorbent was weighed in the range of 1-10 g/L. Then, 10.0 mL of 0.03 M KNO_3 solution was added into the various masses of the modified adsorbent. The aqueous suspension was shaken for 24 hours with a shaking speed of 30 rpm to reach the equilibrium pH then filtered and measured for the equilibrium solution pH using a pH meter. The pH of point of zero charge is the plateau of pH value which is achieved when plotting the adsorbent mass versus equilibrium pH of the solution.

3.6 Adsorption of anti-inflammatory drugs using chitosan-modified waste tire crumb rubber adsorbent

Anti-inflammatory drug adsorption was carried out by mixing approximately 30 mg of adsorbent with 10.0 mL of the anti-inflammatory drug solution (ibuprofen, diclofenac and naproxen were adsorbed separately from each other). The mixture was shaken at 300 rpm under room temperature ($25 \pm 2\ ^{o}C$) and the pH of solution was appropriately adjusted by 1 M HCl or 1 M NaOH. The sample was filtered through a 0.45-μm nylon syringe membrane filter after the adsorption process and then analyzed for the remaining concentration of ibuprofen, diclofenac, and naproxen in the filtrate by ultraviolet-visible spectroscopy (UV-Vis) at 222 nm, 276 nm, and 230 nm, respectively. The percentage of anti-inflammatory drug removal was calculated using the following equation,

$$\%\text{Removal} = \frac{C_0 - C_e}{C_0} \times 100 \qquad (3.1)$$

Where C_0 is the initial concentration of anti-inflammatory drugs (mg/L)

C_e is the equilibrium concentration of anti-inflammatory drugs (mg/L)

The adsorbed amount of anti-inflammatory drugs were calculated by the following equation,

$$Q_e = (C_0 - C_e) \times \frac{v}{w} \tag{3.2}$$

Where Q_e is the amount of adsorbed anti-inflammatory drugs (mg/g)

v is the volume of the solution (L)

w is the dose of adsorbent (g)

and C_0 and C_e are the initial and equilibrium concentrations of anti-inflammatory drugs (mg/L)

3.6.1 Effect of chitosan types

Different types of chitosan, oligomer chitosan; low molecular weight chitosan; moderate molecular weight chitosan; and high MW molecular weight chitosan, were used as modifiers for enhancing the anti-inflammatory drugs adsorption efficiency from aqueous solution. Each chitosan was dissolved by a 5% acetic acid solution to obtain a 2% (w/w) chitosan solution. The waste tire crumb rubber was then added into this chitosan solution at the ratio of 1:10 (waste tire crumb rubber to chitosan). The mixture was stirred at room temperature for 1 hour and then it was dried in an oven at 100 °C for 24 hours to obtain the chitosan-modified adsorbent.

The efficiency of these chitosan-modified adsorbents for anti-inflammatory drugs removal was studied by the adsorption process. The anti-inflammatory drug solution was added into 30 mg of prepared adsorbent. The suspension was shaken at room temperature (25 ± 2 °C). After 24 hours, the solution was filtered through a 0.45-μm membrane filter. The remaining concentration of anti-inflammatory drugs in the filtrate were analyzed by ultraviolet-visible spectrometry technique (UV-Vis) at respective wavelengths as mentioned above. The equation (3.1) and (3.2) were applied to estimate the adsorption efficiency of the prepared adsorbent. The chitosan which demonstrated the highest anti-inflammatory drugs removal efficiency was then used as the modifier for the remaining of this research.

3.6.2 Effect of chitosan amount

The appropriate chitosan amount for modifying the waste tire crumb rubber adsorbent was investigated to maximize the removal of anti-inflammatory drugs. For the adsorbent preparation, 10.0 g of waste tire crumb rubber was mixed with various amount of 2% chitosan solution, i.e. 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, and 10.0 g. After 1 hour, the mixture was dried in an oven at 100 ^{o}C for 24 hours.

The optimum chitosan amount for the preparation of the modified adsorbents was determined by comparing the adsorption efficiency obtained from different ratios of the modified adsorbent. In the adsorption process, 30.0 mg of adsorbent which is chitosan-modified waste tire crumb rubber was added into 10.0 mL of each anti-inflammatory drug solution. The mixture was shaken with 300 rpm speed at room temperature (25 ± 2 ^{o}C) for 24 hours. After that the suspension was filtered and the remaining concentration of anti-inflammatory drugs in the solution were determined using ultraviolet-visible spectrometer (UV). The adsorption efficiency was calculated according to equations (3.1) and (3.2).

3.6.3 Effect of solution pH

In this work, the effect of pH was optimized by varying the pH of anti-inflammatory drug solution in the range of 1-12. The pH of solution was adjusted using 1 M NaOH and/or 1 M HCl. Thirty milligrams of adsorbent was added into 10.0 mL of each drug solution and shaken (~300 rpm) at room temperature (25 ± 2 ^{o}C) for 24 hours. The solution was filtered through a 0.45-μm nylon syringe filter membrane then the remaining concentration of anti-inflammatory drugs in the filtrate were determined using ultraviolet-visible spectrometer. The efficiency of drug adsorption by this modified adsorbent was calculated from the equation shown in the previous section.

3.6.4 Effect of adsorption time

The effect of adsorption time or contact time was investigated in the range of 0-24 hours for the removal of anti-inflammatory drugs. The adsorbent which is chitosan-modified waste tire crumb rubber was weighted 30.0 mg and added into 10.0 mL of each anti-inflammatory drug solution. The mixture was shaken at room temperature (25 ± 2 °C) with ~300 rpm speed and sampled at the time intervals of 0, 5, 10, 15, 30, 60, 120, 180, 300, 360, 600, 720 and 1,440 minutes. The sampling solutions were analyzed for the remaining concentration of anti-inflammatory drugs using ultraviolet-visible spectrometry. The remaining concentration was compared with the initial concentration of anti-inflammatory drugs in terms of adsorption efficiency according to the previous equation.

3.6.5 Adsorption isotherm

The adsorption isotherm of the anti-inflammatory drug removal was investigated under its optimal adsorption condition at room temperature (25 ± 2 °C). Thirty milligrams of the chitosan-modified waste tire crumb rubber adsorbent was mixed with 10.0 mL of solution containing various initial concentration of anti-inflammatory drug as shown in Table 3.4. The anti-inflammatory drug solutions were adjusted to pH 6 before use in the experiment. The mixture of adsorbent and drug solutions were shaken for 3 hours to ensure that the adsorption process reached the equilibrium. Then, the suspension were filtered and the filtrate was analyzed by an ultraviolet-visible spectrometer. The results were fitted with each of the adsorption isotherm models, Langmuir and Freundlich, for investigating the interactive behavior between the adsorbent and adsorbate or its adsorption mechanism for the removal of anti-inflammatory drugs from aqueous solution.

Table 3.4 Initial concentrations of anti-inflammatory drugs for the adsorption isotherm investigation.

No.	**Initial concentration (mg/L)**		
	Ibuprofen	Diclofenac	Naproxen
1	15	5	1
2	20	10	1.5
3	25	15	2
4	30	20	2.5
5	35	25	3
6	40	30	
7		35	
8		40	

3.7 Anti-inflammatory drug removal from real wastewater samples

In this work, the real water samples of various quality were obtained from different sources. The chitosan-modified waste tire crumb rubber was used as the adsorbent for the adsorption of anti-inflammatory drugs in these samples. Because the real water samples used in this work contain a significantly low amount of anti-inflammatory drugs, the stock standard solution was spiked to obtain the final concentrations of ibuprofen, diclofenac, and naproxen at 400, 400, and 30 mg/L in the sample before the study of adsorption process. The concentration of naproxen used was noticeably lower than the others as a result of its limited solubility. After the treatment with the modified adsorbent, the remaining concentrations of anti-inflammatory drugs in the samples were analyzed by a high-performance liquid chromatograph coupled with an ultraviolet-visible spectrometer (HPLC-UV). All of the anti-inflammatory drug species were detected at 227 nm with the operating parameters as shown in the Table 3.2.

The real wastewater sample obtained from a canal was treated with the chitosan-modified waste tire crumb rubber adsorbent for the removal of anti-inflammatory drugs. This real sample is the representative water from households. The adsorption procedure started with the real wastewater sample being filtered to remove any sediments. Then, the filtrate was spiked with 100 mg/L of naproxen and 1000 mg/L of ibuprofen and diclofenac solutions. The pH of this spiked sample was adjusted to 6 before being used in the adsorption process. 10.0 mL of water sample was loaded with 30 mg of chitosan-modified waste tire crumb rubber adsorbent and shaken for 3 hours at ~300 rpm at the room temperature. The remaining concentrations of anti-inflammatory drugs in the solution were determined by HPLC-UV after filtration.

A Chulalongkorn University's pond water sample was also used for evaluating the anti-inflammatory drug removal efficiency of the prepared adsorbent. The pond water sample was initially filtered and then 100 mg/L of naproxen and 1000 mg/L of ibuprofen and diclofenac solutions were spiked into this filtrate. Later, the spiked solution was adjusted to pH 6 by 1 M HCl or/and 1 M NaOH solution. Thirty milligrams of chitosan-modified waste tire crumb rubber adsorbent was added into the spiked sample and then shaken for 3 hours to reach the equilibrium at room temperature. The remaining concentration was determined by HPLC-UV.

In addition, a tap water sample was used as a real sample for this study. The sample was filtered before use in the experiment. The filtered real sample was spiked with 100 mg/L of naproxen and 1000 mg/L of ibuprofen and diclofenac solutions. The appropriate pH was adjusted. The water sample was loaded with 30 mg of chitosan-modified waste tire crumb rubber adsorbent and continuously shaken for 3 hours at room temperature. The mixture solution was filtered and the remaining concentration of anti-inflammatory drugs in the filtrate were analyzed by HPLC-UV.

CHAPTER IV

RESULT AND DISCUSSION

4.1 Preparation of chitosan-modified waste tire crumb rubber adsorbents

The chitosan powder was initially dissolved in 5% acetic acid which resulted in a yellowish solution. The modified adsorbents were then prepared by mixing a varying amount of this chitosan solution into the waste tire crumb rubber. The physical appearances of this chitosan-modified waste tire crumb rubber adsorbent along with its precursors were shown in Figure 4.1.

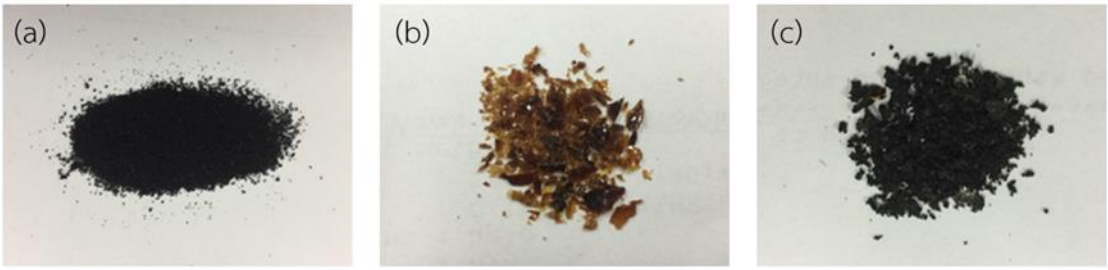


Figure 4.1 The physical appearances of (a) bare waste tire crumb rubber (b) dried activated chitosan (c) chitosan-modified waste tire crumb rubber adsorbent.

4.2 Characterization of the adsorbent

4.2.1 Fourier transform infrared spectroscopy (FT-IR)

The chemical structure of the adsorbent is a key component to understand its adsorption process, the fourier transform infrared technique was thus employed to identify the characteristic functional groups of this sorbent. The FT-IR spectra in attenuated total reflectance (ATR) mode of the waste tire crumb rubber, chitosan, and the chitosan-modified adsorbent are presented in Figure 4.2 (a), (b), and (c), respectively.

The spectra of waste tire crumb rubber in Figure 4.2 (a) showed C-H stretching vibrations peaks at 2917 and 2841 cm^{-1}. While the adsorption bands of chitosan [118], Figure 4.2 (b), revealed a stretching broad band at around 3327 cm^{-1}

which indicated the presence of O-H groups and N-H groups on the adsorbent surface. In addition, it showed the C-H stretching band at 2875 cm^{-1}, N-H bending band at 1584 cm^{-1}, C-N stretching at 1423 cm^{-1}, and a group of C-O-C and C-O stretching bands between 1100 to 1020 cm^{-1}. When comparing the spectra of the chitosan-modified adsorbent with waste tire crumb rubber and plain chitosan, the characteristic absorption bands of the waste tire crumb rubber and chitosan were also observed in the absorption bands of the chitosan-modified adsorbent. The additional absorption bands of chitosan-modified adsorbent [Figure 4.2 (c)] were observed at around 3257 cm^{-1} (O-H and N-H stretching vibrations), 2908 cm^{-1} (C-H stretching vibrations), 1533 cm^{-1} (N-H bending vibrations), 1423 cm^{-1} (C-N stretching vibrations) and a group of bands from 1100 to 1020 cm^{-1} (C-O-C and C-O stretching vibrations). However, no new absorption band that indicated the bonding between the waste tire crumb rubber and chitosan molecules was found. Therefore, this suggested that the chitosan was only assembled onto the waste tire crumb rubber by van der Waals interaction without bonding between the waste tire crumb rubber and the chitosan molecules.

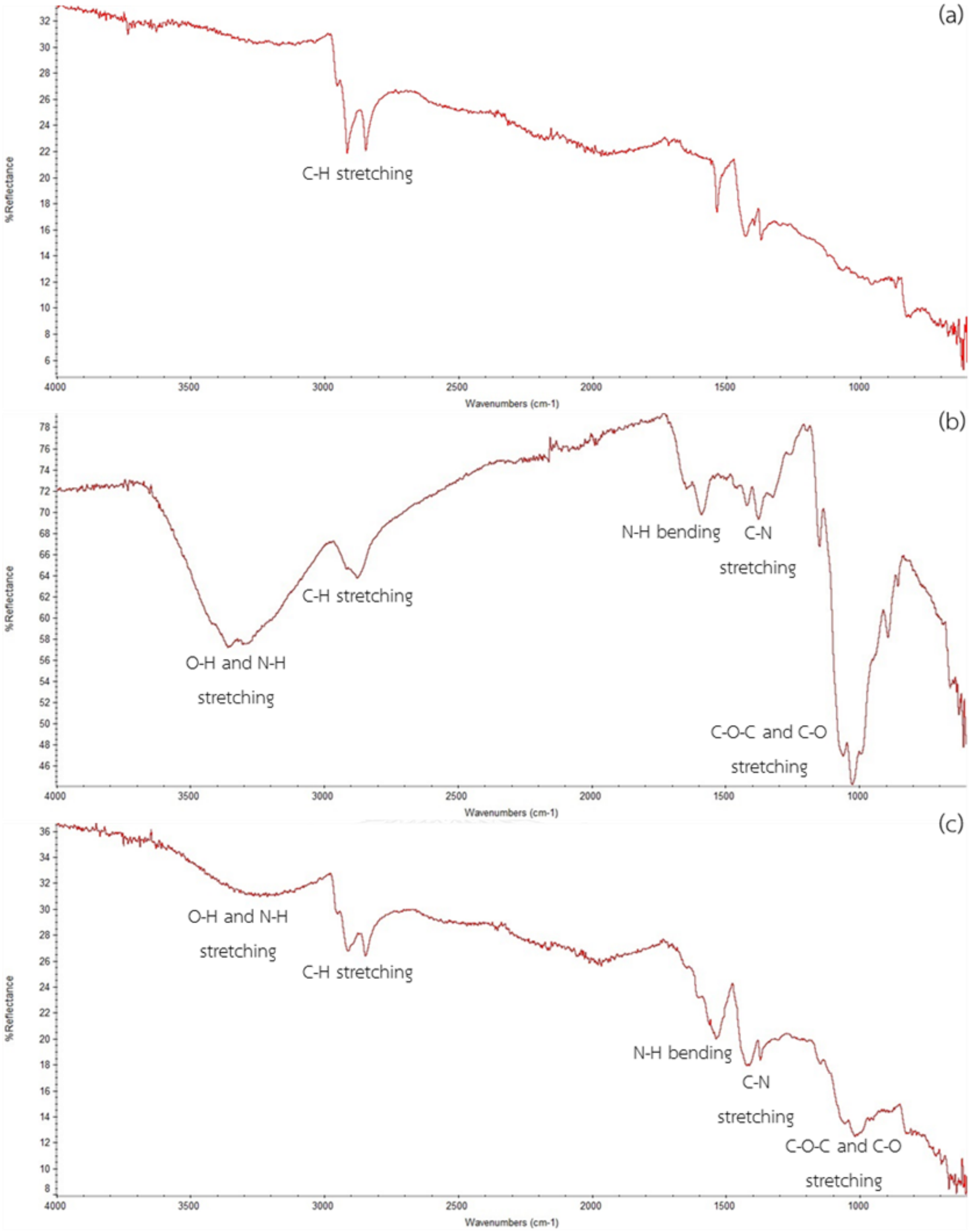


Figure 4.2 FT-IR spectra of (a) waste tire crumb rubber, (b) chitosan, and (c) chitosan-modified waste tire crumb rubber adsorbent.

4.2.2 Elemental analysis (EA)

Elemental analysis was used to confirm the success of the modification process. The elemental composition of non-modified and chitosan-modified adsorbents are given in Table 4.1. The percentages of both carbon (C) and hydrogen (H) decreased from 80.11% carbon and 7.13% hydrogen of the non-modified adsorbent to 68.84% carbon and 6.79% hydrogen of the modified counterpart. Meanwhile, the percentage of nitrogen (N) increased from 0.53% in the non-modified adsorbent to 1.76% in the chitosan-modified adsorbent. The changing percentage of these elements in the modified adsorbent can be attributed to the presence of chitosan molecules deposited on the waste tire crumb rubber surface. This finding evidently validates the successful modification of tire rubber by chitosan.

Table 4.1 The percentages of carbon (C), hydrogen (H), and nitrogen (N) in the non-modified and the chitosan-modified adsorbents.

	%Carbon	%Hydrogen	%Nitrogen
Non-modified waste tire crumb rubber adsorbent	80.11	7.13	0.53
Chitosan-modified waste tire crumb rubber adsorbent	68.84	6.79	1.76

4.2.3 Themogravimetric analysis (TGA)

The thermal analysis of both bare waste tire crumb rubber and chitosan-modified waste tire crumb rubber were investigated by thermogravimetry operating within the temperature range of 35-950 ^{o}C and a heating rate of 10 ^{o}C/min. The results are shown in Figure 4.3. Both thermograms exhibited similar pattern of weight loss. At the initial stage, a small weight loss of 2-5% was observed between 30-100 ^{o}C, due primarily to the loss of moisture. The weight loss by the decomposition of chitosan-modified waste tire crumb rubber adsorbent which occured in the temperature range of 217 to 350 ^{o}C was more substantial than that of bare waste tire crumb rubber. In Figure 4.3 (b), nearly 23% weight loss of the chitosan-modified adsorbent occurred at this temperature range presumably due to the decomposition of chitosan polymer assembled onto the adsorbent [119]. The final weight loss of both materials appeared around 350-575 °C which could be ascribed to the decomposition of the waste tire crumb rubber. Approximately 8% (w/w) of the residual solid remaining in the crucible were defined as the metals and fixed carbon from the composition of tire.

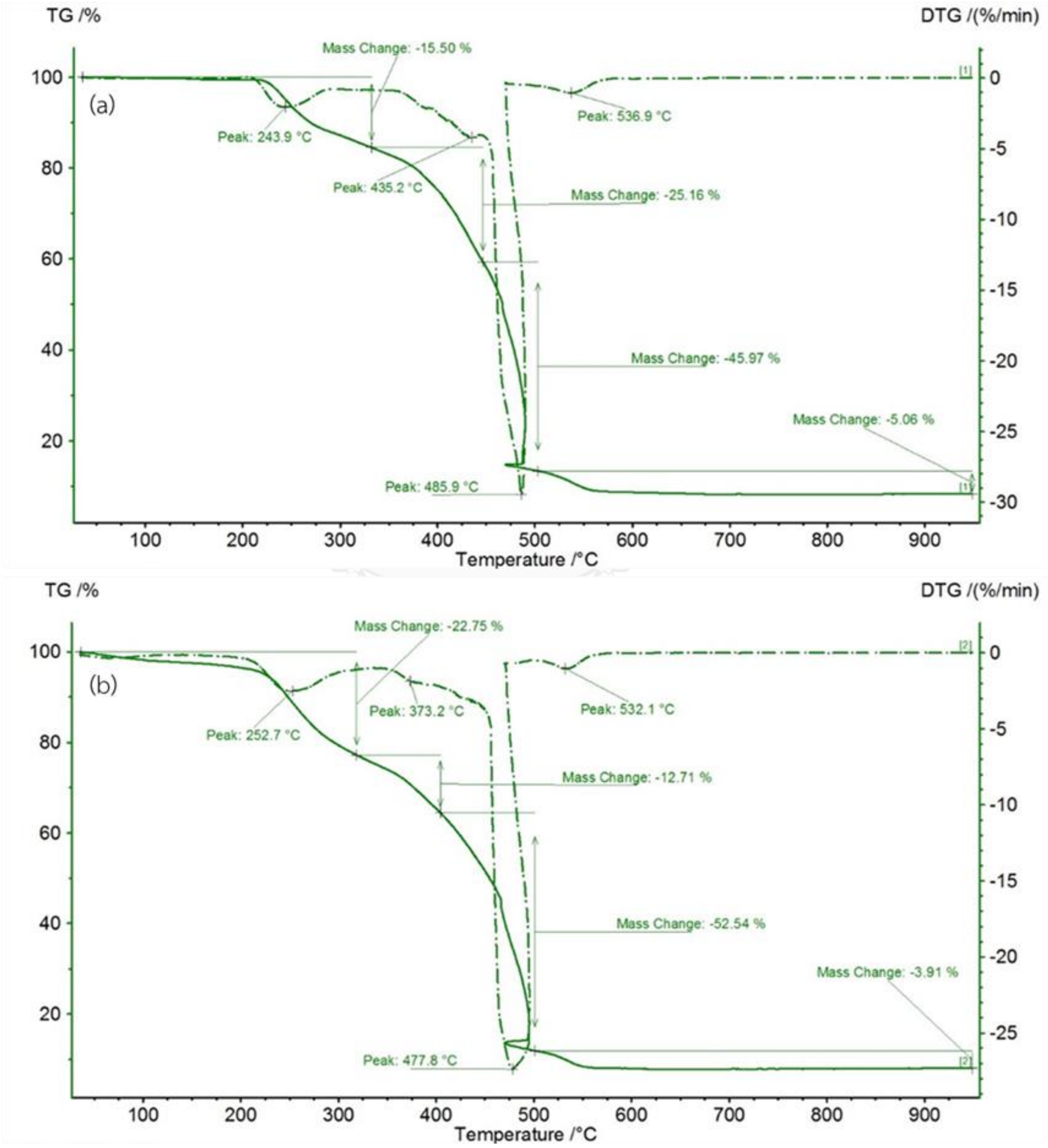


Figure 4.3 Thermograms of (a) waste tire crumb rubber and (b) chitosan-modified waste tire crumb rubber (heating rate of 10 °C/min under ambient environment)

4.2.4 Determination of the point of zero charge (pH_{pzc})

The point of zero charge, pH_{pzc}, is the pH where the surface of adsorbent has a net neutral charge. The adsorbent surface becomes negatively charged if the pH of the solution is above this pH_{pzc} and conversely becomes positively charged if the solution pH is below this value. The charge imposed on the adsorbent plays a significant role on its adsorption efficiency. Therefore, the pH_{pzc} can be used to define the adsorption mechanism of anti-inflammatory drugs onto the chitosan-modified waste tire crumb rubber adsorbent.

In this research, the mass titration curve (shown in Figure 4.4) indicated that the pH_{pzc} of the chitosan-modified waste tire crumb rubber, chitosan, and waste tire crumb rubber were approximately 6.01, 5.69, and 7.72, respectively. The fact that pH_{pzc} of the modified adsorbent lies between those of the chitosan and the waste tire crumb rubber is probably because the modified adsorbent surface was not fully covered by chitosan. The pH_{pzc} of the modified adsorbent was closer to the pH_{pzc} of chitosan than the waste tire crumb rubber which suggested a predominant coating of chitosan on the material. Therefore the behavior of the modified adsorbent would likely be more similar to that of chitosan which means that the surface of adsorbent will be positively charged when the pH is lower than 6.01 ($pH<pH_{pzc}$) while having negative charge when the pH is above 6.01 ($pH>pH_{pzc}$).

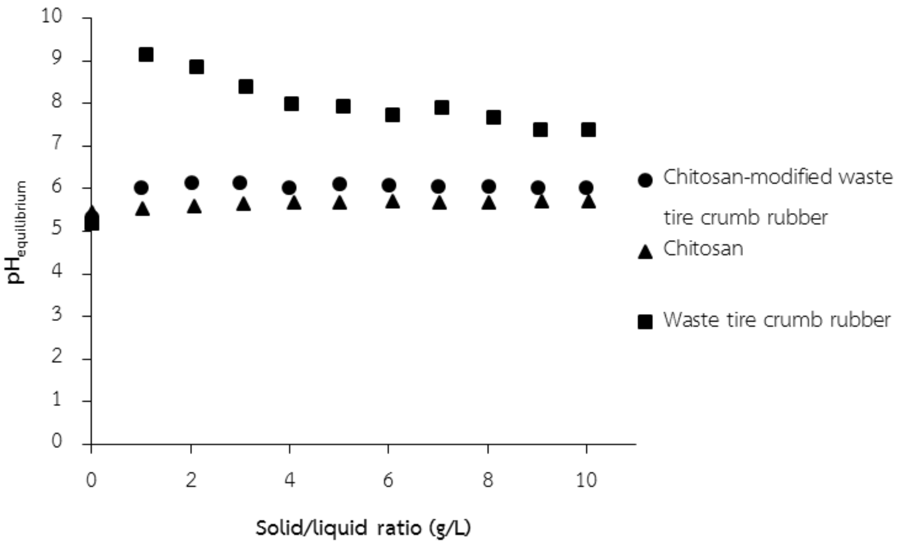


Figure 4.4 Mass titration curve of the chitosan-modified waste tire crumb rubber.

The results implicitly indicated that the assembling of chitosan onto the waste tire crumb rubber was achieved. The novel material, chitosan-modified waste tire crumb rubber adsorbent, was further used for the anti-inflammatory drug removal through the adsorption process in a batch system. The evaluation results and discussions are shown in the following sections.

4.3 Adsorption of anti-inflammatory drugs using chitosan-modified waste tire crumb rubber adsorbent

The key factors that could have influences toward the anti-inflammatory drug adsorption, such as the type of chitosan, chitosan amount, pH of solution, contact time, and initial concentration of the anti-inflammatory drugs were studied in order to optimize the conditions for the adsorption process as detailed hereafter.

4.3.1 Effect of chitosan types

The types of chitosan which was used as a modifier in the waste tire crumb rubber modification process were investigated firstly as this could play a decisive role to the adsorption efficiency of anti-inflammatory drugs. In this research, various types of chitosan, i.e. oligomer, low molecular weight (low MW), moderate molecular weight (moderate MW), and high molecular weight (high MW) chitosans were investigated for their removal efficiency against diclofenac. Each type of chitosan was mixed with the waste tire crumb rubber in the weight ratios 1:5 and 1:10 of the waste tire crumb rubber to chitosan (approximately 83% and 91% weight of chitosan in the modified adsorbent, respectively). The findings are presented in Figure 4.5.

At the ratio of 1:5 (83% weight of chitosan), the oligomer chitosan was able to remove only around 37% of diclofenac in aqueous solution while the low MW, moderate MW, and high MW provided similar adsorption efficiency of roughly 56% removal. On the other hand, when the ratio of the waste tire crumb rubber to chitosan weight was increased to 1:10 (91% weight of chitosan), the removal efficiency was collectively improved. The oligomer chitosan and low MW chitosan imparted only a slight increase (40% and 59% removal) while the moderate MW and high MW chitosans demonstrated a much more significant improvement with roughly 71% and 72% of diclofenac removal, respectively. The high molecular weight chitosan was therefore chosen as the model modifying agent for the preparation of the chitosan-modified waste tire crumb rubber in this study.

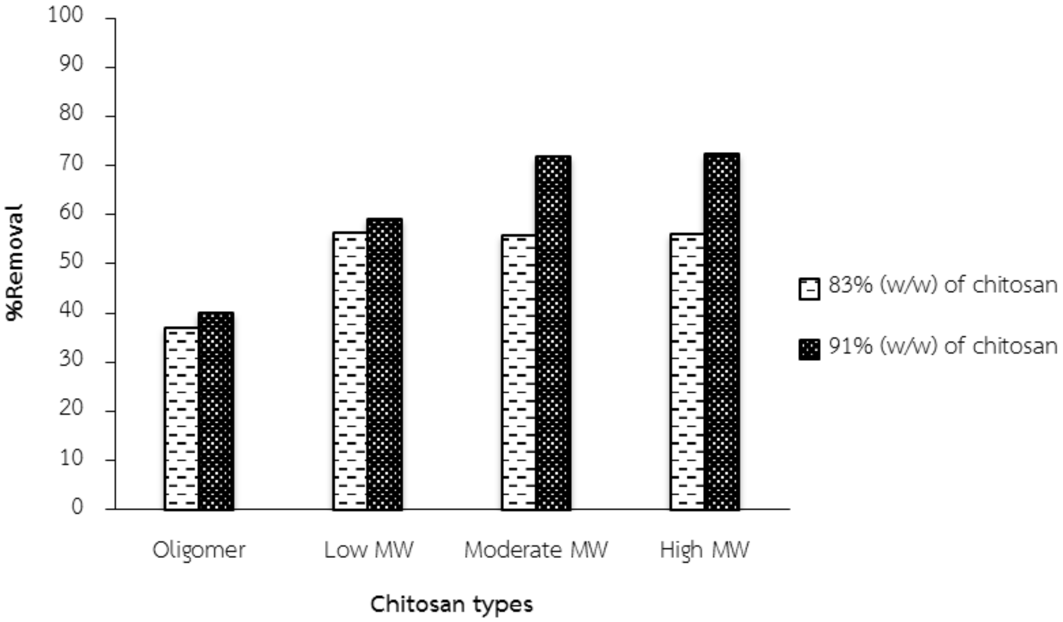


Figure 4.5 The effect of chitosan types on the removal percentage.

4.3.2 Effect of chitosan amount

The chitosan amount is one of the important factors that should be optimized to obtain the highest adsorption efficiency of the adsorbent. The effect of chitosan amount used for the preparation of chitosan-modified adsorbent was studied by varying the quantity of chitosan in the modified adsorbent in the range of 0-50% [10:0 to 10:10 of the waste tire crumb rubber to 2% (w/w) of chitosan solution]. Each adsorbent which contains a differing amount of chitosan was added into ibuprofen, diclofenac, or naproxen solution and then shaken at ~300 rpm for 24 hours at room temperature. The remaining concentration of each drug was analyzed by a UV-Vis spectrometer. The percentage of anti-inflammatory drug removal versus the chitosan content loaded onto the adsorbent is shown in Figure 4.6.

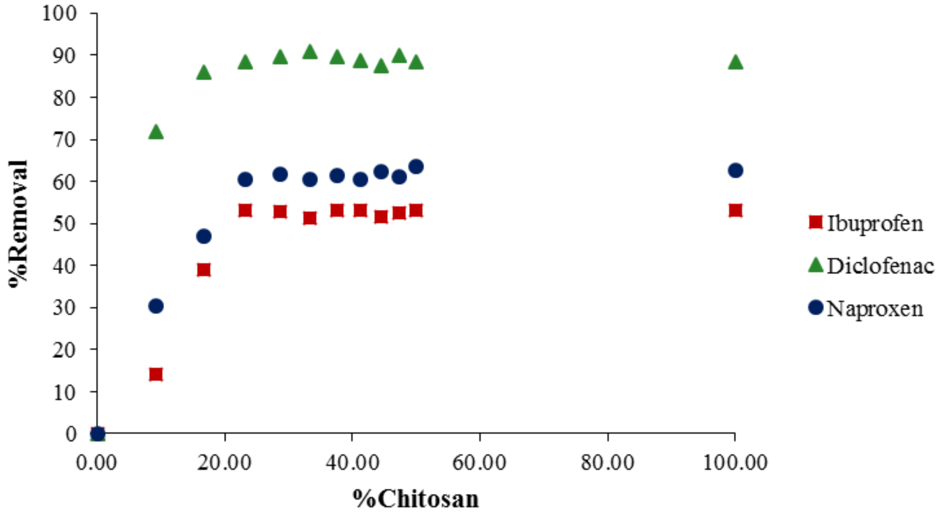


Figure 4.6 %Removal of anti-inflammatory drugs as a function of %chitosan.

As can be seen from Figure 4.6, the removal percentage, which is indicative of the adsorption efficiency, of these anti-inflammatory drugs by the modified adsorbent increased proportionally with the chitosan amount from 0 to 23% (w/w) presumably due to the enhanced electrostatic interactions between the carboxyl groups on anti-inflammatory drugs and the increased amino groups on chitosan. Up to 90% of diclofenac in aqueous solution was removed using the chitosan-modified adsorbent comprising at least 23% (w/w) chitosan (10:3 of the waste tire crumb rubber to chitosan). Meanwhile, approximately 60% and 50% of naproxen and ibuprofen were eliminated from aqueous solution by the identical percentage of chitosan on the modified adsorbent. Nevertheless, as the chitosan amount was higher, i.e. above 23% (w/w), the anti-inflammatory drug removal became almost constant. This is probably due to the fact that the chitosan molecules may have been fully deposited on all the surface of the waste tire crumb rubber and thus the adsorption efficiency would be limited by the number of chitosan active sites on this adsorbent surface. Hence, further increase of the chitosan amount, even the use of pure chitosan (100%) which largely floated over the surface of the solution, proved to be no beneficial to the removal of these substances. In fact, the assembling of chitosan on the waste tire crumb rubber provided another advantageous aspect in that the chitosan density and surface area was increased by the rubber particles to which they are attached, and thus allowed significantly better contact with the drug molecules in the solution. Therefore, the chitosan-modified waste tire crumb rubber adsorbent was prepared with 23% (w/w) of chitosan for further use in the anti-inflammatory drug removal in this study.

4.3.3 Effect of solution pH

The solution pH has always been a crucial parameter in an adsorption process as it can manipulate the presence of particular species of the adsorbate and the adsorbent active sites. For this reason the effect of pH of solution on the anti-inflammatory drug removal was investigated in the pH range of 1-12 with fixed amount of the adsorbent. In order to study this effect, 30 mg of the chitosan-modified adsorbent was added into 10 mL of solution with a fixed initial concentration of ibuprofen, diclofenac, or naproxen at 30 mg/L, 40 mg/L, or 3 mg/L, respectively. The result is depicted in Figure 4.7. The modified adsorbent significantly adsorbed ibuprofen in the pH range 4-9 while diclofenac and naproxen were adsorbed onto this material in the range of pH 5-10 and 3-10, respectively. The optimal solution pH for the adsorption of ibuprofen, diclofenac, and naproxen collectively is at pH 6. At this pH, diclofenac was greatly removed from aqueous solution, reaching approximately 78.20%, while those obtained for the naproxen and ibuprofen at this pH were 50.71% and 33.21%, respectively.

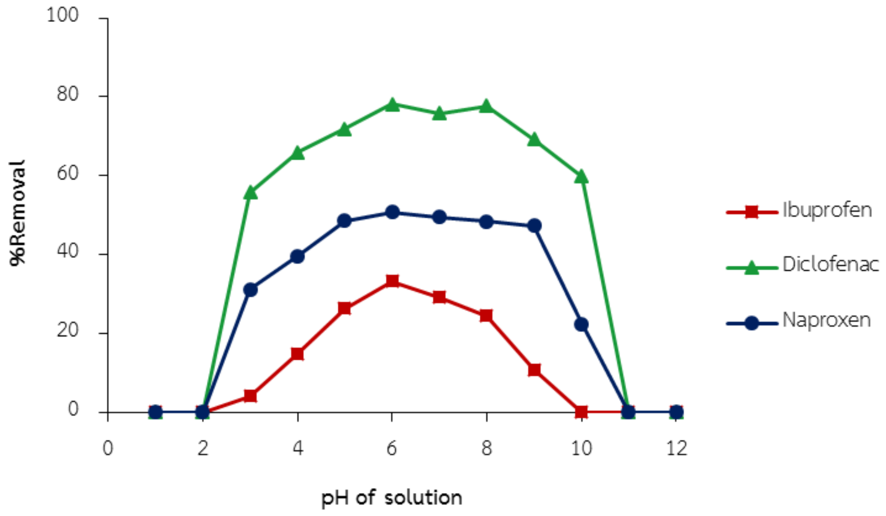


Figure 4.7 Effect of solution pH on anti-inflammatory drug removal by chitosan-modified waste tire crumb rubber adsorbent.

The adsorption vs. pH results can be rationalized with reference to the charge states of the surface and the molecular adsorbates as a function of pH. According to the point of zero charge principle, the adsorbent surface is literally neutral at the pH_{pzc} (~6.1). Under the condition where the solution pH is less than pH_{pzc}, the adsorbent surface become positively charged. Under strong acidic condition, the adsorption process is unfavorable because the amino groups on the chitosan structure are protonated and become positively charged whereas the carboxyl functional on the anti-inflammatory drugs remain uncharged as carboxylic acids. The pK_a values for the carboxylic acid groups on each of the three NSAID compounds are similar, i.e. 4.35 for ibuprofen, 4.27 for naproxen and 4.7 for diclofenac. Hence, over the pH range 3-6, the carboxyl groups on the drugs are progressively converted from being in neutral protonated form to negatively charged deprotonated form. Moving across this pH interval towards more basic solutions, the adsorption for each compound increases, because the negative charges of carboxylate groups interact strongly with the positively charged amino groups of the surface-bound chitosan polymers. Therefore, the electrostatic interactions between chitosan and the drugs enhances the removal of anti-inflammatory drugs from solution. Above pH 6 ($pH>pH_{pzc}$), the adsorbent surface becomes negatively charged while the drugs also contain negative functional groups, thereby the adsorption becomes increasingly unfavorable due to the increasing electrostatic repulsions under these higher pHs. However, the hydrogen bonding between the deprotonated carboxyl groups of drugs and uncharged amino groups of chitosan are also believed to have taken place, resulting in substantial adsorption up to pH values ≈ 8. The driving force for adsorption may have also contained a component from interactions via dispersion forces between non-polar regions of the adsorbate molecules and chitosan-modified surfaces.

In addition, the fact that this modified adsorbent performed relatively well over a wide pH range (i.e. pH 3-10) proved to be very advantageous particularly for the wastewater treatment applications. Normally the pH adjustment of the wastewater is an integral part of the treatment process to maximize the adsorbent efficiency. This process inevitably requires a large amount of chemicals and high operating cost. Thus the adsorbent which functions optimally over a wide range of pH is preferred making this modified adsorbent desirable for such wastewater treatment process.

4.3.4 Effect of adsorption time

The adsorption time or contact time is one of the important factors for the removal process. The adsorption time for the anti-inflammatory drug removal was investigated in the range of 0-1,440 minutes (0-24 hours) with fixed amount of the chitosan-modified waste tire crumb rubber adsorbent. The adsorption of each anti-inflammatory drug was independently studied.

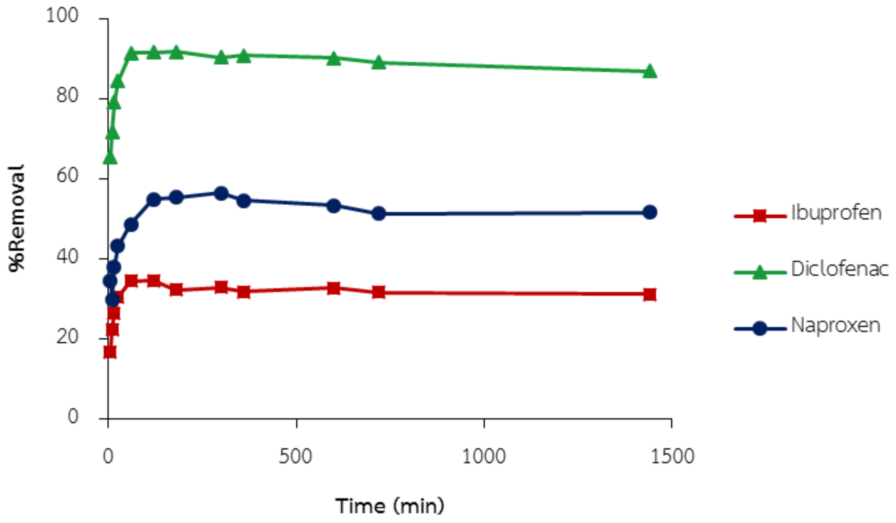


Figure 4.8 Effect of adsorption time on anti-inflammatory drugs removal.

Figure 4.8 displays the removal percentages of ibuprofen, diclofenac, and naproxen as a function of time (min). The removal percentage, which indicated the absorption efficiency of the modified adsorbent, increased gradually during the first two hours then became relatively steady afterwards. The rapid adsorption during the first period could be related to the abundant active sites available on the chitosan-modified adsorbent surface together with a strong interaction between active sites and the target drugs. The optimum contact time for ibuprofen, diclofenac, and naproxen adsorption were roughly 1, 1, and 2 hours in which the elimination of approximately 30%, 90%, and 50% for ibuprofen, diclofenac, and naproxen, respectively, from aqueous solution were attained.

4.3.4.1 Adsorption kinetics

To investigate the factors that could be related to the adsorption rate, the adsorption kinetics was examined by fitting the experimental data to the first-order and second-order kinetic models. The linear equations of first-order and second-order kinetic models can be expressed in equations (4.1) and (4.2), respectively.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4.1}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{2}} + \frac{1}{q_e} t \tag{4.2}$$

Where q_t is the adsorption capacity at time t or adsorbed amount of adsorbate at time t (mg/g)

q_e is the equilibrium adsorption capacity or adsorbed amount of adsorbate at equilibrium (mg/g)

t is the elapsed time in minutes

k_1 is the adsorption rate constant of first-order kinetic model (min^{-1})

and k_2 is the adsorption rate constant of second-order kinetic model (g/mg·min)

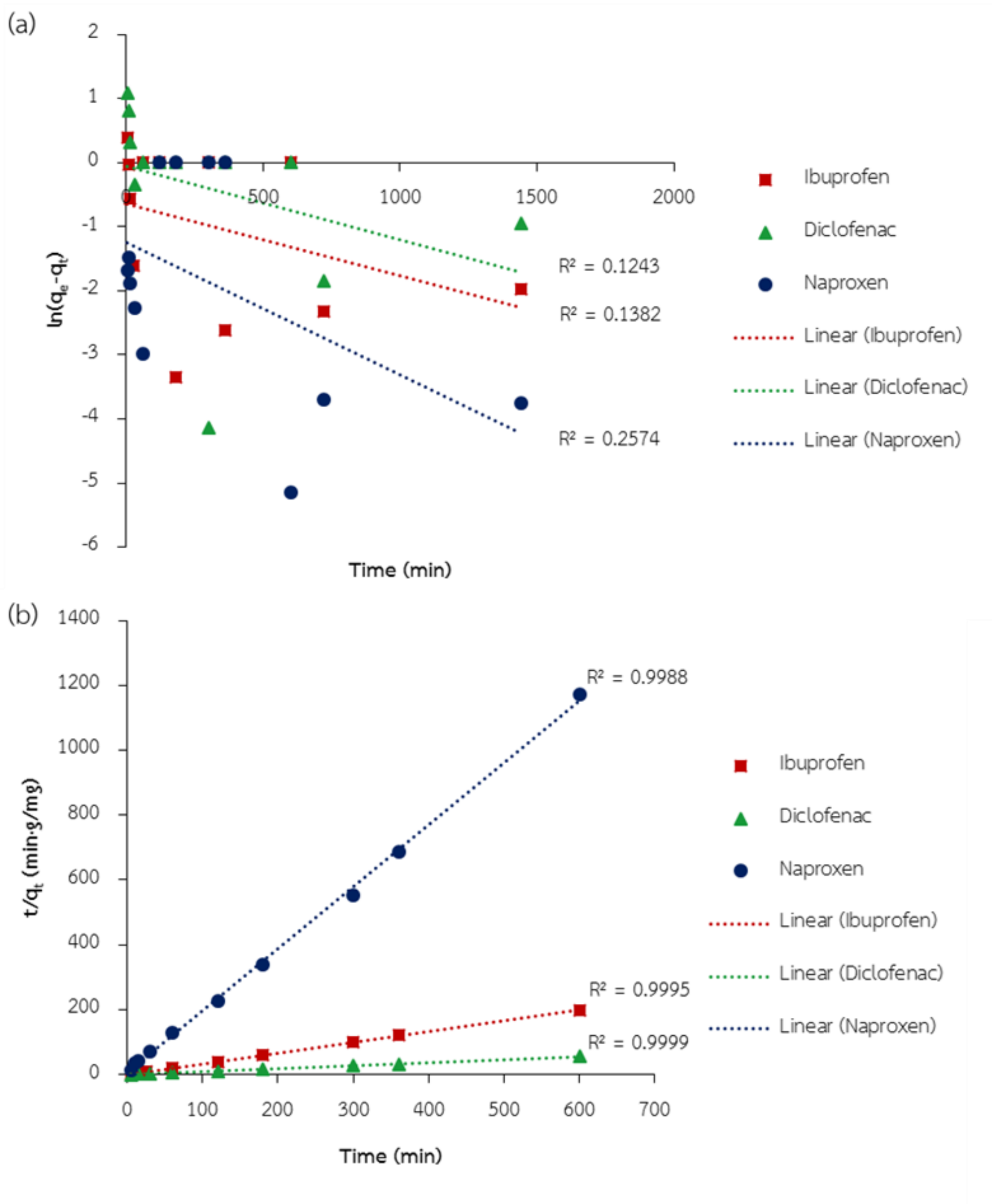


Figure 4.9 The linear regression of (a) first-order kinetic model and (b) second-order kinetic model, for the anti-inflammatory drug removal

The experimental adsorption data of anti-inflammatory drugs by the modified adsorbent was fitted in both first-order and second-order kinetic models as shown in Figure 4.9 (a) and (b), respectively. This fitting provided the adsorption kinetic parameters as shown in Table 4.2. The correlation coefficient (R^2) was used as a criteria to decide the kinetic model of the adsorption of these anti-inflammatory drugs. The R^2 obtained from first-order kinetic model of ibuprofen, diclofenac, and naproxen species were 0.1382, 0.1243, and 0.2574, respectively, while the second-order kinetic model presented the R^2 of 0.9995, 0.9999, and 0.9988 for ibuprofen, diclofenac, and naproxen, respectively. This clearly suggested that such adsorption processes are in compliance with second-order kinetic model. Moreover, the equilibrium adsorption capacity obtained from the experiment [q_e(exp)] of second-order kinetic model was identical to the equilibrium adsorption capacity from the calculation [q_e(cal)]. These results reiterated that the adsorption kinetics of ibuprofen, diclofenac, and naproxen are best described by the second-order kinetic model. Therefore, the adsorption of these anti-inflammatory drugs on the modified adsorbent is based on the assumption that the adsorption capacities of chitosan-modified waste tire crumb rubber adsorbent were proportionally related to the number of active sites on the surface [120] and the rate limiting step of these processes may be defined by chemisorption through the sharing or exchanging of valence electrons between adsorbent and adsorbate [121]. In addition, the second-order rate constant (k_2) of naproxen was higher than that of ibuprofen and diclofenac thus indicating that the removal of naproxen through the adsorption process using the chitosan-modified adsorbent was faster than the ibuprofen and diclofenac, respectively.

Table 4.2 Adsorption kinetic parameters for the adsorption of anti-inflammatory drugs using chitosan-modified waste tire crumb rubber.

Anti-inflammatory drugs	First-order kinetic model				Second-order kinetic model			
	q_e(exp) (mg/g)	q_e(cal) (mg/g)	k_1 (min^{-1})	R^2	q_e(exp) (mg/g)	q_e(cal) (mg/g)	k_2 (g/mg·min)	R^2
Ibuprofen	3.03	0.52	0.0011	0.1382	3.03	3.03	0.21404	0.9995
Diclofenac	10.80	0.95	0.0012	0.1243	10.80	10.87	0.08162	0.9999
Naproxen	0.52	0.29	0.0021	0.2574	0.52	0.52	0.58182	0.9988

4.3.5 Adsorption isotherm

Under the optimum conditions, the interactive behavior between the modified adsorbent and adsorbates were predicted using the adsorption isotherm model. The initial concentrations of the anti-inflammatory drugs were varied as shown in Table 3.4 and the remaining concentration after the adsorption by the modified sorbent was determined using UV-Visible spectrometry. The relationship between the adsorption capacity (q_e) (mg/g) and the equilibrium concentration (C_e) (mg/L) is shown in Figure 4.10 (a). The adsorption efficiency of the anti-inflammatory drugs onto the modified adsorbent surface increased with increasing initial concentration of ibuprofen, diclofenac, and naproxen.

The Langmuir adsorption isotherm model is used to describe the monolayer adsorption and homogeneous surface of adsorbent with limited interaction between the active sites and adsorbed molecules. The linear equation of this isotherm is shown in equation (4.3) [122].

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \qquad (4.3)$$

Where C_e is the equilibrium concentration of anti-inflammatory drug (mg/L)

q_e is the amount of anti-inflammatory drugs adsorbed on the adsorbent (mg/g)

q_m is the maximum adsorption capacity of the adsorbent (mg/g)

and K_L is the Langmuir constant related to the free energy and affinity of binding sites (L/mg).

The Freundlich adsorption isotherm model, on the other hand, is associated with the multilayer adsorption and heterogeneous surface of adsorbent with different active sites and several adsorption energies. The Freundlich adsorption equation is shown below [69].

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad (4.4)$$

Where	K_F	is	the Freundlich constant related to adsorption capacity (mg/g)
	n	is	dimensionless constant related to adsorption intensity
	C_e	is	the equilibrium concentration of anti-inflammatory drug (mg/L)
and	q_e	is	the amount of anti-inflammatory drugs adsorbed on the adsorbent (mg/g)

From Figure 4.10 (b) and (c), the correlation coefficient (R^2) of each curve is used to determine the interactive behavior between the modified adsorbent and the anti-inflammatory drugs. The Langmuir plot provided a linear regression with R^2 of 0.9534, 0.9171, and 0.8577 while the Freundlich plot produced R^2 of 0.9949, 0.9878, and 0.9863 for ibuprofen, diclofenac, and naproxen, respectively. Therefore, the adsorption of these anti-inflammatory drugs on the chitosan-modified waste tire crumb rubber agreed well with the Freundlich isotherm model rather than the Langmuir isotherm model. Thus, the adsorption of these anti-inflammatory drugs can be ascribed to a multilayer adsorption process on the heterogeneous surface. The Langmuir and Freundlich isotherm constants obtained for these anti-inflammatory drugs are summarized in Table 4.3. The reciprocal of n (1/n) from Freundlich isotherm is used for determining the applicability of the adsorbent and the feasibility of the adsorption process. From this table, 1/n of these anti-inflammatory drugs adsorption is greater than unity. These values indicated that the adsorption process was favorable for the high concentrations range than the low concentrations range of the adsorbate studied [67].

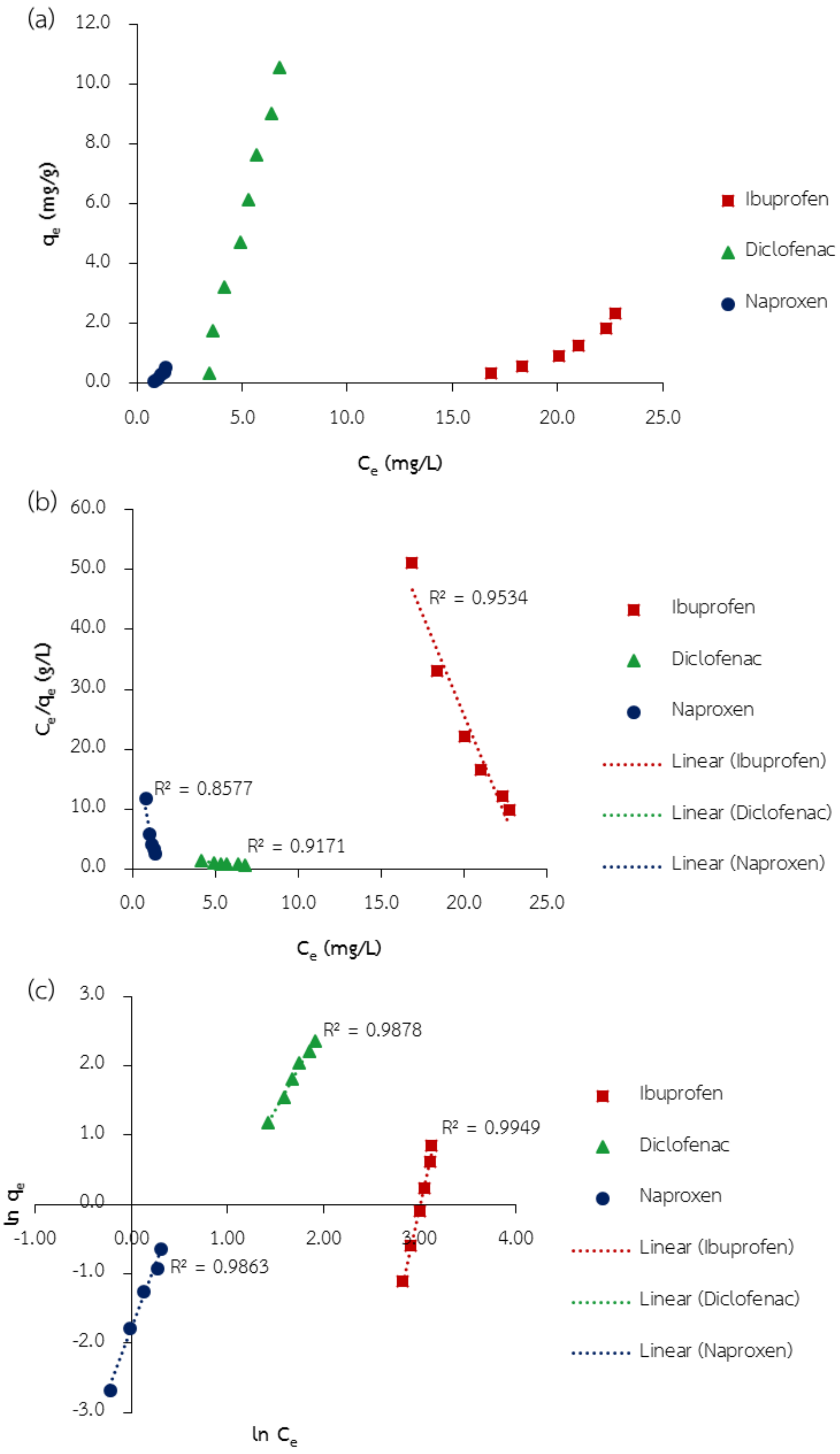


Figure 4.10 Adsorption efficiency of anti-inflammatory drugs at different concentrations; (a) adsorption isotherm; (b) Langmuir isotherm plot; (c) Freundlich isotherm plot.

Table 4.3 Adsorption isotherm parameters for the adsorption of anti-inflammatory drugs onto the chitosan-modified waste tire crumb rubber.

Anti-inflammatory drugs	Langmuir isotherm model			Freundlich isotherm model		
	q_m (mg/g)	K_L	R^2	1/n	K_F	R^2
Ibuprofen	2.32	0.003	0.9534	6.349	5.21×10^{-9}	0.9949
Diclofenac	10.57	0.04	0.9171	2.780	0.056	0.9878
Naproxen	0.52	0.09	0.8577	3.647	0.165	0.9863

4.4 Anti-inflammatory drug removal from real wastewater samples

The anti-inflammatory drug removal efficiency of the chitosan-modified waste tire crumb rubber adsorbent was assessed with the real water samples including Chulalongkorn University's pond, canal water (untreated water), and tap water. A standard spike of each anti-inflammatory drug was applied with the real water samples due to a low amount of these drugs was present in the tested samples. Then the solution was adjusted to pH 6 and the adsorption process was performed under the optimum conditions. The remaining concentrations of these drugs were determined by HPLC-UV.

The removal of each anti-inflammatory drug by the modified adsorbent was determined. The adsorption efficiency of the modified adsorbent in single standard spiked samples were presented in Table 4.4 while those of the mixed standard spiked samples given in Table 4.5. As can be seen from Table 4.4, diclofenac in every real water samples was preferentially adsorbed onto the chitosan-modified adsorbent surface over ibuprofen and naproxen, respectively. Nevertheless, the adsorption amount of the anti-inflammatory drugs diminished when the mixed standard of anti-inflammatory drugs was employed, as shown in Table 4.5. This can simply be attributed to the competitive binding between the drugs to occupy the active sites of the modified adsorbent leading to the declined adsorption efficiency of each drug.

Even so, the overall removal efficiency of these drugs were still superior to those obtained by the other adsorbents from previous works as exemplified in Table 4.6.

Table 4.4 The anti-inflammatory drug removal of single standard spiked water samples.

Water sample	**Adsorption amount (mg/g) (n=3)**		
	Ibuprofen	Diclofenac	Naproxen
Pond water	12.82 ± 0.7	63.11 ± 0.9	1.91 ± 0.1
Canal water	17.70 ± 0.8	56.22 ± 1.1	2.31 ± 0.1
Tap water	14.63 ± 0.8	61.95 ± 1.1	2.08 ± 0.1

Table 4.5 The anti-inflammatory drug removal of mixed standard spiked water samples.

Water sample	**Adsorption amount (mg/g) (n=3)**		
	Ibuprofen	Diclofenac	Naproxen
Pond water	11.37 ± 1.1	49.02 ± 1.0	1.98 ± 0.2
Canal water	12.96 ± 1.1	53.10 ± 1.2	2.16 ± 0.2
Tap water	13.31 ± 0.9	57.47 ± 1.1	2.36 ± 0.1

Table 4.6 The adsorption amount of anti-inflammatory drugs by the adsorbents from previous works.

Adsorbents	**Adsorption amount (mg/g)**			**References**
	Ibuprofen	Diclofenac	Naproxen	
Polyaniline	-	42.918	-	[12]
Mesoporous silica SBA-15	0.41	0.34	-	[123]
Olive-waste cakes	12.6	56.2	39.5	[124]
Grape bagasse	-	23.77	-	[125]
Hexagonal mesoporous silicate (HMS)	-	0.032	-	[126]
Pine wood fast pyrolysis biochar	10.74	-	-	[127]
Chitosan-modified adsorbent	14.63	61.95	2.08	-

CHAPTER V
CONCLUSION AND SUGGESTION

5.1 Conclusion

A chitosan-modified waste tire crumb rubber adsorbent was developed and demonstrated as an efficient low-cost adsorbent for the removal of anti-inflammatory drugs in aqueous solution. The modified sorbent was prepared by assembling chitosan onto the tire crumb rubber by simply blending a 2% (w/w) chitosan solution with the rubber at a given ratio.

The chitosan-modified waste tire crumb rubber adsorbent was then characterized using Fourier transform infrared spectroscopy (FT-IR), elemental analysis (EA), themogravimetric analysis (TGA), the point of zero charge (pH_{pzc}) determination. The FT-IR spectrum revealed characteristic adsorption bands of chitosan on the modified adsorbent; nonetheless, there was no indication that the chitosan was chemically bound but instead only assembled onto the rubber by van der Waals interaction. The elemental analysis disclosed a significantly higher percentage of nitrogen in the modified adsorbent as compared to those in the tire crumb rubber alone, which evidently signified the presence of chitosan molecules on the material after the modification. The thermogram also exhibited additional weight loss of the chitosan polymer from the modified adsorbent. All of these results conclusively confirmed that the chitosan-modified waste tire crumb rubber adsorbent was successfully prepared.

Various parameters potentially affecting the anti-inflammatory drug removal using the chitosan-modified waste tire crumb rubber were investigated through a batch system. All of the experiments were performed at room temperature. The high molecular weight chitosan was the chitosan of choice for modifying the waste tire crumb rubber at the ratio of 10:3 (w/w). The adsorption of anti-inflammatory drugs by the chitosan-modified adsorbent was established over a wide range of solution pH: i.e. 4-9 for ibuprofen, 5-10 for diclofenac, and 3-10 for naproxen. However, the collectively optimal pH for the removal of these anti-inflammatory drugs by the developed adsorbent was 6. The equilibration time for ibuprofen or diclofenac adsorption was approximately 1 hour while that of naproxen was roughly 2 hours.

The adsorption kinetics for these anti-inflammatory drugs were best described by the second-order kinetic model. In addition, this result showed that the removal of naproxen through the adsorption process using the chitosan-modified adsorbent was faster than the ibuprofen and diclofenac, respectively.

The adsorption isotherm of the chitosan-modified waste tire crumb rubber adsorbent for these anti-inflammatory drugs followed the Freundlich adsorption isotherm model. Thus, the adsorption of these anti-inflammatory drugs can be ascribed to multilayer adsorption process on the heterogeneous surface.

In addition, the real water samples including Chulalongkorn University's pond water, canal water, and tap were evaluated for the anti-inflammatory drug removal using the chitosan-modified waste tire crumb rubber adsorbent. The efficiency of anti-inflammatory drug removal from the single standard spiked of real water samples is better than those of the mixed standard spiked samples because the drugs competed with each other to occupy the active sites of the modified adsorbent leading to the diminished adsorption efficiency of each drug. Therefore, the chitosan-modified adsorbent performed more effectively toward the anti-inflammatory drug removal when no interference was present in water samples. All of these results convincingly indicate that the chitosan-modified waste tire crumb rubber adsorbent is an efficient low-cost adsorbent for the removal of anti-inflammatory drugs including ibuprofen, diclofenac, and naproxen in aqueous solution.

5.2 Suggestion for the future work

- Improvement on the adsorption efficiency of the anti-inflammatory drugs.
- Extensive investigation on the effect of interferences.
- The chitosan-modified waste tire crumb rubber adsorbent should be applied as the low-cost adsorbent in column system for the anti-inflammatory drug removal from aqueous solution.
- The desorption study of the chitosan-modified adsorbent for the reuse purpose.
- The large-scale preparation of the chitosan-modified waste tire crumb rubber adsorbent for the wastewater treatment plant applications.

REFERENCES

[1] Ferrari, B.t., Paxéus, N., Giudice, R.L., Pollio, A., and Garric, J. Ecotoxicological Impact of Pharmaceuticals Found in Treated Wastewaters: Study of Carbamazepine, Clofibric Acid, and Diclofenac. Ecotox. Environ. Safe. 55(3) (2003): 359-370.

[2] Mailler, R., Gasperi, J., Chebbo, G., and Rocher, V. Priority and Emerging Pollutants in Sewage Sludge and Fate during Sludge Treatment. Waste Manag. 34(7) (2014): 1217-1226.

[3] Rizzo, L. Bioassays as a Tool for Evaluating Advanced Oxidation Processes in Water and Wastewater Treatment. Water Res. 45(15) (2011): 4311-4340.

[4] Boyd, G.R., Reemtsma, H., Grimm, D.A., and Mitra, S. Pharmaceuticals and Personal Care Products (PPCPs) in Surface and Treated Waters of Louisiana, USA and Ontario, Canada. Sci. Total Environ. 311(1-3) (2003): 135-149.

[5] Beltran, F.J., Pocostales, P., Alvarez, P., and Oropesa, A. Diclofenac Removal from Water with Ozone and Activated Carbon. J. Hazard. Mater. 163(2-3) (2009): 768-776.

[6] Liscio, C., Abdul-Sada, A., Al-Salhi, R., Ramsey, M.H., and Hill, E.M. Methodology for Profiling Anti-Androgen Mixtures in River Water Using Multiple Passive Samplers and Bioassay-Directed Analyses. Water Res. 57 (2014): 258-269.

[7] Postigo, C. and Richardson, S.D. Transformation of Pharmaceuticals during Oxidation/Disinfection Processes in Drinking Water Treatment. J. Hazard. Mater. 279 (2014): 461-475.

[8] Sotelo, J.L., Rodríguez, A., Álvarez, S., and García, J. Modeling and Elimination of Atenolol on Granular Activated Carbon in Fixed Bed Column. Int. J. Environ. Res. 6(4) (2012): 961-968.

[9] Khatem, R., Miguel, R.O., and Bakhti, A. Use of Synthetic Clay for Removal of Diclofenac Anti-Inflammatory. Eurasian J. Soil Sci. 4(2) (2015): 126-136.

[10] Torrellas, S.A., Rodriguez, A.R., Escudero, G.O., Martin, J.M., and Rodriguez, J.G. Comparative Evaluation of Adsorption Kinetics of Diclofenac and Isoproturon

by Activated Carbon. J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng. 50(12) (2015): 1241-1248.

[11] Sotelo, J.L., Rodríguez, A., Álvarez, S., and García, J. Removal of Caffeine and Diclofenac on Activated Carbon in Fixed Bed Column. Chem. Eng. Res. Des. 90(7) (2012): 967-974.

[12] Bajpai, S.K. and Bhowmik, M. Adsorption of Diclofenac Sodium from Aqueous Solution Using Polyaniline as a Potential Sorbent. I. Kinetic Studies. J. Appl. Polym. Sci. (2010): 3615-3622.

[13] Cuerda-Correa, E.M., Dominguez-Vargas, J.R., Olivares-Marin, F.J., and de Heredia, J.B. On the Use of Carbon Blacks as Potential Low-Cost Adsorbents for the Removal of Non-Steroidal Anti-Inflammatory Drugs from River Water. J. Hazard. Mater. 177(1-3) (2010): 1046-1053.

[14] Karaman, R., et al. Removal of Diclofenac Potassium from Wastewater Using Clay-Micelle Complex. Environ. Technol. 33(10-12) (2012): 1279-1287.

[15] National Science and Technology Development Agency. Tire: Components and Chemical Hazards [Online]. 2015. Available from: http://www.nstda.or.th/sci-kids-menu/1636-tyre [30 Nov 2015]

[16] Vieno, N.M., Harkki, H., Tuhkanen, T., and Kronberg, L. Occurrence of Pharmaceuticals in River Water and Their Elimination in a Pilot-Scale Drinking Water Treatment Plant. Environ. Sci. Technol. 41 (2007): 5077-5084.

[17] Scheytt, T., Mersmann, P., Lindsta, R., and Heberer, T. 1-Octanol/Water Partition Coefficients of 5 Pharmaceuticals from Human Medical Care: Carbamazepine, Clofibric Acid, Diclofenac, Ibuprofen, and Propyphenazone. Water Air Soil Pollut. 165 (2005): 3-11.

[18] Vieno, N., Tuhkanen, T., and Kronberg, L. Removal of Pharmaceuticals in Drinking Water Treatment: Effect of Chemical Coagulation. Environ. Technol. 27(2) (2006): 183-192.

[19] Shalaeva, M., Kenseth, J., Lombardo, F., and Bastin, A. Measurement of Dissociation Constants (pKa Values) of Organic Compounds by Multiplexed Capillary Electrophoresis Using Aqueous and Cosolvent Buffers. J. Pharm. Sci. 97(7) (2008): 2581-606.

[20] Kamal, M.A.H.M., Iimura, N., Nabekura, T., and Kitagawa, S. Enhanced Skin Permeation of Diclofenac Further Enhancement by Microemulsion. Chem. Pharm. Bull. 55(3) (2007): 368-371.

[21] pKa Definition [Online]. 2017. Available from: http://www.sirius-analytical.com/pka [1 Feb 2017]

[22] Madhavan, J., Grieser, F., and Ashokkumar, M. Combined Advanced Oxidation Processes for the Synergistic Degradation of Ibuprofen in Aqueous Environments. J. Hazard. Mater. 178(1-3) (2010): 202-208.

[23] Loraine, G.A. and Pettigrove, M.E. Seasonal Variations in Concentrations of Pharmaceuticals and Personal Care Products in Drinking Water and Reclaimed Wastewater in Southern California. Environ. Sci. Technol. 40 (2006): 687-695.

[24] Roberts, P.H. and Thomas, K.V. The Occurrence of Selected Pharmaceuticals in Wastewater Effluent and Surface Waters of the Lower Tyne Catchment. Sci. Total Environ. 356(1-3) (2006): 143-153.

[25] Triebskorn, R., Casper, H., Heyd, A., Eikemper, R., Kohler, H.R., and Schwaiger, J. Toxic Effects of the Non-Steroidal Anti-Inflammatory Drug Diclofenac. Part II: Cytological Effects in Liver, Kidney, Gills and Intestine of Rainbow Trout (Oncorhynchus Mykiss). Aquat. Toxicol. 68(2) (2004): 151-166.

[26] Sawchuk, R.J., Maloney, J.A., Cartier, L.L., Rackley, R.J., Chan, K.K.H., and Lau, H.S.L. Analysis of Diclofenac and Four of Its Metabolites in Human Urine by HPLC. Pharmaceut. Res. 12(5) (1995): 756-762.

[27] Fent, K., Weston, A.A., and Caminada, D. Ecotoxicology of Human Pharmaceuticals. Aquat. Toxicol. 76(2) (2006): 122-159.

[28] Schwaiger, J., Ferling, H., Mallow, U., Wintermayr, H., and Negele, R.D. Toxic Effects of the Non-Steroidal Anti-Inflammatory Drug Diclofenac. Part I: Histopathological Alterations and Bioaccumulation in Rainbow Trout. Aquat. Toxicol. 68(2) (2004): 141-150.

[29] Yu, Z., Peldszus, S., and Huck, P.M. Adsorption Characteristics of Selected Pharmaceuticals and an Endocrine Disrupting Compound-Naproxen, Carbamazepine and Nonylphenol-on Activated Carbon. Water Res. 42(12) (2008): 2873-2882.

[30] Isidori, M., Lavorgna, M., Nardelli, A., Parrella, A., Previtera, L., and Rubino, M. Ecotoxicity of Naproxen and Its Phototransformation Products. Sci. Total Environ. 348(1-3) (2005): 93-101.

[31] Boxall, A.B., et al. Pharmaceuticals and Personal Care Products in the Environment: What are the Big Questions? Environ. Health Perspect. 120(9) (2012): 1221-1229.

[32] Heberer, T. Occurrence, Fate, and Removal of Pharmaceutical Residues in the Aquatic Environment: A Review of Recent Research Data. Toxicol. Lett. 131 (2002): 5-17.

[33] Moldovan, Z. Occurrences of Pharmaceutical and Personal Care Products as Micropollutants in Rivers from Romania. Chemosphere 64(11) (2006): 1808-1817.

[34] Ziylan, A. and Ince, N.H. The Occurrence and Fate of Anti-Inflammatory and Analgesic Pharmaceuticals in Sewage and Fresh Water: Treatability by Conventional and Non-Conventional Processes. J. Hazard. Mater. 187(1-3) (2011): 24-36.

[35] Jones, O.A., Lester, J.N., and Voulvoulis, N. Pharmaceuticals: A Threat to Drinking Water? Trends Biotechnol. 23(4) (2005): 163-167.

[36] Zhang, Y., Geissen, S.U., and Gal, C. Carbamazepine and Diclofenac: Removal in Wastewater Treatment Plants and Occurrence in Water Bodies. Chemosphere 73(8) (2008): 1151-1161.

[37] Heberer, T. Tracking Persistent Pharmaceutical Residues from Municipal Sewage to Drinking Water. J. Hydrol. 266 (2002): 175-189.

[38] Liu, J.L. and Wong, M.H. Pharmaceuticals and Personal Care Products (PPCPs): A Review on Environmental Contamination in China. Environ. Int. 59 (2013): 208-224.

[39] Choong, A.M., Teo, S.L., Leow, J.L., Koh, H.L., and Ho, P.C. A Preliminary Ecotoxicity Study of Pharmaceuticals in the Marine Environment. J. Toxicol. Environ. Health A 69(21) (2006): 1959-1970.

[40] Daughton, C.G. and Ternes, T.A. Pharmaceuticals and Personal Care Products in the Environment: Agents of Subtle Change? Environ. Health Persp. 107 (1999): 907-938.

[41] Sebastine, I.M. and Wakeman, R.J. Consumption and Environmental Hazards of Pharmaceutical Substances in the UK. Process Saf. Environ. 81(4) (2003): 229-235.

[42] Taggart, M.A., et al. Diclofenac Residues in Carcasses of Domestic Ungulates Available to Vultures in India. Environ. Int. 33(6) (2007): 759-765.

[43] Oaks, J.L., et al. Diclofenac Residues as the Cause of Vulture Population Decline in Pakistan. Nature 427 (2004): 630-633.

[44] Cleuvers, M. Mixture Toxicity of the Anti-Inflammatory Drugs Diclofenac, Ibuprofen, Naproxen, and Acetylsalicylic Acid. Ecotox. Environ. Safe. 59(3) (2004): 309-315.

[45] Sein, M.M., Zedda, M., Tuerk, J., Schmidt, T.C., Golloch, A., and Sonntag, C.V. Oxidation of Diclofenac with Ozone in Aqueous Solution. Environ. Sci. Technol. 42 (2008): 6656-6662.

[46] Ternes, T.A., et al. Ozonation: A Tool for Removal of Pharmaceuticals, Contrast Media and Musk Fragrances from Wastewater? Water Res. 37(8) (2003): 1976-1982.

[47] Beltran, F.J., Pocostales, J.P., Alvarez, P.M., and Jaramillo, J. Mechanism and Kinetic Considerations of TOC Removal from the Powdered Activated Carbon Ozonation of Diclofenac Aqueous Solutions. J. Hazard. Mater. 169(1-3) (2009): 532-538.

[48] Huber, M.M., Canonica, S., Park, G.Y., and Gunten, U.V. Oxidation of Pharmaceuticals During Ozonation and Advanced Oxidation Processes. Environ. Sci. Technol. 37 (2003): 1016-1024.

[49] Ikehata, K., Jodeiri, N.N., and Gamal, E.D.M. Degradation of Aqueous Pharmaceuticals by Ozonation and Advanced Oxidation Processes: A Review. Ozone Sci. Eng. 28(6) (2006): 353-414.

[50] Zwiener, C. and Frimmel, F.H. Oxidative Treatment of Pharmaceuticals in Water. Wat. Res. 34(6) (2000): 1881-1885.

[51] Reungoat, J., Escher, B.I., Macova, M., Argaud, F.X., Gernjak, W., and Keller, J. Ozonation and Biological Activated Carbon Filtration of Wastewater Treatment Plant Effluents. Water Res. 46(3) (2012): 863-872.

[52] Nakada, N., et al. Removal of Selected Pharmaceuticals and Personal Care Products (PPCPs) and Endocrine-Disrupting Chemicals (EDCs) During Sand Filtration and Ozonation at a Municipal Sewage Treatment Plant. Water Res. 41(19) (2007): 4373-4382.

[53] Rigobello, E.S., Dantas, A.D., Di Bernardo, L., and Vieira, E.M. Removal of Diclofenac by Conventional Drinking Water Treatment Processes and Granular Activated Carbon Filtration. Chemosphere 92(2) (2013): 184-191.

[54] Hijosa-Valsero, M., Matamoros, V., Martin-Villacorta, J., Becares, E., and Bayona, J.M. Assessment of Full-Scale Natural Systems for the Removal of PPCPs from Wastewater in Small Communities. Water Res. 44(5) (2010): 1429-1439.

[55] Carballa, M., Omil, F., Ternes, T., and Lema, J.M. Fate of Pharmaceutical and Personal Care Products (PPCPs) during Anaerobic Digestion of Sewage Sludge. Water Res. 41(10) (2007): 2139-2150.

[56] Langenhoff, A., et al. Microbial Removal of the Pharmaceutical Compounds Ibuprofen and Diclofenac from Wastewater. Biomed Res. Int. 2013 (2013): 1-9.

[57] Schwarzenbach, R.P., et al. The Challenge of Micropollutants in Aquatic Systems. Science 313 (2006): 1072-1077.

[58] Safoniuk, M. Wastewater Engineering: Treatment and Reuse. 4th ed. McGraw Hill, New York, NY, USA, 2003.

[59] Ternes, T.A., et al. Removal of Pharmaceuticals during Drinking Water Treatment. Environ. Sci. Technol. 36 (2002): 3855-3863.

[60] Omidvar Borna, M., et al. Batch and Column Studies for the Adsorption of Chromium(VI) on Low-Cost Hibiscus Cannabinus Kenaf, a Green Adsorbent. J. Taiwan Inst. Chem. Eng. 68 (2016): 80-89.

[61] Sag, Y. and Aktay, Y. Mass Transfer and Equilibrium Studies for the Sorption of Chromium Ions onto Chitin. Process Biochem. 36 (2000): 157-173.

[62] Doğan, M., Özdemir, Y., and Alkan, M. Adsorption Kinetics and Mechanism of Cationic Methyl Violet and Methylene Blue Dyes onto Sepiolite. Dyes Pigments 75(3) (2007): 701-713.

[63] Berger, A.H. and Bhown, A.S. Comparing Physisorption and Chemisorption Solid Sorbents for Use Separating CO_2 from Flue Gas Using Temperature Swing Adsorption. Energy Procedia 4 (2011): 562-567.

[64] Nageeb, M. Adsorption Technique for the Removal of Organic Pollutants from Water and Wastewater. in *INTECH open science open minds*. 2013.

[65] Dabrowski, A. Adsorption-from Theory to Practice. Adv. Colloid Interfac. 93 (2001): 135-224.

[66] Dogan, M., Alkan, M., Turkyilmaz, A., and Ozdemir, Y. Kinetics and Mechanism of Removal of Methylene Blue by Adsorption onto Perlite. J. Hazard. Mater. 109(1-3) (2004): 141-148.

[67] Mittal, H., Maity, A., and Sinha, R.S. The Adsorption of Pb^{2+} and Cu^{2+} onto Gum Ghatti-Grafted Poly(Acrylamide-Co-Acrylonitrile) Biodegradable Hydrogel: Isotherms and Kinetic Models. J. Phys. Chem. B 119(5) (2015): 2026-2039.

[68] Kannan, N. and Sundaram, M.M. Kinetics and Mechanism of Removal of Methylene Blue by Adsorption on Various Carbons—A Comparative Study. Dyes Pigments 51 (2001): 25-40.

[69] Wang, X.S. and Qin, Y. Equilibrium Sorption Isotherms for of Cu^{2+} on Rice Bran. Process Biochem. 40(2) (2005): 677-680.

[70] Gupta, V.K., Carrott, P.J., Singh, R., Chaudhary, M., and Kushwaha, S. Cellulose: A Review as Natural, Modified and Activated Carbon Adsorbent. Bioresource Technol. 216 (2016): 1066-1076.

[71] Moharami, S. and Jalali, M. Removal of Phosphorus from Aqueous Solution by Iranian Natural Adsorbents. Chem. Eng. J. 223 (2013): 328-339.

[72] Ratola, N., Botelho, C.l., and Alves, A. The Use of Pine Bark as a Natural Adsorbent for Persistent Organic Pollutants - Study of Lindane and Heptachlor Adsorption. J. Chem. Technol. Biot. 78(2-3) (2003): 347-351.

[73] Montes-Atenas, G. and Schroeder, S.L.M. Sustainable Natural Adsorbents for Heavy Metal Removal from Wastewater: Lead Sorption on Pine Bark (*Pinus Radiatad.Don*). Surf. Interface Anal. 47(10) (2015): 996-1000.

[74] Asubiojo, O.I. and Ajelabi, O.B. Removal of Heavy Metals from Industrial Wastewaters Using Natural Adsorbents. Toxicol. Environ. Chem. 91(5) (2009): 883-890.

[75] Chol, H.M. and Cloud, R.M. Natural Sorbents in Oil Spill Cleanup. Environ. Sci. Technol. 26 (1992): 772-776.

[76] Singha, B., Naiya, T.K., Bhattacharya, A.k., and Das, S.K. Cr(VI) Ions Removal from Aqueous Solutions Using Natural Adsorbents – FTIR Studies. J. Environ. Prot. 2(6) (2011): 729-735.

[77] Silva, J.P., et al. Characterization of Commercial Ceramic Adsorbents and its Application on Naphthenic Acids Removal of Petroleum Distillates. Mater. Res. 10(2) (2007): 219-225.

[78] Ravančić, M.E. and Habuda-Stanić, M. Equilibrium and Kinetics Studies for the Adsorption of Fluoride onto Commercial Activated Carbons Using Fluoride Ion-Selective Electrode. Int. J. Electrochem. Sci. 10 (2015): 8137-8149.

[79] Zamani, C., Illa, X., Abdollahzadeh-Ghom, S., Morante, J.R., and Romano Rodriguez, A. Mesoporous Silica: A Suitable Adsorbent for Amines. Nanoscale Res. Lett. 4(11) (2009): 1303-1308.

[80] Ahmed, M.N. and Ram, R.N. Removal of Basic Dye from Waste-Water Using Silica as Adsorbent. Environ. Pollut. 77 (1992): 79-86.

[81] Raut, P.A., Dutta, M., Sengupta, S., and Basu, J.K. Alumina-Carbon Composite as an Effective Adsorbent for Removal of Methylene Blue and Alizarin Red-S from Aqueous Solution. Indian J. Chem. Techn. 20 (2013): 15-20.

[82] Gupta, V.K. and Suhas. Application of Low-Cost Adsorbents for Dye Removal--a Review. J. Environ. Manage. 90(8) (2009): 2313-2342.

[83] Ali, I., Asim, M., and Khan, T.A. Low Cost Adsorbents for the Removal of Organic Pollutants from Wastewater. J. Environ. Manage. 113 (2012): 170-183.

[84] Gupta, S. and Babu, B.V. Economic Feasibility Analysis of Low Cost Adsorbents for the Removal of Cr(VI) from Wastewater. (2008): 1-7.

[85] Mousavi, H.Z., Hosseynifar, A., Jahed, V., and Dehghani, S.A.M. Removal of Lead from Aqueous Solution Using Waste Tire Rubber Ash as an Adsorbent. Braz. J. Chem. Eng. 27(1) (2010): 79-87.

[86] Wu, B. and Zhou, M.H. Recycling of Waste Tyre Rubber into Oil Absorbent. Waste Manag. 29(1) (2009): 355-359.

[87] Bharathi, K.S. and Ramesh, S.T. Removal of Dyes Using Agricultural Waste as Low-Cost Adsorbents: A Review. Appl. Water Sci. 3(4) (2013): 773-790.

[88] Wan, N.W.S. and Hanafiah, M.A. Removal of Heavy Metal Ions from Wastewater by Chemically Modified Plant Wastes as Adsorbents: A Review. Bioresour Technol. 99(10) (2008): 3935-3948.

[89] El-Sherif, I.Y. and Fathy, N.A. Modification of Adsorptive Properties of Bagasse Fly Ash for Uptaking Cadmium from Aqueous Solution. Environ. Res. Eng. Manag. 64(2) (2013).

[90] Argun, M.E. and Dursun, Ş. Removal of Heavy Metal Ions Using Chemically Modified Adsorbents. J. Int. Environ. Appl. Sci. 1(1-2) (2006): 27-40.

[91] Kong, H., et al. Surfactant Modification of Banana Trunk as Low-Cost Adsorbents and Their High Benzene Adsorptive Removal Performance from Aqueous Solution. RSC Adv. 6(29) (2016): 24738-24751.

[92] You, H., Chen, J., Yang, C., and Xu, L. Selective Removal of Cationic Dye from Aqueous Solution by Low-Cost Adsorbent Using Phytic Acid Modified Wheat Straw. Colloids Surface A 509 (2016): 91-98.

[93] Agarry, S.E., Owabor, C.N., and Ajani, A.O. Modified Plantain Peel as Cellulose-Based Low-Cost Adsorbent for the Removal of 2,6-Dichlorophenol from Aqueous Solution: Adsorption Isotherms, Kinetic Modeling, and Thermodynamic Studies. Chem. Eng. Commun. 200(8) (2013): 1121-1147.

[94] Zuorro, A., Battista, A.D., and Lavecchia, R. Magnetically Modified Coffee Silverskin for the Removal of Xenobiotics from Wastewater. Chem. Eng. Trans. 35 (2013): 1375-1380.

[95] Abdul-Raheim, A.R.M., Shimaa, M.E.S., K, F.R., and Manar, E.A.R. Low Cost Biosorbents Based on Modified Starch Iron Oxide Nanocomposites for Selective

Removal of Some Heavy Metals from Aqueous Solutions. Adv. Mat. Lett. 7(5) (2016): 402-409.

[96] Te, B., Wichitsathian, B., and Yossapol, C. Modification of Natural Common Clays as Low Cost Adsorbents for Arsenate Adsorption. IJESD. 6(11) (2015): 799-804.

[97] Sae-oui, P. Types and Application of Tires [Online]. 2015. Available from: http://www.rubbercenter.org/files/technologys.pdf [9 Dec 2015]

[98] Sukges, S. Tire Industry in India [Online]. 2014. Available from: http://www.thaiembassy.org/mumbai/contents/files/information-20140714-115027-937992.pdf [23 Feb 2017]

[99] The Schumacher Centre for Technology & Development. Recycling Rubber [Online]. Available from: http://answers.practicalaction.org/our-resources/item/recycling-of-rubber [1 Dec 2015]

[100] Yilmaz, A. and Degirmenci, N. Possibility of Using Waste Tire Rubber and Fly Ash with Portland Cement as Construction Materials. Waste Manag. 29(5) (2009): 1541-1546.

[101] Sukontasukkul, P. and Chaikaew, C. Properties of Concrete Pedestrian Block Mixed with Crumb Rubber. Constr. Build. Mater. 20(7) (2006): 450-457.

[102] Rinaudo, M. Chitin and Chitosan: Properties and Applications. Prog. Polym. Sci. 31(7) (2006): 603-632.

[103] Dutta, P.K., Dutta, J., and Tripathi, V.S. Chitin and Chitosan: Chemistry, Properties and Applications. J. Sci. Ind. Res. India 63 (2004): 20-31.

[104] Rinaudo, M. Physical Properties of Chitosan and Derivatives in Sol and Gel States. in Sarmento, B. and Neves, J.d. (eds.),Chitosan-Based Systems for Biopharmaceuticals: Delivery, Targeting and Polymer Therapeutics, pp. 23-43, 2012.

[105] Unob, F. Adsorbents and Adsorption Processes for Water Treatment. 1 ed. Protexts, Bangkok, 2558.

[106] Jin, Y. and Row, K.H. Adsorption Isotherm of Ibuprofen on Molecular Imprinted Polymer. Korean J. Chem. Eng. 22(2) (2005): 264-267.

[107] Mestre, A.S., Pires, J., Nogueira, J.M.F., and Carvalho, A.P. Activated Carbons for the Adsorption of Ibuprofen. Carbon 45(10) (2007): 1979-1988.

[108] Hasan, Z., Jeon, J., and Jhung, S.H. Adsorptive Removal of Naproxen and Clofibric Acid from Water Using Metal-Organic Frameworks. J. Hazard. Mater. 209-210 (2012): 151-157.

[109] Reza, R.A., Ahmaruzzaman, M., Sil, A.K., and Gupta, V.K. Comparative Adsorption Behavior of Ibuprofen and Clofibric Acid onto Microwave Assisted Activated Bamboo Waste. Ind. Eng. Chem. Res. 53(22) (2014): 9331-9339.

[110] Knocke, W.R. and Hemphill, L.H. Mercury(II) Sorption by Waste Rubber. Water Res. 15 (1981): 275-282.

[111] Calisir, F., Roman, F.R., Alamo, L., Perales, O., Arocha, M.A., and Akman, S. Removal of Cu(II) from Aqueous Solutions by Recycled Tire Rubber. Desalination 249(2) (2009): 515-518.

[112] Gupta, V.K., Gupta, B., Rastogi, A., Agarwal, S., and Nayak, A. Pesticides Removal from Waste Water by Activated Carbon Prepared from Waste Rubber Tire. Water Res. 45(13) (2011): 4047-4055.

[113] Gupta, V.K., Ali, I., Saleh, T.A., Siddiqui, M.N., and Agarwal, S. Chromium Removal from Water by Activated Carbon Developed from Waste Rubber Tires. Environ. Sci. Pollut. Res. Int. 20(3) (2013): 1261-1268.

[114] Pietrelli, L., Francolini, I., and Piozzi, A. Dyes Adsorption from Aqueous Solutions by Chitosan. Separ. Sci. Technol. 50(8) (2014): 1101-1107.

[115] Zhang, S., Dong, Y., Yang, Z., Yang, W., Wu, J., and Dong, C. Adsorption of Pharmaceuticals on Chitosan-Based Magnetic Composite Particles with Core-Brush Topology. Chem. Eng. J. 304 (2016): 325-334.

[116] Imyim, A., Sirithaweesit, T., and Ruangpornvisuti, V. Arsenite and Arsenate Removal from Wastewater Using Cationic Polymer-Modified Waste Tyre Rubber. J. Environ. Manage. 166 (2016): 574-578.

[117] Fiol, N. and Villaescusa, I. Determination of Sorbent Point Zero Charge: Usefulness in Sorption Studies. Environ. Chem. Lett. 7(1) (2008): 79-84.

[118] Lopez, R.G., et al. Chitosan-Coated Magnetic Nanoparticles Prepared in One Step by Reverse Microemulsion Precipitation. Int. J. Mol. Sci. 14(10) (2013): 19636-19650.

[119] Podust, T.V., et al. Chitosan-Nanosilica Hybrid Materials: Preparation and Properties. Appl. Surf. Sci. 320 (2014): 563-569.

[120] Hong, J., Zhu, Z., Lu, H., and Qiu, Y. Synthesis and Arsenic Adsorption Performances of Ferric-Based Layered Double Hydroxide with A-Alanine Intercalation. Chem. Eng. J. 252 (2014): 267-274.

[121] Ho, Y.S. and McKay, G. Pseudo-Second Order Model for Sorption Processes. Process Biochem. 34 (1999): 451-465.

[122] Boudrahem, F., Aissani-Benissad, F., and Ait-Amar, H. Batch Sorption Dynamics and Equilibrium for the Removal of Lead Ions from Aqueous Phase Using Activated Carbon Developed from Coffee Residue Activated with Zinc Chloride. J. Environ. Manage. 90(10) (2009): 3031-3039.

[123] Bui, T.X. and Choi, H. Adsorptive Removal of Selected Pharmaceuticals by Mesoporous Silica SBA-15. J. Hazard. Mater. 168(2-3) (2009): 602-608.

[124] Baccar, R., Sarrà, M., Bouzid, J., Feki, M., and Blánquez, P. Removal of Pharmaceutical Compounds by Activated Carbon Prepared from Agricultural By-Product. Chem. Eng. J. 211-212 (2012): 310-317.

[125] Antunes, M., Esteves, V.I., Guégan, R., Crespo, J.S., Fernandes, A.N., and Giovanela, M. Removal of Diclofenac Sodium from Aqueous Solution by Isabel Grape Bagasse. Chem. Eng. J. 192 (2012): 114-121.

[126] Suriyanon, N., Punyapalakul, P., and Ngamcharussrivichai, C. Mechanistic Study of Diclofenac and Carbamazepine Adsorption on Functionalized Silica-Based Porous Materials. Chem. Eng. J. 214 (2013): 208-218.

[127] Essandoh, M., Kunwar, B., Pittman, C.U., Mohan, D., and Mlsna, T. Sorptive Removal of Salicylic Acid and Ibuprofen from Aqueous Solutions Using Pine Wood Fast Pyrolysis Biochar. Chem. Eng. J. 265 (2015): 219-227.

APPENDIX

VITA

Miss Warintorn Phasuphan was born on November 16th, 1991 in Bangkok, Thailand. She graduated with a Bachelor of Science Degree in Chemistry (2nd Class Honours) from Chulalongkorn University in 2014. After that, she continued her study with a Master of Science Degree in Analytical Chemistry at Department of Chemistry, Faculty of Science, Chulalongkorn University, at which she became a member of Environmental Analysis Research Unit (EARU). She graduated with a Master of Science Degree in Analytical Chemistry in 2017. Her contact information is 7 Soi Phaholyothin 24 alley 2-2, Phaholyothin Road, Kwaeng Chomphon, Khet Jatujak, Bangkok, 10900 (home address), 086-888-5572 (phone), and ph.warintorn@gmail.com (email).