การดูดซับอะซิตามิโนเฟนและนาลิดิซิกแอซิดบนตัวดูดซับชนิดมีขั้วและไม่มีขั้ว

นางสาวอุมารัจน์ สันติสุขเกษม

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาการจัดการสิ่งแวดล้อม (สหสาขาวิชา)
บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2548

ISBN 974-14-1975-9

SORPTION OF ACETAMINOPHEN AND NALIDIXIC ACID ONTO POLAR AND NONPOLAR ADSORBENTS

Miss Umarat Suntisukaseam

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Environmental Management
(Inter-Department)
Graduate School
Chulalongkorn University
Academic Year 2005

ISBN 974-14-1975-9

Thesis Title	Sorption of Acetaminophen and Nalidixic Acid onto Polar and Nonpolar Adsorbents
By	Miss Umarat Suntisukaseam
Field of Study	Environmental Management
Thesis Advisor	Punjaporn Weschayanwiwat, Ph.D.
Thesis Co-advisor	Professor David A. Sabatini, Ph.D.

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

.....Dean of the Graduate School
(Assistant Professor M.R. Kalaya Tingsabadh, Ph.D.)

THESIS COMMITTEE

..... Chairman
(Chantra Tongcumpou, Ph.D.)

..... Thesis Advisor
(Punjaporn Weschayanwiwat, Ph.D.)

..... Thesis Co-Advisor
(Professor David A. Sabatini, Ph.D.)

..... Member
(Assistant Professor Khemarath Osathaphan, Ph.D.)

..... Member
(Assistant Professor Sangobthip Pongstabodee, Ph.D.)

อุมารัจน์ สันติสุขเกษม: การดูดซับอะซิตามิโนเฟนและนาลิดิซิกแอซิดบนตัวดูดซับชนิดมีขั้วและไม่มีขั้ว (SORPTION OF ACETAMINOPHEN AND NALIDIXIC ACID ONTO POLAR AND NONPOLAR ADSORBENTS) อ. ที่ปรึกษา: ดร. ปัญจพร เวชยันต์วิวัฒน์, อ. ที่ปรึกษาร่วม: Prof. Dr. David A. Sabatini, 76 หน้า ISBN 974-14-1975-9

สารประกอบจำพวกยามีบทบาทสำคัญต่อชีวิตประจำวันของมนุษย์และสัตว์ มีสารประกอบยาปนเปื้อนน้ำใต้ดินและแหล่งน้ำในหลายทวีปอย่างเห็นได้ชัด แม้ว่าจะมีการตรวจพบสารเหล่านี้ที่ความเข้มข้นต่ำจากสิ่งแวดล้อมก็ตามยังไม่มีการศึกษาถึงผลกระทบระยะยาวที่แน่ชัด เนื่องจากไม่มีข้อมูลเรื่องการเคลื่อนที่ของสารประกอบยาที่เพียงพอ การวิจัยนี้เพิ่มความเข้าใจในพฤติกรรมการดูดซับของยาซึ่งเป็นโมเลกุลแอมฟลิไฟล์บนตัวดูดซับชนิดต่างๆ เพื่อประโยชน์ในด้านการบำบัดน้ำผิวดินและน้ำใต้ดินที่ปนเปื้อนด้วยยาด้วยกระบวนการดูดซับ ทั้งนี้เพื่อเป็นการส่งเสริมแนวคิดเรื่องการนำน้ำกลับมาใช้ใหม่ อีกทั้งการวิจัยนี้ยังเพื่อความเข้าใจในเรื่องของการเคลื่อนที่ของยาในสิ่งแวดล้อมโดยใช้การทดลองแบบแบช เพื่อศึกษาพฤติกรรมการดูดซับของยาอะซิตามิโนเฟนและนาลิดิซิกแอซิดบนตัวดูดซับเรซินชนิดมีขั้วที่มีความเป็นขั้วต่างกัน (Amberlite XAD2, XAD7, และ XAD761) และตัวดูดซับชนิดไม่มีขั้ว (ผงถ่านกัมมันต์) ผลการศึกษาแสดงให้เห็นว่านาลิดิซิกแอซิดมีความสามารถในการดูดซับสูงกว่าอะซิตามิโนเฟนบนทุกตัวกลาง เนื่องจากอะซิตามิโนเฟนมีค่าการละลายน้ำสูงและมีค่าสัมประสิทธิ์การแบ่งชั้นของออกทานอลกับน้ำต่ำ ในการศึกษาจลน์หพลศาสตร์ของการดูดซับ พบว่าการดูดซับของอะซิตามิโนเฟนและนาลิดิซิกแอซิดเข้าสู่สภาวะสมดุลภายใน 24 ชั่วโมงสำหรับทุกตัวกลาง การดูดซับของอะซิตามิโนเฟนและนาลิดิซิกแอซิดบนเรซินเป็นไปตาม Langmuir Isotherm ความสามารถในการดูดซับต่อพื้นที่ผิวสัมผัสของยาทั้งสองชนิดขึ้นอยู่กับความเป็นขั้วของเรซิน สำหรับการดูดซับของอะซิตามิโนเฟนและนาลิดิซิกแอซิดบนผงถ่านกัมมันต์เป็นไปตาม Freundlich isotherm โดยสมการการดูดซับของอะซิตามิโนเฟนและนาลิดิซิกแอซิดได้ดังนี้ $q = 131.3107\ (mg/g\ activated\ carbon)(L/g)^{N}xC_{e}^{0.1243}$ และ $q = 78.5578\ (mg/g\ activated\ carbon)(L/g)^{N}xC_{e}^{0.3273}$ ตามลำดับ การดูดซับของยาบนเรซินนั้น แรงกระทำระหว่างส่วนที่มีขั้วในองค์ประกอบของยาและตัวดูดซับมีบทบาทสำคัญมาก ส่วนการดูดซับของยาบนผงถ่านกัมมันต์นั้น แรงกระทำระหว่างส่วนที่ไม่มีขั้วจะเป็นตัวควบคุมการดูดซับของอะซิตามิโนเฟนและนาลิดิซิกแอซิด ผงถ่านกัมมันต์มีความสามารถในการดูดซับยาทั้งสองชนิดได้ดีกว่าเรซิน จากผลการทดลองสรุปได้ว่ายาสามารถถูกดูดซับได้ทั้งบนพื้นผิวที่มีขั้วและไม่มีขั้ว เนื่องมาจากคุณสมบัติแอมฟลิฟิลิกของยา และพฤติกรรมการดูดซับขึ้นอยู่กับโครงสร้างโมเลกุลของยาและคุณสมบัติที่ผิวของตัวดูดซับเป็นสำคัญ

สาขาวิชาการจัดการสิ่งแวดล้อม (สหสาขาวิชา) ลายมือชื่อนิสิต.....

ปีการศึกษา 2548 ลายมือชื่ออาจารย์ที่ปรึกษา.....

ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....

4789503920: MAJOR ENVIRONMENTAL MANAGEMENT

KEY WORD: SORPTION/ PHARMACEUTICAL/ AMPHIPHILE MOLECULE/ AMBERLITE XAD POLYMERIC RESINS/ACTIVATED CARBON

UMARAT SUNTISUKASEAM: SORPTION OF ACETAMINOPHEN AND NALIDIXIC ACID ONTO POLAR AND NONPOLAR ADSORBENTS. THESIS ADVISOR: PUNJAPORN WESCHAYANWIWAT, Ph.D. THESIS CO-ADVISOR: PROF. DAVID A. SABATINI, Ph.D. 76 PP. ISBN 974-14-1975-9

Pharmaceuticals play a vital role in human and animal daily life. Apparently, pharmaceutical compounds show up in groundwater and surface water in many continents. Although these compounds are detected at low concentrations in the environment, a long term effect of such exposures has not yet known. The available information on their fate and transport are still limited and fragmented. The understanding of the sorption of these molecules is greatly important not only in the removal of those compounds from drinking water to support the idea of the water reuse but also in the migration of these compounds in the environment. The sorption of two pharmaceuticals predominantly in the neutral form, acetaminophen and nalidixic acid, have been investigated in the laboratory using batch experiments. The nonionic polymeric resins (Amberlite XAD2, XAD7, and XAD761) and activated carbon were used as polar and nonpolar adsorbents, respectively. The results indicated that nalidixic acid shows greater sorption capability than acetaminophen onto all adsorbents as acetaminophen has higher water solubility with less K_{ow}. The sorption kinetics studies showed that the sorption equilibrium of acetaminophen and nalidixic acid are achieved within 24 hours for all adsorbents. Sorption of acetaminophen and nalidixic acid onto polymeric resins are well fitted with the Langmuir isotherm. The sorption capacity in an area basis corresponds to the polarity of the polymeric adsorbents for both pharmaceuticals. For sorption of acetaminophen and nalidixic acid onto activated carbon, both sorptions follow the Freundlich isotherm with the equation of $q = 131.3107$ (mg/g activated carbon) $(L/g)^N \times C_e^{0.1243}$ for acetaminophen and $q = 78.5778$ (mg/g activated carbon) $(L/g)^N \times C_e^{0.3273}$ for nalidixic acid. In the sorption of pharmaceuticals onto polymeric resins, the interaction caused by the affinity between polar moieties of pharmaceutical compounds and adsorbents plays an important role. Alternatively, the hydrophobic interaction controls the sorption of pharmaceuticals onto activated carbon as the hydrophobic part of both acetaminophen and nalidixic acid partition onto the nonpolar surface of activated carbon. The activated carbon shows the greater sorption capacity than the polymeric resins for the sorption of these two pharmaceuticals. The results thus imply that the pharmaceuticals can truly adsorb on both polar and nonpolar surfaces due to their amphiphilic characteristic and the sorption behavior strongly depends on the molecular structure of pharmaceuticals and the surface properties of adsorbents.

Field of study Environmental management

(Inter Department) Academic year 2005

Student's signature.....

Advisor's signature.....

Co-Advisor's signature.....

ACKNOWLEDGEMENTS

I wish to express my sincere gratitude to my advisor, Punjaporn Weschayanwiwat, Ph.D., for her useful suggestions on research techniques and guidance throughout the entire year of this research. I do would like to express my appreciation to Professor David A. Sabatini, PhD., my co-advisor, who was the most helpful in providing comments and additional information.

Grateful thanks are also to Oranuch Lorphensri, Ph.D., Ms. Walairat Poopa, Ms. Ananya Wanitkorkul, Ms. Ramnaree Netvichian, Ms. Chantana Intim, and my friends at NRC-EHWM laboratory for their technical assistance and invaluable comments during the experiments in laboratory.

I wish to acknowledge thanks every effort to the many Professors who have freely given off their time to help with my research. These include, Chantra Tongcumpou, Ph.D., Assistant Professor Khemarath Osathaphan, Ph.D., and Assistant Professor Sangobthip Pongstabodee, Ph.D. I would like to specially thank the National Research Center for Environmental and Hazardous Waste Management (NRC-EHWM) Program for funding and all useful laboratory facilities.

By no mean least, I would like to express my deeply appreciation and gratitude to my family as my inspiration and encouragement during the entire study.

TABLE OF CONTENTS

Page

Page

Page

LIST OF TABLES

LIST OF FIGURES

Figure **Page**

NOMENCLATURES

q_e	=	mass of chemical sorbed/ mass of sorbent (mg/g sorbent)
C_{eq}	=	solute concentration at equilibrium (mg/L)
K_d	=	linear sorption coefficient (L/g)
K_{fr}	=	Freundlich sorption coefficient (mg/g sorbent)$(L/g)^N$
N	=	Freundlich exponent coefficient
K_L	=	Langmuir sorption coefficient (L/mg)
Q	=	mass of adsorbate required to saturate a unit mass of adsorbent (mg/g sorbent)
K_{ow}	=	octanol-water partition coefficient (dimensionless)
SSA	=	specific surface area (m^2/g)

CHAPTER I

INTRODUCTION

1.1 Pharmaceuticals in the Environment

Pharmaceuticals are becoming emerged pollutants and getting more attention as they are widely used and produced throughout the world. Pharmaceutical compounds are applied mainly for human and animal medical care and treatment. Large amount of pain killers, i.e. paracetamol and aspirin, are prescribed annually. However, they are sold at much higher quantities without prescriptions, which is known as “over the counter” or OTC drugs (Heberer, 2002a). The OTC drugs are sold in EU countries such as the United Kingdom and Germany close to or exceeding 1000 tons/year (Dietrich, 2002).

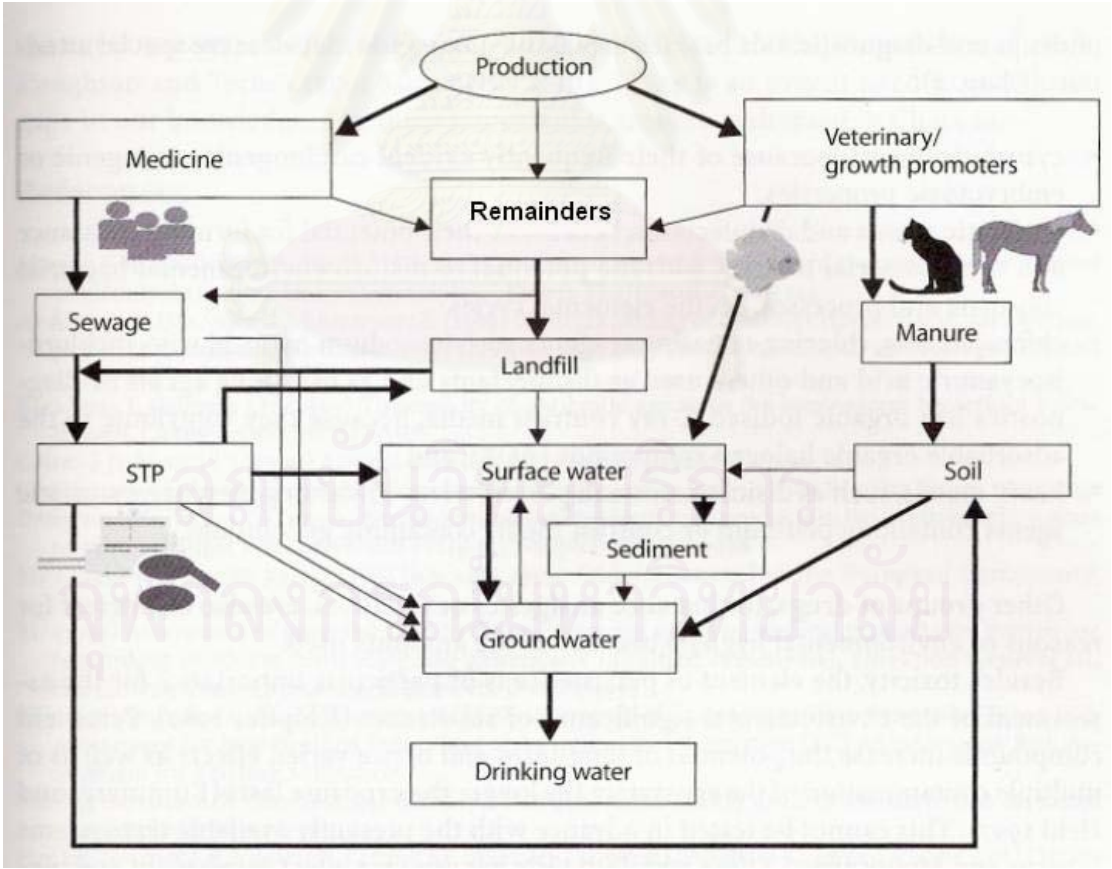


Figure 1.1: Sources, distribution, and sinks of pharmaceuticals in environment (Adapted from Kummerer, 2000)

The release of pharmaceuticals in environment could possibly occur by the metabolic excretion, direct disposal of unused or expired drugs to sewage systems, and terrestrial runoff (Daughton and Jones-Lepp, 2001). In general, pharmaceuticals have high polarity and water solubility because they need to be combined with water. Most pharmaceuticals are metabolized before excreted from the body and the products are often more reactive, more water soluble, and sometimes more toxic than the parent drug (Halling-Sorensen et al., 1998). However, the main functional groups of the compounds still remain unchanged. Some pharmaceuticals are also resisting to biodegradation as metabolic stability is necessary to pharmacological action (Dietrich, 2002). As a result, they are not completely removed in the treatment plants. Furthermore, the general wastewater treatment plants are not specifically engineered to remove pharmaceuticals, thus the effluents are still contaminated with certain amount of the pharmaceutical residues. Therefore, it is released into an aquatic environment, mostly by the effluents from municipal sewage treatment plants (STPs). Eventually, it becomes the receiving water which can be the main sources of potable water production.

The U.S. Geological Survey found 80 % of the sampled streams were contaminated with organic contaminants and the most frequently compounds detected are pharmaceuticals (Kolpin et al., 2002). The drug residues were also identified in a sample taken from a private drinking water tap in Germany (Heberer, 2002b). To date, none of the adverse health effects can be attributed to the consumption of water contaminated by pharmaceuticals at these low concentration levels, but based on precautionary principles, drinking water should be free from all kinds of contaminants. Although, the pharmaceuticals are designed to be biologically active to

the target organism, the unaware effects on the non-target organisms can also be taken place. Thus, it is such an inevitable threat to human health and aquatic life.

1.2 Research Aspect

The concerns on the pharmaceutical removal are still lacked since they are detected in relatively low concentration, from sub to hundreds of micrograms per liter (µg/L) or parts per billion (ppb) (Daughton and Jones-Lepp, 2001). Even though several research have been studied on the occurrence and fate of the pharmaceuticals (Daughton and Jones-Lepp, 2001, Dietrich, 2002, Halling-Sorensen et al., 1998, Heberer, 2002a, Heberer, 2002b, and Kolpin et al., 2002), but the information on their transport is still limited, particularly in the subsurface.

In this century, there are increasing concerns on conserving water due to the scarcity of water resources. Therefore, it is important to protect the water resources from the contamination of pharmaceuticals compounds, as the adverse effects on human and environment are still unknown. The continuing production, consumption, and disposition of numerous pharmaceuticals can be pseudo-persistent pollutants in nature as the new compounds are introduced after the old one is being degraded. Sorption is a mechanism naturally occurred in aquatic and groundwater systems that can substantially retard the transport or spread of adsorbate materials such as organic pollutants and inorganic metals to the uncontaminated regions. It is accordingly considered as an insightful fundamental needed to be clearly understood in order to remedy the problems regarding the transport of contaminants into the environment. The ultimate goal of this research is to study the sorption of pharmaceuticals onto polar and nonpolar adsorbents as one approach to investigate the transport of these pharmaceuticals. In this experiment, the polymeric resins Amberlite XAD2,

Amberlite XAD7, Amberlite XAD761 represented polar adsorbents where powdered activated carbon represented nonpolar adsorbents. Acetaminophen (analgesic) and nalidixic acid (antibiotics) were used as pharmaceutical compounds due to their physicochemical properties, frequency of detection in water and concentration level in the environment.

1.2.1 Objectives

The main purpose of this research was to study the sorption of acetaminophen and nalidixic acid onto pure adsorbents materials (Amberlite XAD2, Amberlite XAD7, Amberlite XAD761 and powdered activated carbon). Three specific objectives were as follows:

1. To study the adsorption behavior of pharmaceutical compounds, acetaminophen and nalidixic acid, onto polar adsorbents varied polarity and nonpolar adsorbent.
2. To investigate the interactions between pharmaceutical compounds and adsorbents.
3. To compare the pharmaceutical adsorption efficiency between the polar and nonpolar adsorbents.

1.2.2 Hypotheses

1. The sorption behavior of pharmaceuticals depends on the interaction between the molecular structure of pharmaceuticals and surface properties of adsorbent.
2. The pharmaceuticals are amphiphile molecules so they can adsorb on both polar and nonpolar surfaces.

1.2.3 Scopes of the Study

The batch experiments were conducted to investigate the sorption of pharmaceuticals in laboratory scale. All experiments were operated at ambient temperature (~25ºC) and triplicate samples were evaluated for all different sets of experiments.

1. The adsorption behavior of acetaminophen and nalidixic acid onto polar adsorbents varied polarity; Amberlite XAD2, XAD7, XAD761, and nonpolar adsorbent; powdered activated carbon, were interpreted by mean of adsorption isotherm.
2. The possible interactions occurred between pharmaceuticals and adsorbents were investigated.
3. The capability to adsorb pharmaceutical compounds between polar and nonpolar adsorbents were compared

1.3 Significance of the Study

The significance of this study was to comprehend the migration of pharmaceuticals in the environment by adsorption study as well as the interaction between pharmaceutical compounds and various types of adsorbent. Therefore, the outcomes of this research can be used as the information to find out an appropriate technique derived from the adsorption phenomenon to remedy the water contaminated by pharmaceutical compounds as regarded to the idea of water reuse.

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Background

2.1.1 Pharmaceuticals

Pharmaceuticals compounds are a diverse group of chemicals designed to be extremely bioactive to the specific biological targets. It is comprised of over-the-counter (OTC) drugs and under the prescriptions drugs (Daughton and Jones-Lepp, 2001). Most of pharmaceuticals are amphiphile molecules, which one portion is hydrophilic and the other portion is hydrophobic (Schwarzenbach et al., 2003).

The medical substances are usually metabolized to phase I or phase II metabolites before being discarded from the body with the urine and may be exposed to the environment as such. Phase I reactions mainly consist of oxidation, reduction, or hydrolysis, and the products are often more reactive and sometimes more toxic than the parent drug. Phase II reactions involve conjugation, which normally results in inactive compounds. However, both phase I and phase II reaction change the physical and chemical behaviors of pharmaceuticals because the metabolism always renders the metabolites to be more water soluble than the parent compounds (Halling-Sorensen et al., 1998). Two pharmaceuticals namely, acetaminophen and nalidixic acid, were used in this experiment.

Acetaminophen (ACE) belongs to a class of drugs called analgesics or pain relievers and antipyretics or fever reducers. It is a colorless, crystalline powder containing a hydroxyl functional group and metabolized primarily by conjugation reactions (Foye, et al. 1995). Acetaminophen is the most widely used drug, particularly for ones who are allergic or sensitive to aspirin. It is available in various

formulations, including liquid, tablet, capsule, and suppository. Acetaminophen is mainly used for the relief of fever, headaches, and other minor aches and pains. It is available without prescriptions. The common trade names are Paracetamol and Tylenol (http://www.medicinenet.com/acetaminophen/article.htm).

Nalidixic acid (NAL) is a quinolone antimicrobial agent used to treat bacterial infections of the urinary tract. It is primarily effective against gram-negative bacteria and its clinical spectrum is primarily reserved for oral treatment of uncomplicated urinary tract infections caused by susceptible microorganisms (usually *E.Coli*) (Foye, et al. 1995). It does not work for colds, flu, or other viral infections. It is pale-yellow, crystalline substances possessed a carboxylic functional group, thus being a very weak organic acid. It is available only with doctor's prescriptions. The common trade name is NegGram. (http://www.rxlist.com/cgi/generic2/nalidixicacid.htm)

2.1.2 Adsorbents

Amberlite XAD resins are nonionic polymeric resins with porous structure whose internal surfaces can adsorb and desorb a wide variety of different species depending on the affinity between resins and adsorbate species. They are generally used for adsorption of organic substances from aqueous solution and polar solvents. Their binding capacity is affected by three parameters: dipole moment, pore size and surface area. The functional group of the resins justifies the characteristic of resins into two types: polar and nonpolar. The adsorbents possessed styrenic group represents a nonpolar surface and the hydrophobic behavior generally exhibits resulting in the capability of adsorbing the organic species that are sparingly soluble in water. On the other hands, the adsorbents containing acrylic and phenolic groups represent the polar organic surfaces. The occurred behaviors are predominantly

influenced by the hydrophilicity of the surface. Consequently, these adsorbents are capable of adsorbing the organic species with certain degree of polarity (http://www.rohmhaas.com/ionexchange/Pharmaceuticals/AmberliteXAD_download.htm).

Activated Carbon is composed up of a complex network of pores with relatively large surface area (Faust and Aly, 1998). The effectiveness of activated carbon for the removal of organic compounds from fluids by adsorption is resulted by its large surface, which is a critical factor in adsorption process (Cheremisinoff and Cheremisinoff, 1993). Their structure consists of elementary microcrystallines of graphite which stacked together in random orientation and the spaces between these crystals are in the micropores range. The surface of carbon is essentially nonpolar. As a result, the activated carbon adsorbent tends to have hydrophobic and organophilic behaviors (Ruthven, 1984). There are two kinds of activated carbon: granular and powdered.

The use of powdered activated carbon in water treatment is more applicable as compared to the granular one especially when coped with a relatively low contaminant level that requires less amount of carbon. Also when applications are periodical or seasonal in nature, such as taste and odor problems in some surface water supplies, the capital investment in equipment is relatively small, and the carbon addition can be adjusted to change the water quality. They are therefore widely used for the adsorption of organics in sugar decolorization, water purification, and solvent recovery systems as well as for the adsorption of gasoline vapors in automobiles and as a general purpose adsorbent in many purification systems (Ruthven, 1984). As a result, almost 90% of worldwide water treatment plants used the powdered form of activated carbon (Sontheimer, 1976).

2.1.3 Sorption Phenomenon

Sorption interactions generally occur among all phases presented in any subsurface system and at the interfaces between these phases (Weber Jr. et al., 1991). The sorption phenomena can be categorized into two broad cases: adsorption, a process in which solute accumulation is generally restricted to a surface or interface and absorption, a process in which the solute penetrates into the sorbent (Grathwohl, 1998). The sorbent is defined as the soil or sediment solid and the sorbate is the solute sorbed onto the solids. For adsorption process, the adsorbent is soil or sediment solid and the adsorbate is the solute in form of gas or liquid phase. Sorption to solid surfaces is the main process affecting transport and fate of pharmaceuticals in an aquifer system. The adsorption of pharmaceuticals may be resulted from various types of attractive forces between sorbent and sorbate. In groundwater, sorption of pharmaceuticals depends on the aquifer media properties, pharmaceutical properties, and groundwater properties. In general, the sorption mechanism can be classified into three main categories: physical, chemical, and electrostatic (Weber Jr. et al., 1991). The physical sorption deals mainly with the dispersion forces between the sorbates and sorbents. The chemical and electrostatic sorption involves the chemical bonding and ion-exchanging between sorbates and sorbents, respectively.

2.1.4 Sorption and Retardation

The dissolved contaminants may interact with an aquifer solids encountered along the flow path through adsorption process. This phenomenon results in the distribution of the contaminants between an aqueous phase and the aquifer solids, diminution of concentrations in the aqueous phase, and retardation of the movement of the contaminant relative to the groundwater flow (Mackay et al., 1985). The

retardation is referred to the phenomenon of diminished chemical transport speed relative to the water seepage velocity (Schwarzenbach et al., 2003). It is commonly discussed using the correction factor known as a retardation factor (r_f) which simply indicates the mobility of the species at the reciprocal rate of the flow of groundwater at any instant. The retardation factor takes into account how much the velocity of contaminants is affected by the sorption process in the groundwater. As the adsorption increases, the r_f is high, thus the effectively velocity of the chemical decreases as it is retarded by the adsorbents. The chemical is more significantly retarded relative to the groundwater (Knox et al., 1993). The higher the fraction of the contaminant sorbed, the more retarded in its transport is achieved.

2.1.5 Sorption of Amphiphile Molecules onto Nonpolar Surfaces

Adsorption of amphiphilic molecules onto nonpolar surfaces occurs as a result of dispersion force interactions. The hydrophobic portion of the adsorbate will be associated with the solid surface with the hydrophilic group directed toward the aqueous phase. In the early stage of adsorption, it is likely that the hydrophobic group is lying on the surface much like “trains” or lying more or less flat on the surface as shown in Figure 2.1(a). As the degree of adsorption increases, the compounds will gradually become oriented more perpendicular to the surface or “L”, in which the significance portions of the molecule remain adsorbed parallel to the surface as demonstrated in Figure 2.1 (b) until, at or near saturation condition, an approximately close-packed assembly will result in a vertical or perpendicular in which the major portion of the chain has no direct contact with the solid surfaces as shown in Figure 2.1(c) (Myers, 1999).

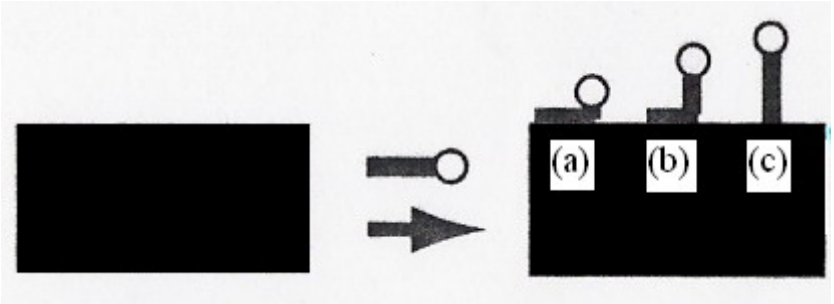


Figure 2.1: Sorption of amphiphile molecules onto nonpolar surfaces (Myers, 1999)

2.1.6 Sorption of Amphiphile Molecules onto Polar Surfaces

The mechanism of adsorption onto these surfaces can be much more complex than that of the nonpolar discussed above, since such factors as orientation will be determined by a balance of several forces.

The potential forces operating at a polar surface include the dispersion forces, dipolar interactions, hydrogen bonding and other acid-base interactions. The determination of sorption onto polar surfaces depends strongly on the relative balance between the dispersion forces and the uniquely polar interactions. If dispersion forces predominate, adsorption will occur in a manner essentially equivalent to that for the nonpolar surfaces as shown in Figure 2.1. On the other hand, if the polar interactions dominate, adsorption may occur in a reverse mode; that is, the hydrophilic group will adsorb at the solid surface and the hydrophobic group oriented toward the aqueous phase as shown in Figure 2.2 (Myers, 1999).

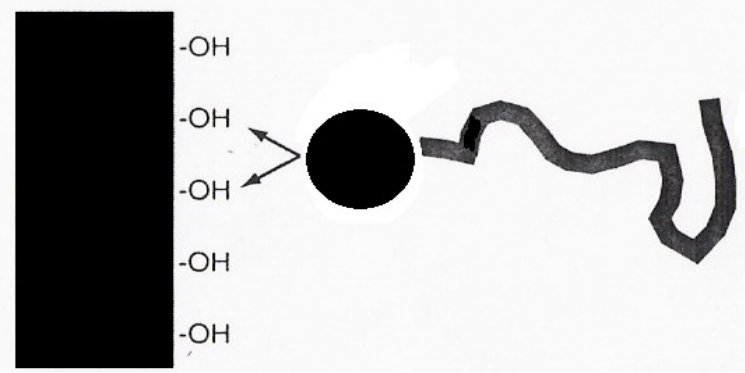


Figure 2.2: Sorption of amphiphile molecules onto polar surfaces (Myers, 1999)

2.1.7 Sorption Isotherm

The equilibrium distribution of the adsorbate among the phases is typically evaluated at a fixed system temperature according to various models known as sorption "isotherm" (Weber Jr. et al., 1991). The most common models founded in adsorption of organic contaminants in environmental media are Linear, Langmuir, and Freundlich models. Examples of these isotherms are shown below.

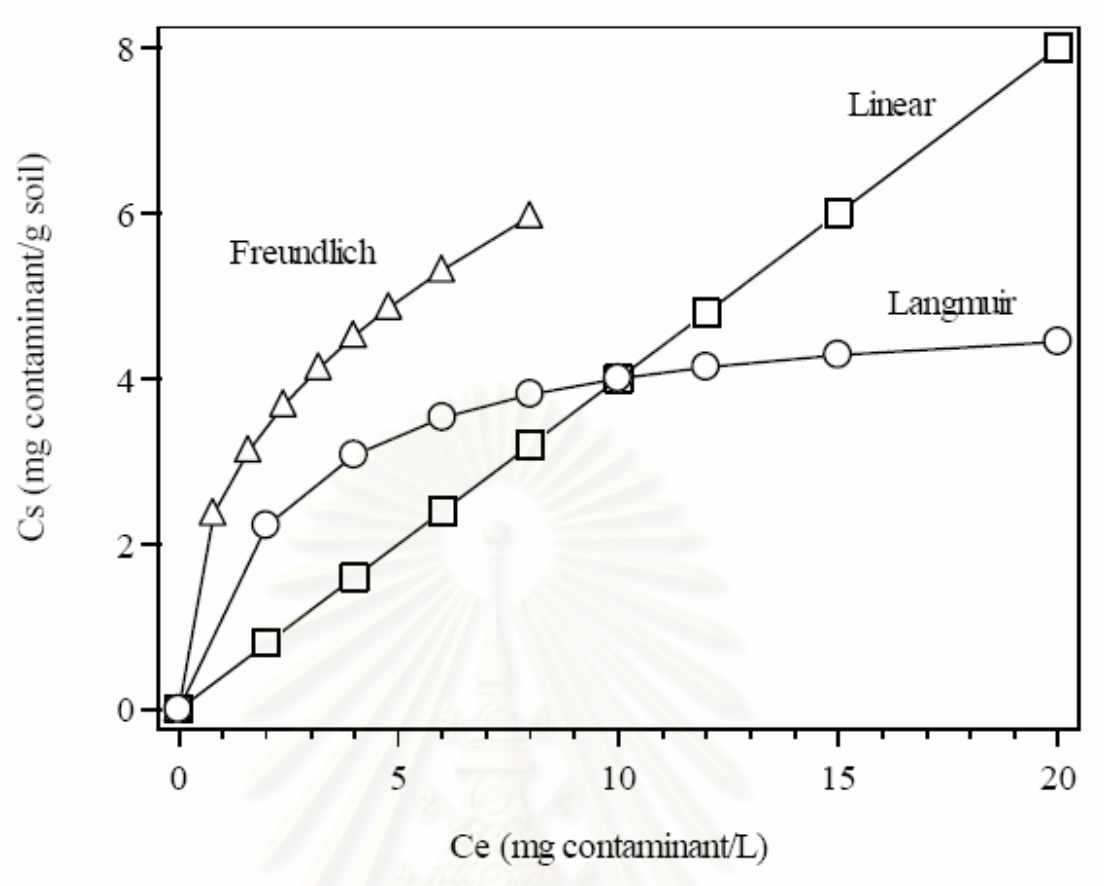


Figure 2.3: The plot of the three most common isotherms: Linear, Langmuir, and Freundlich (Adapted from www.engineering.uiowa.edu/~cee158/sorption_ws.pdf)

The simplest model is the linear model, which describes the accumulation of sorbate by the sorbent as directly proportional to the solution phase concentration:

$$q_e = K_d C_e$$

Where q_e = the amount of solute adsorbed per unit weight of adsorbent (mass/mass)

K_d = linear sorption coefficient (volume/mass)

C_e = equilibrium concentration of the solute (mass/volume)

The Langmuir model provides the basic assumptions that the sorption energy of each molecule is the same, occurs on localized sites and involves no interactions between sorbed molecules. The sorption leads to the deposition of a single layer of sorbate molecules on the surface of sorbent as monolayer coverage (Weber Jr. et al., 1991). The Langmuir expression is:

$$q_e = \frac{QK_LC_e}{1+K_LC_e}$$

Where q_e = the amount of solute adsorbed per unit weight of adsorbent (mass/mass)

K_L = Langmuir sorption coefficient (volume/mass)

C_e = equilibrium concentration of the solute (mass/volume)

Q = amount of solute adsorbed per unit weight of adsorbent required for monolayer capacity (mass/mass)

The Freundlich model is an empirical expression that encompasses the heterogeneity of the surface and the exponential distribution of sites and their energies (Faust and Aly, 1998). The Freundlich expression is:

$$q_e = K_{fr}C_e^{N}$$

Where q_e = the amount of solute adsorbed per unit weight of adsorbent (mass/mass)

K_{fr} = Freundlich sorption coefficient (volume/mass)

C_e = equilibrium concentration of the solute (mass/volume)

N = Freundlich constant (dimensionless)

2.2 Literature Review

2.2.1 Occurrence of Pharmaceuticals in the Aquatic Environment

Heberer (2002a) detected several pharmaceutically active compounds (PhACs) from the investigations in the aquatic environment in Austria, Brazil, Canada, Croatia, England, Germany, Greece, Italy, Spain, Switzerland, The Netherlands, and the United States of America. More than 80 compounds, including several pharmaceuticals and drug metabolites have been found at concentration up to the µg/L-level in sewage influent and effluent samples and also in several surface waters located downstream from municipal sewage treatment plants (STPs). The studies showed that some PhACs originating from human therapy are not eliminated completely in the STPs and eventually are, discharged as contaminants in the receiving waters.

Heberer (2002b) collected the water samples in urban areas of Berlin, Germany. He concluded that the pharmaceuticals residues cannot be eliminated completely in the municipal sewage treatment plants (STPs). As a result, there is a potential risk of drinking water contaminated by polar organic compounds when the receiving water is used as a source of drinking water production. Several pharmaceuticals were detected at concentrations up to the mg/L-level. A few were also identified at ng/L-level in tap water.

Stumpf et al. (1999) studied the occurrence of eleven polar drugs and two metabolites by investigating in treated and untreated sewage as well as natural waters in the state of Rio de Janeiro, Brazil. The drug residues in raw sewage, treated wastewater and river water were detected at concentrations in the ng/L-range.

Kolpin et al. (2002) provided the first nationwide reconnaissance of the occurrence of pharmaceuticals, hormones, and other organic wastewater contaminants

(OWCs) in U.S. streams. The U.S. Geological Survey found several groups of pharmaceutical compounds, namely antibiotics, nonprescription drugs, other prescription drugs and reproductive hormones. Nonprescription drugs, i.e. acetaminophen, were found with greatest frequency.

Carballa et al. (2004) observed the behavior of pharmaceuticals, cosmetics, and hormones, in a sewage treatment plant (STP) located in Galicia (NW Spain). The overall removal efficiencies of the STP ranged from 70%-90% for the fragrances, 40-65% for the anti-inflammatories, around 60% for the antibiotic sulfamethoxazole and 65% for 17β-estradiol. This indicated that the STP cannot remove 100% of these pharmaceuticals and personal care products and finally leach to the aquatic environment.

2.2.2 Sorption of Pharmaceuticals onto Solid Surfaces

Tolls (2001) reviewed the sorption of veterinary pharmaceuticals (VPs) in soils. He suggested that mechanisms other than hydrophobic partitioning play a significant role in sorption of VPs. The estimation of log K_{oc} based on the hydrophobicity parameter log K_{ow} is not successful and thus fails to predict the adsorption coefficient K_d. It can be concluded that the adsorption behavior of pharmaceuticals is different from that of the nonpolar adsorbate.

Intravichit (2003) had investigated the sorption of three pharmaceuticals (Acetaminophen, Nalidixic acid, and 17-alpha-ethynylestradiol) onto three different adsorbents (silica, alumina, and porapak). Alumina and Silica are positively and negatively charged surfaces, respectively at neutral pH. Porapak is the organic polymer adsorbent. Acetaminophen shows no significant adsorption onto all adsorbents indicating that the transport of this pharmaceutical cannot be retarded if

the subsurface aquifer is composed of these adsorbents. Nalidixic acid has a significant adsorption on the positively charged alumina where 17-alpha-ethynylestradiol strongly sorbs onto porapak.

Lunn et al. (1994) studied the decontamination of pharmaceuticals aqueous solutions by polymeric resins. Amberlite resins XAD2, XAD4, XAD7, and XAD16 were tested for their ability to decontaminate solutions of various drugs (antibacterials: ampicillin, trimethoprim; antineoplastics: bleomycin, carmustine, lomustine, streptozotocin; oral contraceptives: norethindrone; and antianginal: verapamil). All solutions were decontaminated with difference degree of success. He had concluded that the Amberlite resins are promising adsorbent for decontaminating large volumes of dilute aqueous solutions containing pharmaceuticals.

Otero et al. (2004) carried out the adsorption of salicylic acid onto polymeric adsorbents and activated charcoal. Salicylic acid ($C_7H_6O_3$) represents a pharmaceutical compound and the polymeric adsorbents used were Sephabeads SP206 and SP207. These two adsorbents are synthetic adsorbents based on a styrene and divinylbenzene (DVB) copolymer. It could be summarized that the activated charcoal has higher capacity than the polymeric adsorbents and the adsorption equilibrium data fit well with the Nitta isotherm model rather than the Langmuir isotherm model. Nitta isotherm is the multisite Langmuir model for homogenous adsorbents derived by Nitta using statistical thermodynamic arguments. It is a model based on the mass-action law. The salicylic acid adsorptive capacity of all the adsorbents considered increases with decreasing temperature, especially for these polymeric adsorbents due to the effects of the temperature.

Juang and Shiau (1999) measured the amounts of equilibrium adsorption of phenol and 4-chlorophenol from water on non-ionic polymeric resins, Amberlite

XAD4 (hydrophobic) and Amberlite XAD7 (moderately polar) in the controlled temperature (288-318K). The affinity for the more hydrophobic solute 4-chlorophenol is stronger with hydrophobic resins, XAD4. However, it was found that XAD7 and XAD4 give comparable q_e for both phenols. In fact, the adsorption capacity per unit area of XAD7 is comparatively high because the specific surface area of XAD7 is much smaller than XAD4. The data from adsorption studies cannot be fit by the conventional Langmuir, Freundlich, BET, and Redlich-Peterson isotherms but are well fitted by combined the BET isotherm or its modified form with the Langmuir or Freundlich isotherm.

2.2.3 Adsorbents Properties

Xu et al. (2003) reviewed the applications of porous resin sorbents in industrial wastewater and water resource recovery. The survey of several literatures indicated that the resins are physically and chemically stable. They have long life due to the hard and durable structure. They can be tailor-made for specific application which provides the possibility of controlling the resin structure, internal surface area, and pore size distribution. In addition, it can be regenerated and can recover valuable chemicals from waste streams. They also concluded several case studies discussed mainly on the resins durability. Streat and Sweetland (1998) concluded that the resin sorbent had no apparent degradation after two years of operation in treating a phenol-laden wastewater over 1,300 cycles of regeneration. The resins regeneration can be operated by either solvent elution or pH adjustment. Dow chemical (2001) summarized that the annual resin sorbent replacement needed for a fluidized-bed operation is less than 5%. These cases are confirmed by a full scale operation in

China that these resins can be use for over five years with more than 2,000 cycles of regeneration.

Trochimczuk et al. (2001) reported that the polymeric adsorbents that based on styrene-divinylbenzene, i.e. Amberlite XAD2 have been extensively used in the decontamination of wastewater containing phenol and its derivatives. Furthermore, it is accepted that the presence of functional groups on the surface of styrene-divinylbenzene copolymers results in an increase of surface polarity and hydrophilicity and thus enhancing the sorption of polar sorbates onto these polymers. Some of these polymers, i.e. Amberlite XAD7, are commercially available and widely used in solid phase extraction of polar compounds.

CHAPTER III

METHODOLOGY

3.1 Materials

3.1.1 Adsorbents

The commercial adsorbents, non-ionic polymeric resins: Amberlite XAD2, XAD7, and XAD761 represented polar surfaces and powdered activated carbon (PAC) represented nonpolar surface were used in this study. Amberlite XAD2 and XAD761 were purchased from Supelco and have a surface area of 330 $m^2 g^{-1}$ and 200 $m^2 g^{-1}$, respectively. Amberlite XAD7 was obtained from Fluka and has a surface area of 450 $m^2 g^{-1}$. The powdered activated carbon has a surface area of 600 $m^2 g^{-1}$. It was purchased from Aldrich Chemical Co. Amberlite XAD2, XAD7, and powdered activated carbon were used as received. Amberlite XAD761 was prepared by grinding and passing through the sieves. The used material was one which passed through the sieve number 40 but retained on the sieve number 70. The surface area of Amberlite XAD761 after treating is 118 $m^2 g^{-1}$ as measured in duplicate by BET surface area analyzer. All resins were pretreated prior using by washing several times with distilled water, drying over night at 60ºC, and cooling down in desiccators. The properties of adsorbents are listed in Table 3.1.

Table 3.1: Adsorbents properties

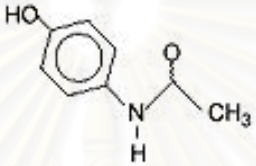
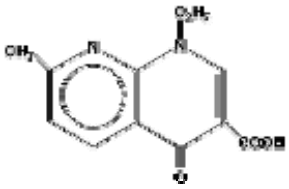
Adsorbents	Matrix	Dipole Moment	Surface Area ($m^2 g^{-1}$)	Average Pore Diameter (Å)
XAD2	Polyaromatic	0.3	330	90
XAD7	Acrylic ester	1.8	450	90
XAD761	Phenol-formaldehyde	N/A	118	600
AC	Graphite micro-crystallites [a]	N/A	600	N/A

References: Sigma-Aldrich Product Data Sheet
a. Sontheimer, 1976
N/A: Not Available

3.1.2 Pharmaceutical Compounds

Acetaminophen (analgesics) and Nalidixic acid (antibiotics) were pharmaceutical compounds used in these experiments. Both acetaminophen and nalidixic acid were purchased from Aldrich Chemical Co and were used as received. Table 3.2 listed the pharmaceutical properties.

Table 3.2: Pharmaceuticals properties

Properties	Acetaminophen	Nalidixic Acid
Structure		
CAS Number	103-90-2	389-08-2
Chemical Formula	$C_8H_9NO_2$	$C_{12}H_{12}N_2O_3$
Molecular Weight (g)	151.16	232.24
Molecular Size (Å) [a]	10.1-11.1	11.9-12.9
Water Solubility (mg L^{-1})[b]	12742.79	99.98
Melting point	168-172°C	227-229°C
Log K_{ow}	0.46	1.59
pKa [c]	9.71	6.00

References: Sigma-Aldrich Product Data Sheet
a. ChemDrawUltra Program
b. Rytting et al. 2005
c. Hansch et al. 1990

3.1.3 Chemicals

Reagent grade MeOH (99% purity) was obtained from Fisher Scientific and was used as a solvent in preparing nalidixic acid stock solution. The acid and basic adjustment was conducted using the hydrochloric acid (HCl) and sodium hydroxide (NaOH), respectively. The hydrochloric acid was purchased from Carlo Erba and sodium hydroxide was purchased from Univar.

3.2 Experimental Methods

The experiments were divided into three main parts which are equilibrium sorption study, solid to solution ratio determination, and sorption isotherm study.

3.2.1 Experimental Conditions and Methodology

The batch experiments were conducted to investigate the sorption behavior of two pharmaceutical compounds onto various types of adsorbents. All experiments were operated at ambient temperature (≈25°C) and at least triplicate samples were evaluated for all different sets of experiment. Blank solutions were used for correction of background interferences. Acetaminophen was prepared in distilled water as a stock solution at concentration of 1000 mg L^{-1}. Nalidixic acid was prepared in MeOH as a stock solution at concentration of 1000 mg L^{-1}. The pH was measured using the pH-meter (Hach; Sension1). The pH was adjusted to be less than pKa so the pharmaceuticals are predominantly in neutral form and the dissociated forms are presumably negligible. The nalidixic acid was adjusted to have a pH at 5 using the 0.02 M dilute solution of HCl and NaOH, while the pH of acetaminophen solution was not adjusted since the solution already exists at the pH lower than its pKa.

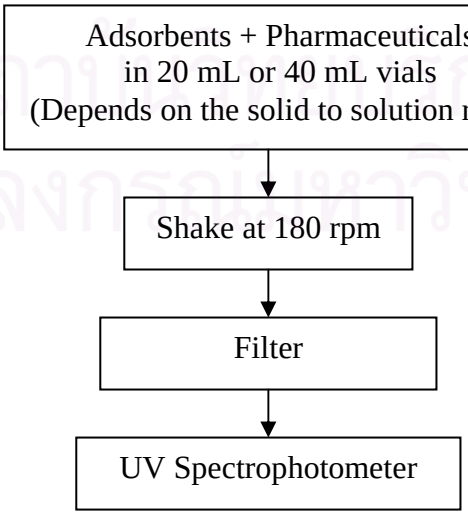


Figure 3.1: The schematic diagram for sample preparation

All parts of the experiment followed the same procedure as shown in Figure 3.1. The pH of the pharmaceutical solutions were adjusted and mixed with the adsorbents in a series of 20 mL or 40 mL vials and shaken at 180 rpm until the solutions reach the equilibrium. Then the samples were filtered through a glass microfibre filters (GF/C Whatman) with the diameter of 1.2 µm. Then the unadsorbed concentrations of pharmaceuticals in the supernatant solution were measured by Helios Alpha UV-visible spectrophotometer (ThermoSpectronic). The wavelength of 242 nm and 258 nm were used to analyze the concentration of acetaminophen and nalidixic acid, respectively.

3.2.2 Equilibrium Sorption Study

The equilibrium sorption study was conducted at certain pharmaceutical concentration and adsorbent mass. The contact time was varied (i.e. 6, 12, 24, 36, and 48 hours) to determine an equilibrium time of adsorption. The equilibrium time is defined as the time in which there is no concentration change with respect to time. The concentration of pharmaceuticals and mass of adsorbents were constant at 10 ppm and 0.1 g, respectively. The samples were prepared following the experimental procedure as shown in Figure 3.1.

3.2.3 Solid to Solution Ratio Determination

In this part, the determination followed the trials and errors rule of thumb. The solid to solution ratio was conducted at constant pharmaceuticals concentration at certain solution volume but varied mass of adsorbent to determine appropriate amount of solid required to obviously seen the adsorption phenomena. If the amount of adsorbent is too high, the concentrations of unadsorbed pharmaceuticals approach

zero. On the other hand, if the amount of adsorbent is too low, there is no adsorption at all due to an inadequate amount of solid as evidenced by exactly equal concentration of sample as the initial concentration. The experiments were followed the schematic flow shown in Figure 3.1. The samples were shaken at equilibrium time of 24 hours, which was predetermined from the previous section.

3.2.4 Sorption Isotherm Study

The sorption isotherm study was conducted by applying the solid to solution ratio obtained from previous experiments with varied pharmaceuticals concentration. The Amberlite XAD2, XAD7, and XAD761 had a constant solid to solution ratio of 0.01:20 g mL^{-1} and 0.2:20 g mL^{-1} for nalidixic acid and acetaminophen, respectively. The pharmaceutical concentrations were varied in the range of 5-20 ppm. The solid to solution ratio of 0.02:40 g mL^{-1} was used for activated carbon where the pharmaceuticals concentrations were varied in the range of 100-800 ppm.

The experimental were followed the flow diagram shown in figure 3.1. The mass of pharmaceuticals sorbed, q_e, was determined by mass balance equation shown below:

$$q_e = \left[\frac{(C_t - C_e)}{M}\right](V_l)$$

Where q_e = mass of pharmaceuticals sorbed (mg g^{-1})

C_t = initial concentration (mg L^{-1})

C_e = equilibrium concentration (mg L^{-1})

M = mass of adsorbent (g)

V_l = total volume of liquid in sample (L)

3.3 Analytical Apparatus and Instruments

The pH was adjusted by using pH-meter (Hach; Model Sension1). The Helios Alpha UV-visible spectrophotometer (ThermoSpectronic) was used to analyze the concentration of acetaminophen and nalidixic acid at the wavelength of 242 nm and 258 nm, respectively.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Sorption Equilibrium

The preliminary study on sorption equilibrium was conducted to determine the equilibrium time of adsorption indicated as when there is no further change in sorbate concentration with respect to time. The sorption kinetics studies were conducted with both pharmaceuticals; acetaminophen and nalidixic acid; and all pure adsorbents including Amberlite XAD2, XAD7, XAD761 and powdered activated carbon.

Figures 4.1-4.4 shows the sorption of pharmaceuticals onto various sorbents in terms of equilibrium sorption q_e, amount of pharmaceuticals sorbed per gram of sorbent, on y-axis versus time in hours on x-axis. The sorption kinetics of acetaminophen onto polymeric resins and activated carbon are shown in Figure 4.1-4.2, respectively. Figure 4.3-4.4 indicates the sorption kinetics of nalidixic acid onto polymeric resins and activated carbon, respectively. Both acetaminophen and nalidixic acid show sorption onto all sorbents.

According to Figure 4.1 and 4.2, the sorptions of acetaminophen onto all adsorbents show the negligible change in the amount of adsorbate sorbed per gram of adsorbent with respect to time. So, it can be assumed that the sorption reaches the equilibrium since the first sample analysis at 6 hours for all adsorbents.

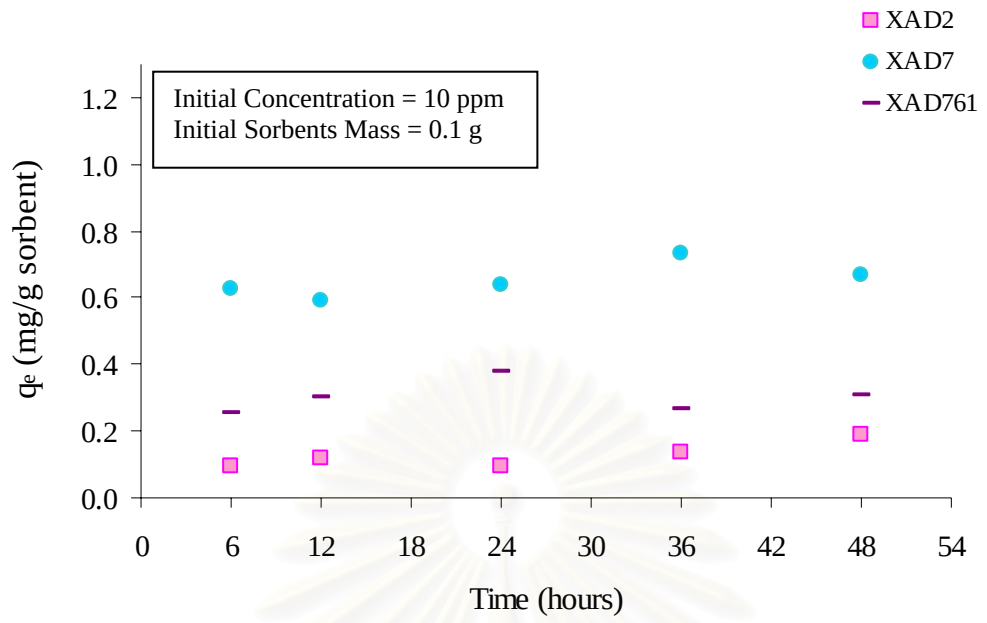


Figure 4.1: The sorption kinetics of acetaminophen onto Amberlite XAD2, XAD7, and XAD761

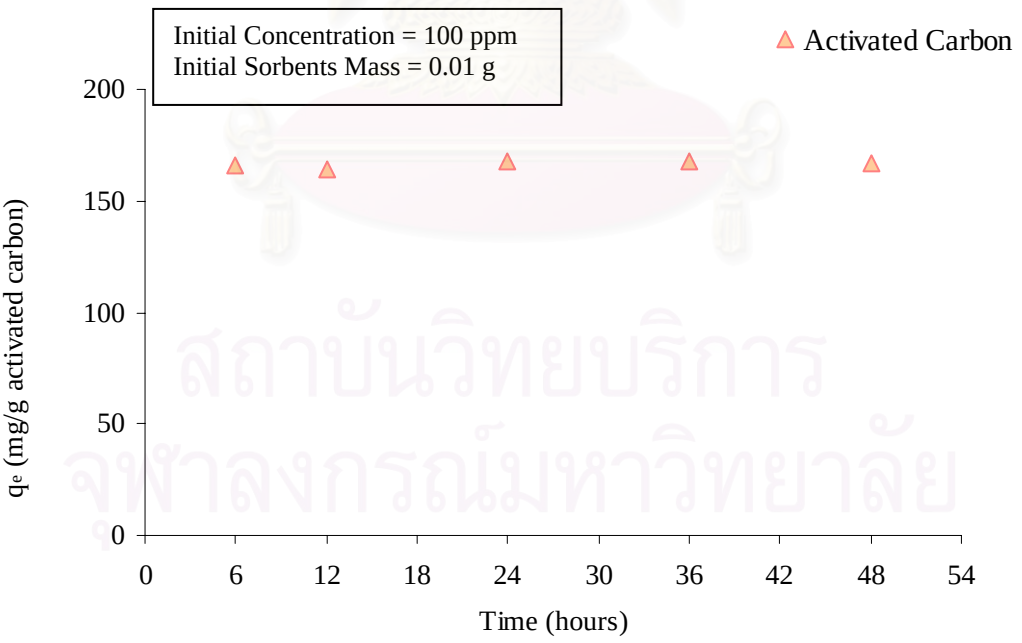


Figure 4.2: The sorption kinetics of acetaminophen onto activated carbon

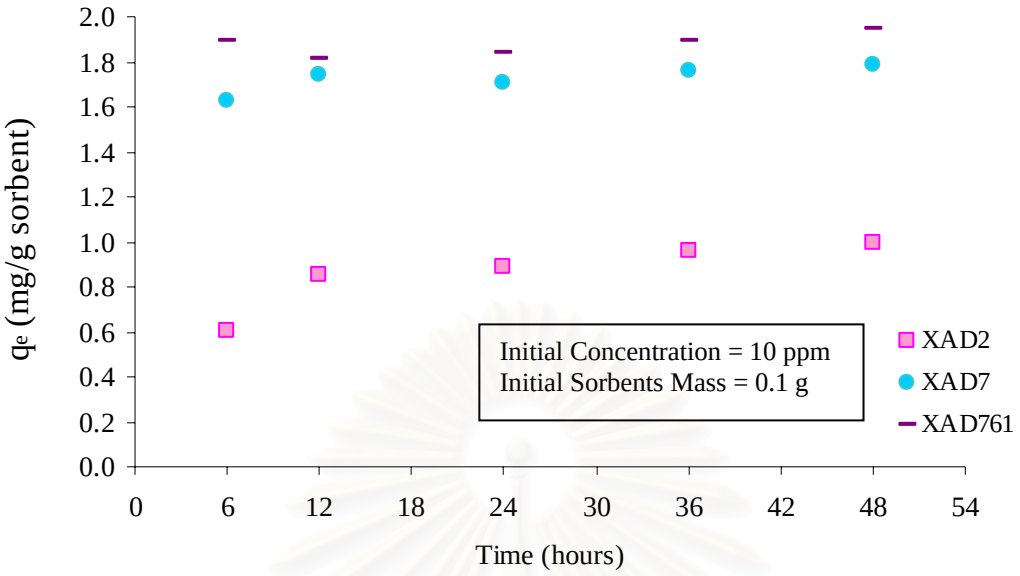


Figure 4.3: The sorption kinetics of nalidixic acid onto Amberlite XAD2, XAD7, and XAD761

The sorptions kinetics of nalidixic acid was shown in Figure 4.3 and 4.4. The plot also revealed the similar trend as acetaminophen. After 24 hours, there is only insignificance change in the amount of adsorbate sorbed per gram of adsorbent with respect to time for polymeric adsorbents. For activated carbon, the equilibrium is reached since the first 6 hours.

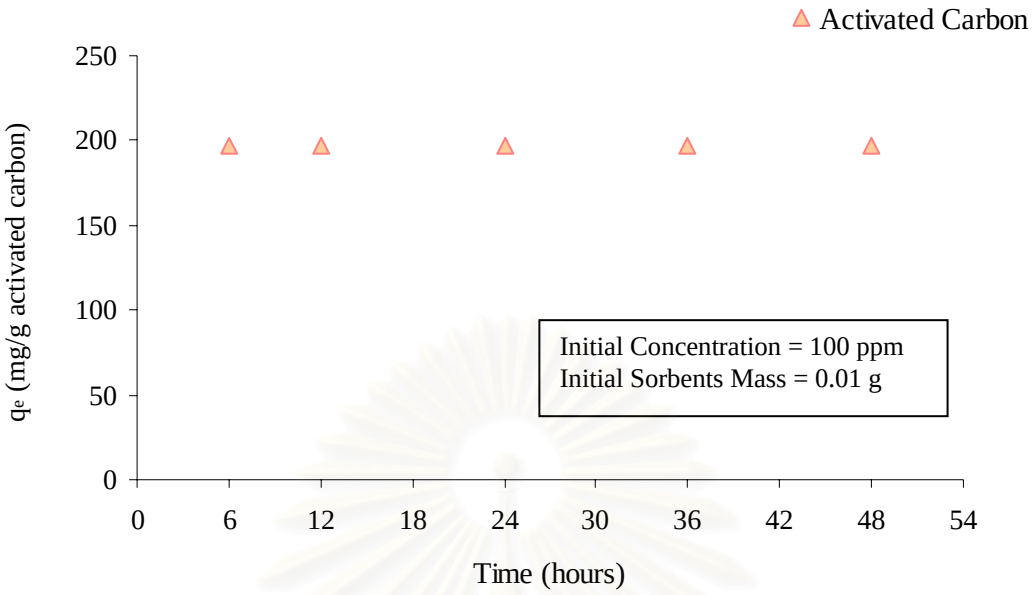


Figure 4.4: The sorption kinetics of nalidixic acid onto activated carbon

The results yield that the equilibrium occurred quite fast, therefore the sorption kinetics at a range of time prior to six hours (i.e. 15, 30, 45, and 60 minutes) was conducted for sorption of nalidixic acid onto XAD7 in order to confirm that the sorption occurs with respect to time. Figure 4.5 illustrated the sorption kinetics of nalidixic acid onto Amberlite XAD7 at the time interval of 15 minutes to 48 hours.

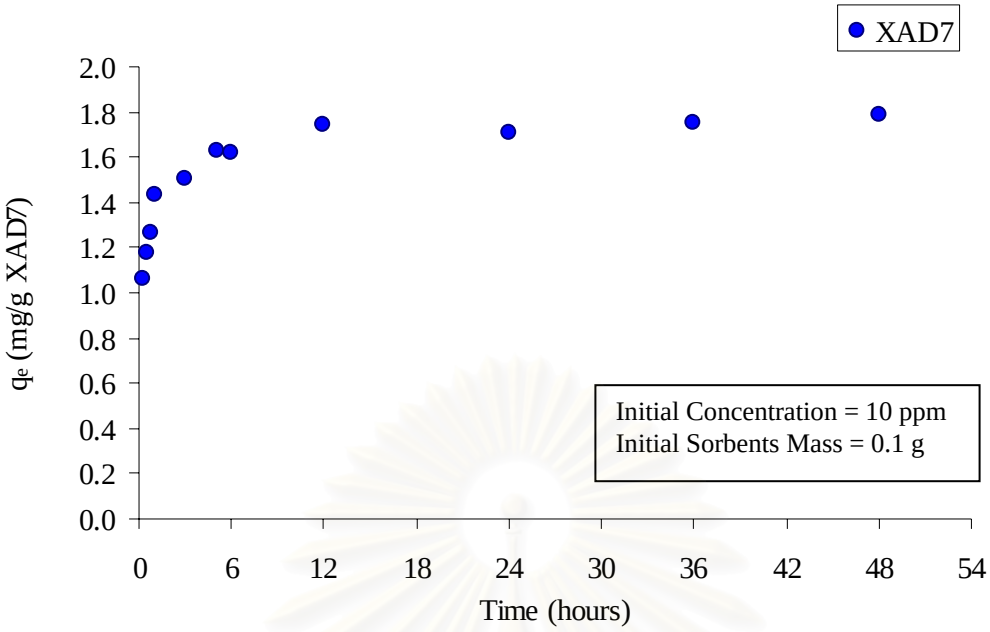


Figure 4.5: The sorption kinetics of nalidixic acid onto Amberlite XAD7 at frequent time interval prior to 6 hours.

According to these sorption equilibrium studies, it could be summarized that the equilibrium time of 24 hours were selected to use for both acetaminophen and nalidixic acid onto all sorbents in order to assure that the adsorption truly undergoes the equilibrium.

4.2 Solid to Solution Ratio

The solid to solution ratio determination was conducted using two pharmaceuticals (acetaminophen and nalidixic acid) and four adsorbents (Amberlite XAD2, XAD7, XAD761, and activated carbon) to determine the ratio of suitable amount of solid to appropriate volume of solution which was capable of observing the sorption phenomena. In this experiment, the results were obtained by variation of the ratio of sorbent mass to solution volume at certain concentration of pharmaceuticals in the range of 5-20 ppm.

There are two specific scenarios of inappropriate solid to solution ratio: the amount of solid is too high and the amount of solid is too low. For the first case, when the amount of solid is too high, the sorption capacity provided by sorbent is too high to sorb all pharmaceuticals. In this case, the equilibrium concentrations of pharmaceutical are close to or equal to zero, $C_{eq} \approx 0$. It thus yields the high amount of mass sorbed per gram of sorbent (q_e). As a result, the sorption cannot be seen as the data lie on the y-axis. An example of this scenario was shown in Figure 4.6, which is a plot of q_e (mg/g sorbents) versus C_{eq} (ppm) obtained from the sorption study of nalidixic acid onto activated carbon. It was found that the solid to solution ratio of 0.01 g activated carbon to 20 mL of nalidixic acid solution at initial concentration of 5-20 ppm is not suitable as the result falls into this scenario. Therefore, the range of concentrations for activated carbon is changed to 100-800 ppm.

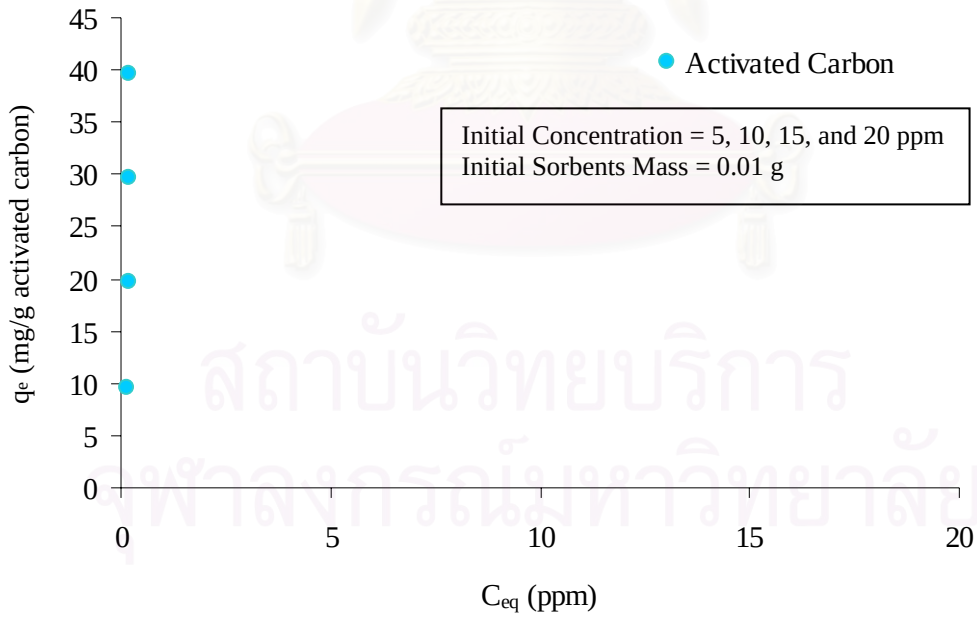


Figure 4.6: The inappropriate solid to solution ratio in sorption of nalidixic acid onto activated carbon (the amount of solid is too high)

On the other hand, when the mass of sorbent is too low, it is not capable to sorb the pharmaceuticals. The result indicates that the equilibrium pharmaceutical concentrations are close to or equal to the initial concentrations, $C_{eq} \approx C_i$. Therefore, the amount of mass sorbed per gram of sorbent (q_e) approaches to zero, $q_e \rightarrow 0$. Then with this scenario, the data lie on the x-axis and the sorption trends are also invisible.

Those two perspectives mentioned earlier are the main criteria for solid to solution ratio selection. The proper ratio needs to fall in between these two criteria. An example of appropriate solid to solution ratio selection was shown for acetaminophen and nalidixic acid onto Amberlite XAD7 as illustrated in Figure 4.7.

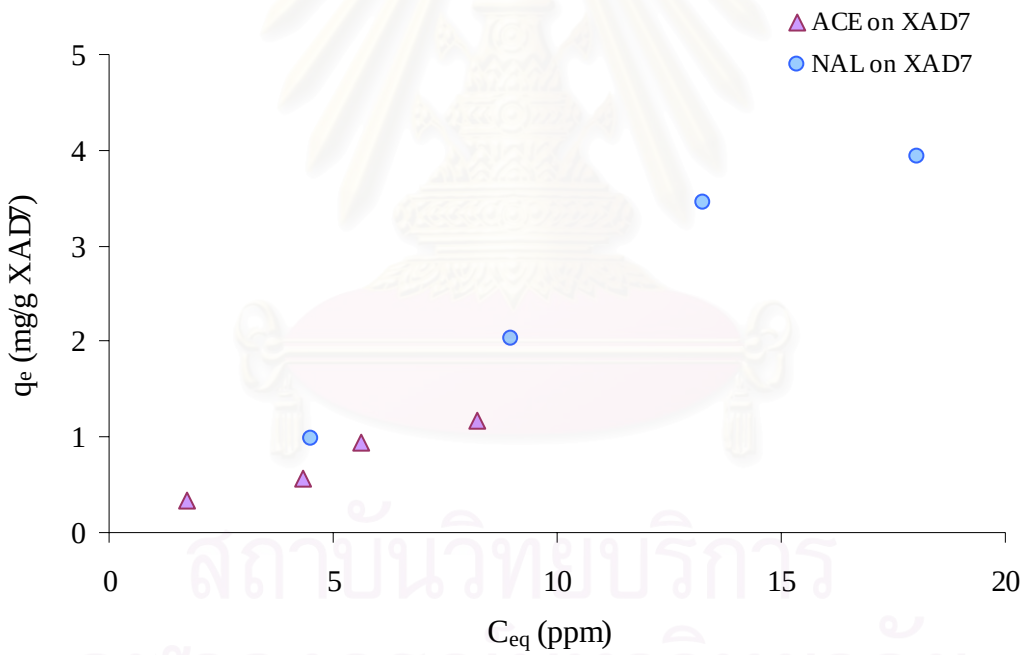


Figure 4.7: The appropriate solid to solution ratio in sorption of acetaminophen and nalidixic acid onto Amberlite XAD7

The solid to solution ratio for each adsorbent and pharmaceutical were listed in the following table:

Table 4.1: The solid to solution ratio of acetaminophen and nalidixic acid onto various adsorbents

Adsorbents	Solid to Solution Ratio	
	Acetaminophen	**Nalidixic Acid**
Amberlite XAD2	0.2 g:20 mL	0.01 g:20 mL
Amberlite XAD7	0.2 g:20 mL	0.01 g:20 mL
Amberlite XAD761	0.2 g:20 mL	0.01 g:20 mL
Activated Carbon	0.02 g:40 mL	0.02 g:40 mL

4.3 Sorption Capacity and Sorption Isotherm

The sorption isotherm studies were carried out in batch experiments using two pharmaceuticals (acetaminophen and nalidixic acid) and four adsorbents (Amberlite XAD2, XAD7, XAD761, and activated carbon). The sorption data were fitted to most three common isotherms namely linear isotherm, Langmuir isotherm, and Freundlich isotherm.

The isotherm studies were conducted at pH lower than the pK_a of pharmaceuticals. So, the pharmaceuticals are predominant in neutral form and the dissociated forms are presumably negligible. The pH was adjusted to 5 for nalidixic acid (pK_a = 6.00) and there was no adjustment for acetaminophen (pK_a = 9.71) as the solution is in the neutral pH range which is already lower than the pK_a.

In these experiments, the concentration of pharmaceuticals was varied in the range of 5-50 ppm and the amount of polymeric adsorbents was fixed at 0.01 g for nalidixic acid and 0.2 g for acetaminophen with solution volume of 20 mL. For activated carbon, the amount of adsorbent was 0.02 g in 40 mL of pharmaceutical solution both acetaminophen and nalidixic acid with the concentration in the range of 100-800 ppm.

The plots between q_e (mg/g sorbents) and C_{eq} (ppm) of acetaminophen and nalidixic acid were firstly introduced as aimed to discuss about the sorption capacity of polymeric adsorbents prior investigating the sorption isotherm of each adsorbent.

4.3.1 Sorption Capacity of Polymeric Resins for Acetaminophen and Nalidixic Acid

The sorption data of acetaminophen and nalidixic acid onto Amberlite XAD2, XAD7, and XAD761 are illustrated in Figure 4.8 and 4.9, respectively. It was observed that the sorption behaviors of both pharmaceuticals onto the Amberlite XAD polymeric resins are similar. The XAD7 demonstrates the highest sorption capacity or q_e in mg per gram adsorbent for both pharmaceuticals followed by XAD761 and XAD2, respectively eventhough the XAD7 possesses only an intermediate polarity among three polymeric resins used in this study. However, it is worthwhile to note that the specific surface areas of three commercial resins are totally difference in such a way that the XAD7 has highest specific surface area of 450 m^2/g, followed by 330 m^2/g and 118 m^2/g for XAD2 and XAD761, respectively.

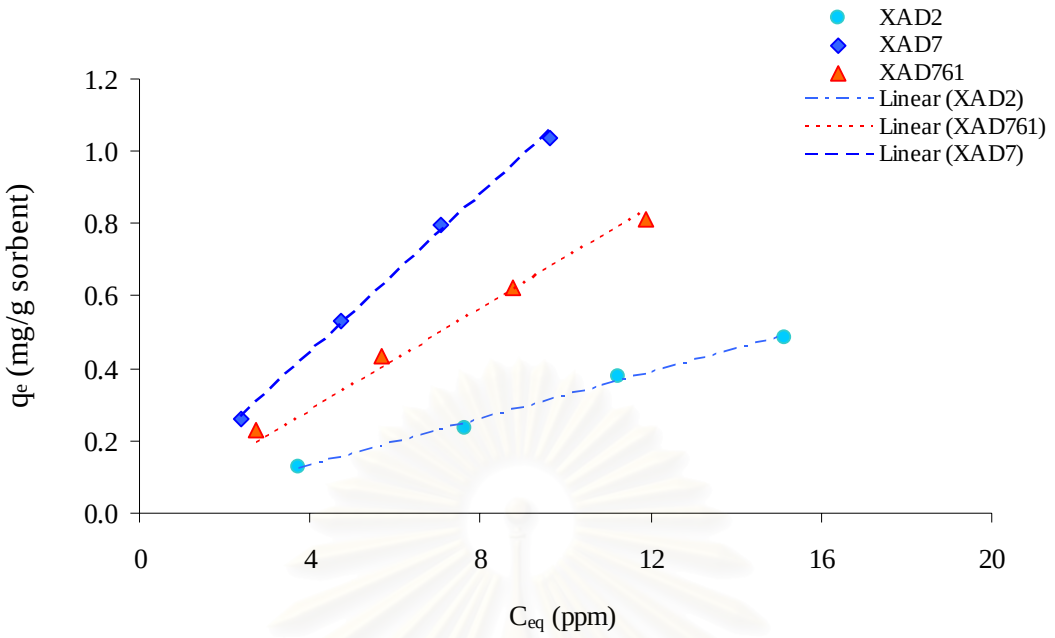


Figure 4.8: The sorption isotherm of acetaminophen onto polymeric sorbents

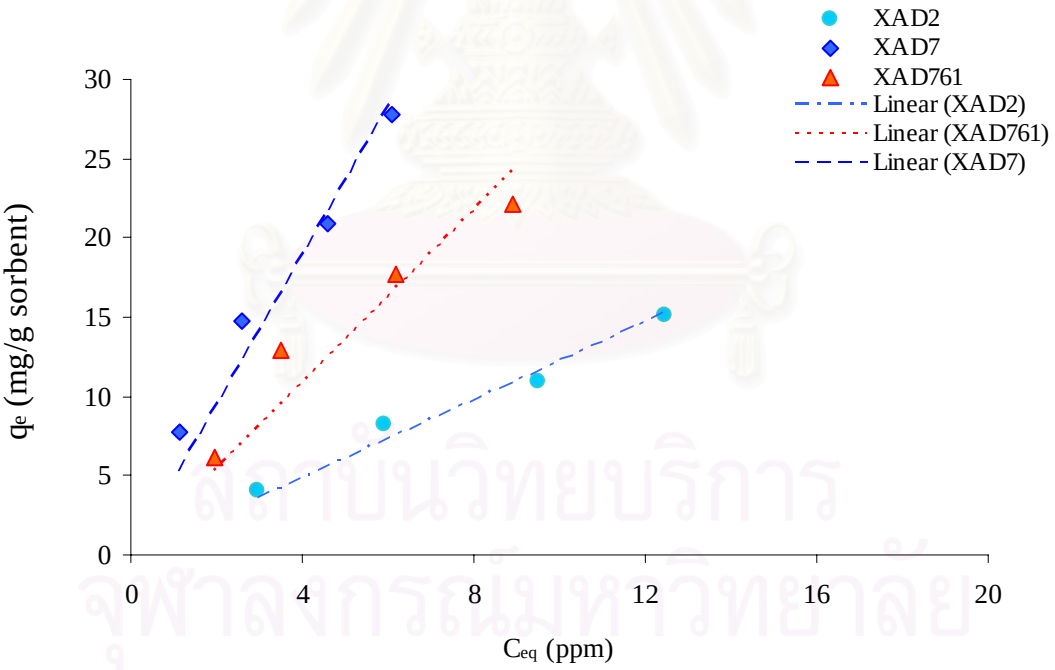


Figure 4.9: The sorption isotherm of nalidixic acid onto polymeric sorbents

Due to the fact that the sorption process is a phenomenon occurred at the surface. So, the surface area is one of the primary properties directly governed the sorption. In order to overcome the effect of unequally of surface area of these polymeric resins, the sorption capacity was interpreted on the area basis by harmonizing the sorption capacity in term of mg adsorbed per square meter of the adsorbent as shown in Figure 4.10 and 4.11 for acetaminophen and nalidixic acid, respectively. The results show that the XAD761, which is a strong polar resin, has highest sorption capacity for both pharmaceuticals, followed by the moderately polar XAD7 resin, and the slightly polar XAD2 resin, respectively.

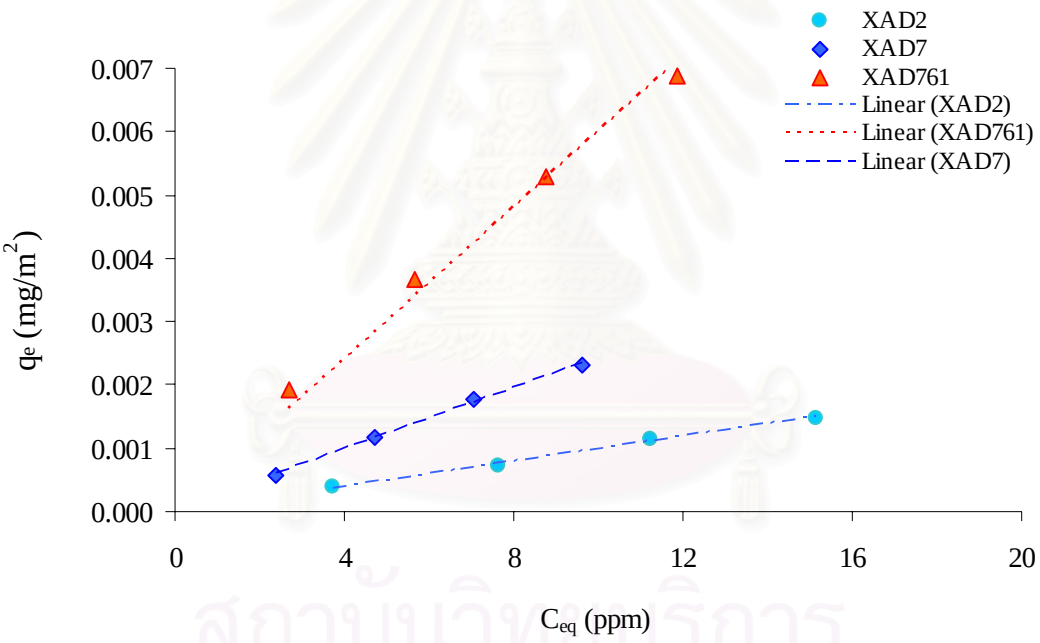


Figure 4.10: The sorption isotherm normalized by surface area of acetaminophen onto polymeric sorbents

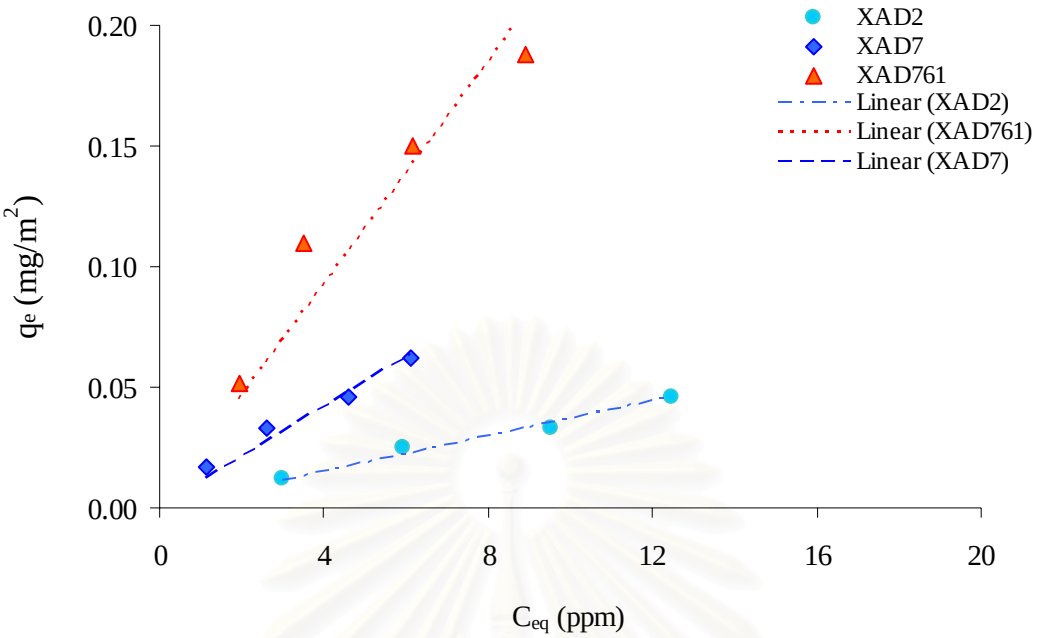


Figure 4.11: The sorption isotherm normalized by surface area of nalidixic acid onto polymeric sorbents

The results were attributed to the chemical structure of these polar resins. Among these three adsorbents, the functional group of XAD761 is the phenol formaldehyde showing the strongest polarity while XAD7 has moderate polarity due to its acrylic ester property and XAD2 has the slightest polarity regarding its polyaromatic matrix. Since acetaminophen and nalidixic acid are amphiphile molecules, they contain both polar and nonpolar moieties within the molecule. The polar or hydrophilic part results in the water solubility properties which are 12743 mg L^{-1} for acetaminophen and 100 mg L^{-1} for nalidixic acid. Therefore, these pharmaceuticals tend to strongly sorb onto XAD761, which provides the strongest polar adsorption sites. Thus, it was comprehensible that regardless to the surface area, the acetaminophen and nalidixic acid more readily adsorb onto the XAD761.

In the sorption of pharmaceuticals onto the polymeric resins, the interaction between polar moieties of adsorbate and adsorbent is dominance (Myers, 1999). In this study, the sorption of both acetaminophen and nalidixic acid onto the polar resins occurs in such a way that their hydrophilic parts are motivated by the adsorbent to adsorb onto its polar surface and the hydrophobic parts of the molecules orient away. It can be summarized that the occurred interaction caused by the affinity between polar moieties of pharmaceutical compounds and adsorbents plays a major role in the sorption of pharmaceuticals onto polymeric resins.

4.3.2 Sorption Capacity of Activated Carbon for Acetaminophen and Nalidixic Acid

Figure 4.12 and 4.13 illustrated the sorption capacity of activated carbon for acetaminophen and nalidixic acid, respectively.

Figure 4.12: The sorption isotherm of acetaminophen onto activated carbon

The surface of activated carbon is considered as nonpolar. Then the sorption of both acetaminophen and nalidixic acid occurs due to the hydrophobic interaction. The hydrophobic part of the pharmaceuticals tends to partition with the nonpolar surface of activated carbon with the hydrophilic group directed toward the aqueous phase. Although the water solubility of these pharmaceuticals is considerably high especially for acetaminophen indicating that the dissolving of these compounds into aqueous solution is of favor, the sorption process is remarkably substantial as the hydrophobic interaction is truly strong, resulting in a favorable accumulation or partitioning of the hydrophobic part of both pharmaceuticals onto the nonpolar surface of activated carbon.

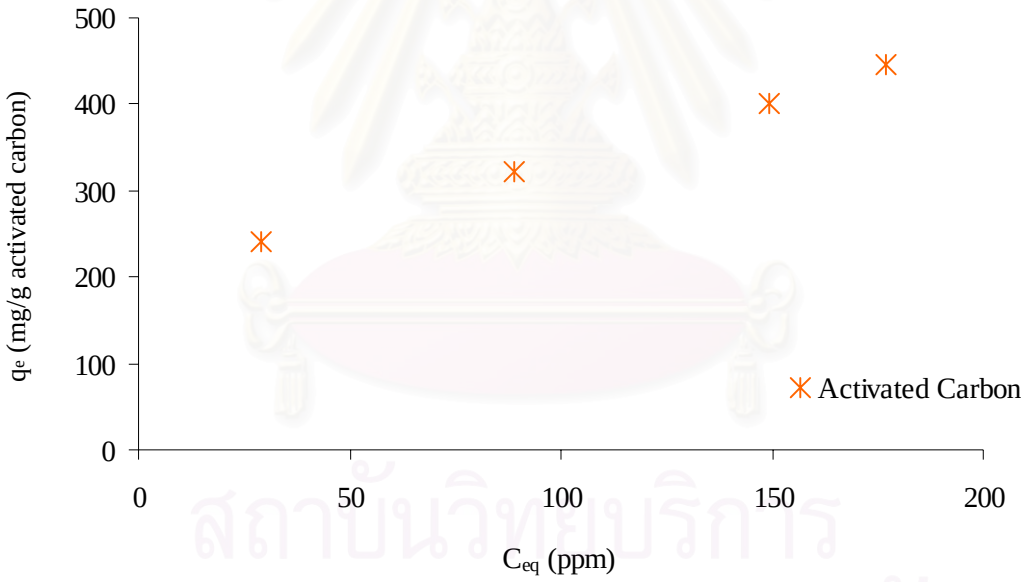


Figure 4.13: The sorption isotherm of nalidixic acid onto activated carbon

It was expected that the activated carbon would provide the highest sorption capacity among all sorbents since it has the highest surface area of 600 $m^2 g^{-1}$. This assumption was confirmed by the q_e value as it is higher in sorption of both acetaminophen and nalidixic acid onto activated carbon than that of onto polymeric resins as shown in Figure 4.14 and 4.15. It is also in agreement with the research

study by Otero et al. (2004) who concluded that the activated charcoal has higher capacity than the polymeric resins in sorption of salicylic acid.

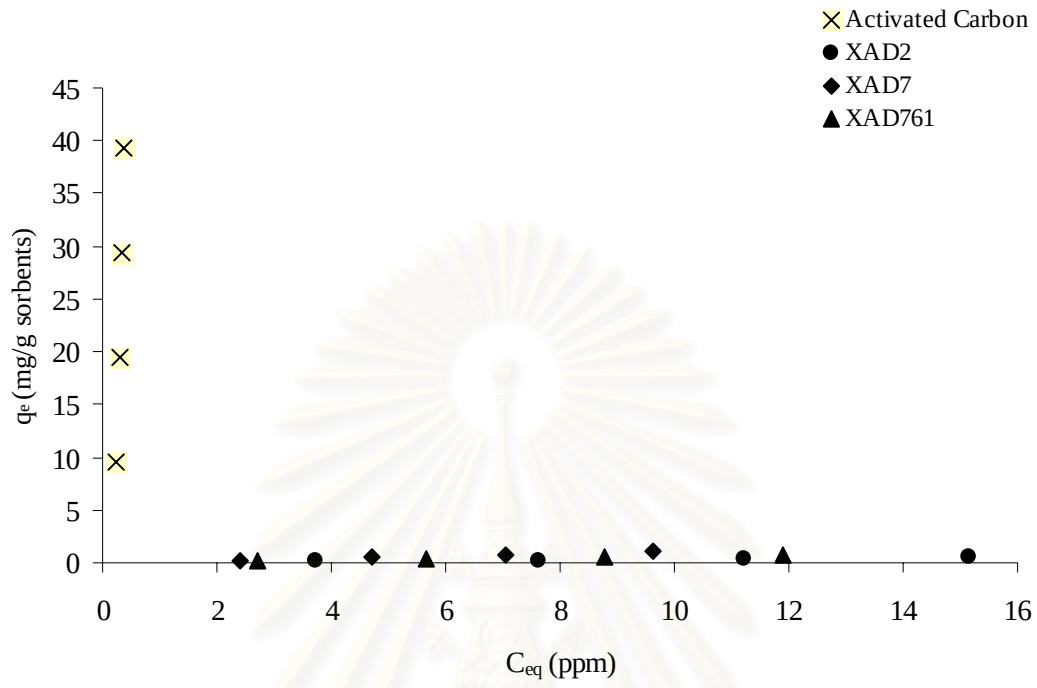


Figure 4.14: The sorption isotherm of acetaminophen onto several adsorbents

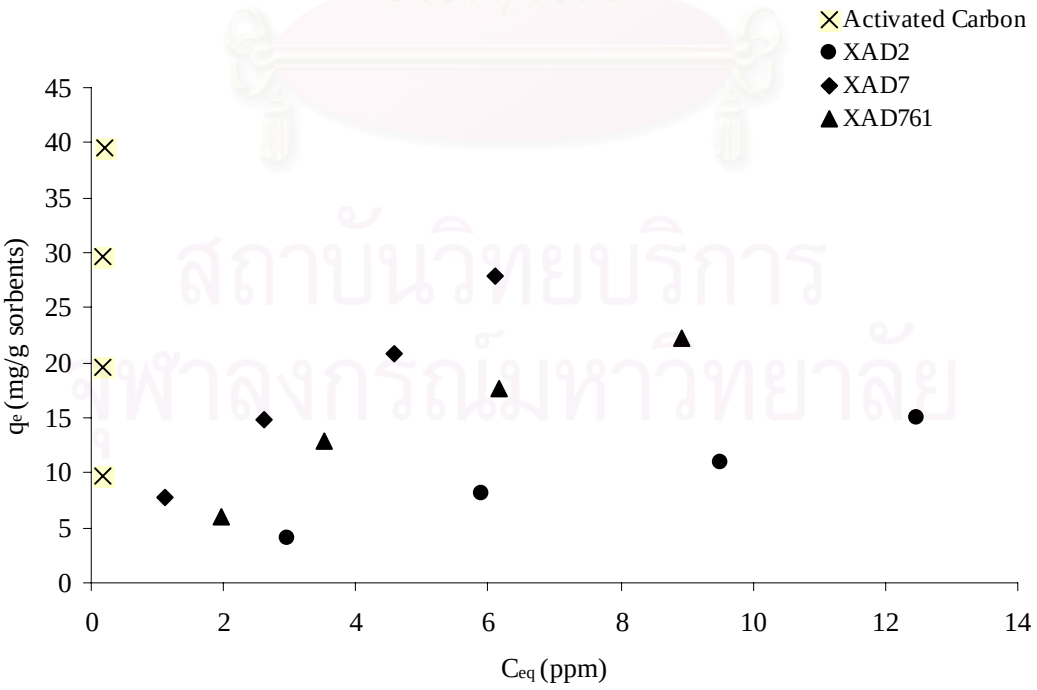


Figure 4.15: The sorption isotherm of nalidixic acid onto several adsorbents

4.3.3 Comparison on Sorption Ability of Acetaminophen and Nalidixic Acid onto Polymeric Resins and Activated Carbon.

Figure 4.16 and 4.17 showed that the nalidixic acid can adsorb onto all polymeric sorbents (XAD2, XAD7, and XAD761) and activated carbon greater than the acetaminophen as indicated by the higher sorption capacity. The results can be explained by the pharmaceuticals properties, i.e. water solubility and octanol-water partition coefficient (K_{ow}).

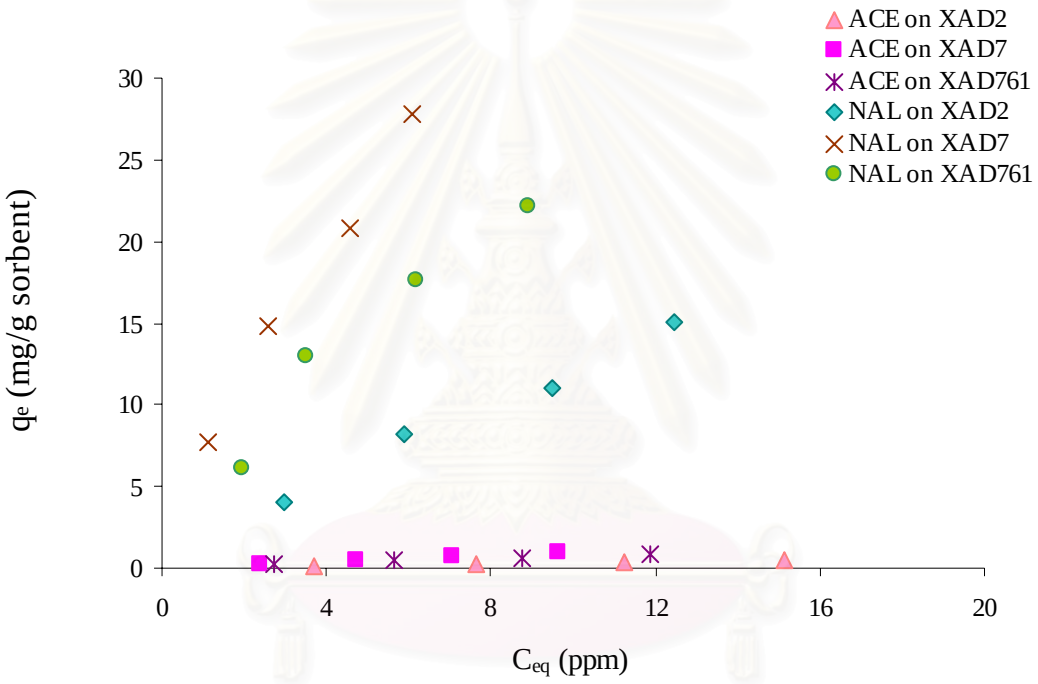


Figure 4.16: The sorption isotherm of acetaminophen and nalidixic acid onto various polymeric sorbents

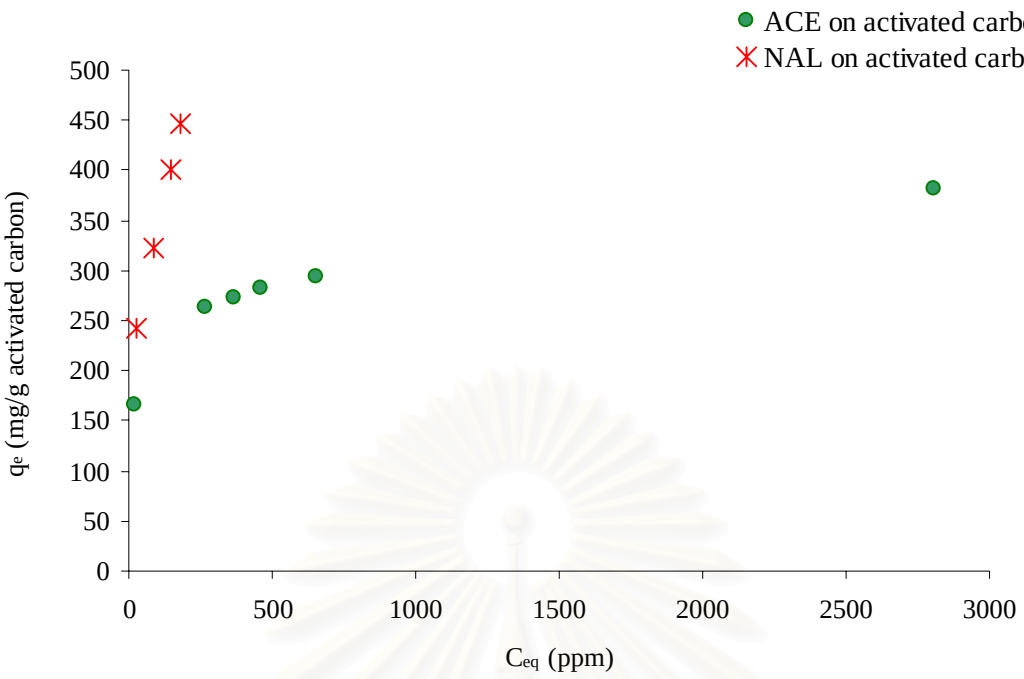


Figure 4.17: The sorption isotherm of acetaminophen and nalidixic acid onto activated carbon

The water solubility of solute is defined as the maximum amount of a solute that can be dissolved in water at a specified temperature (http://ewr.cee.vt.edu/environmental/teach/gwprimer/sorp/sorp.html). The water solubility of compound tends to be inversely proportional to the amount sorbed into organic adsorbents. The water solubility of acetaminophen is 12743 mg L^{-1} where that of nalidixic acid is only 100 mg L^{-1}. Moreover, the acetaminophen has low K_{ow} value of 2.88 while the K_{ow} value of nalidixic acid is very high at 38.90. The K_{ow} or octanol-water partition coefficient is simply a measure of the degree of hydrophobicity (water repulsing) of an organic compound. The more hydrophobic of a compound, the less soluble it is in the water, thus the more likely it adsorbs onto soil particles (Bedient et al., 1984).

The polarity of an organic compound plays a major role in its mobility in the subsurface. Polar organic substances tend to dissolve more readily in water than nonpolar substances. Then, it tends to transport with groundwater rather than adsorbs

onto soil particles. In this study, the acetaminophen has higher polarity as compared to nalidixic acid as it has higher water solubility and has relatively low K_{ow} value. Therefore, acetaminophen is more willingly to dissolve in water than sorb onto organic adsorbents. As a result, the nalidixic acid shows greater sorption ability compared with acetaminophen.

4.3.4 Sorption Isotherm

In the sorption study, the amount of adsorbate sorbed onto a unit mass or unit area of adsorbent at a constant temperature was determined and the data were generally interpreted in term of adsorption isotherm. The isotherm is a mathematical expression that relates the concentration of adsorbate at the solid surface (q_e) to its equilibrium concentration in the liquid phase (C_{eq}). In this research, three most common isotherms were considered including a linear isotherm and the nonlinear isotherms namely Langmuir and Freundlich isotherms.

4.3.4.1 Linear Sorption Isotherm

Linear isotherm is the simplest expression of equilibrium sorption. A plot between q_e and C_{eq} in this expression will result in a straight line with a slope of K_d. The linear isotherm is appropriate for sorption relationships in which the energetic of sorption is uniform with increasing concentration and the loading of the sorbent is low (Weber Jr. et al., 1991). It is commonly occurred at very low solute concentration and for solid of low sorption potential, which are similar to the actual environment scenario.

In this experiment, the sorption of acetaminophen and nalidixic acid at low concentrations (5-15 ppm) onto various adsorbents show the linear sorption isotherm as expected.

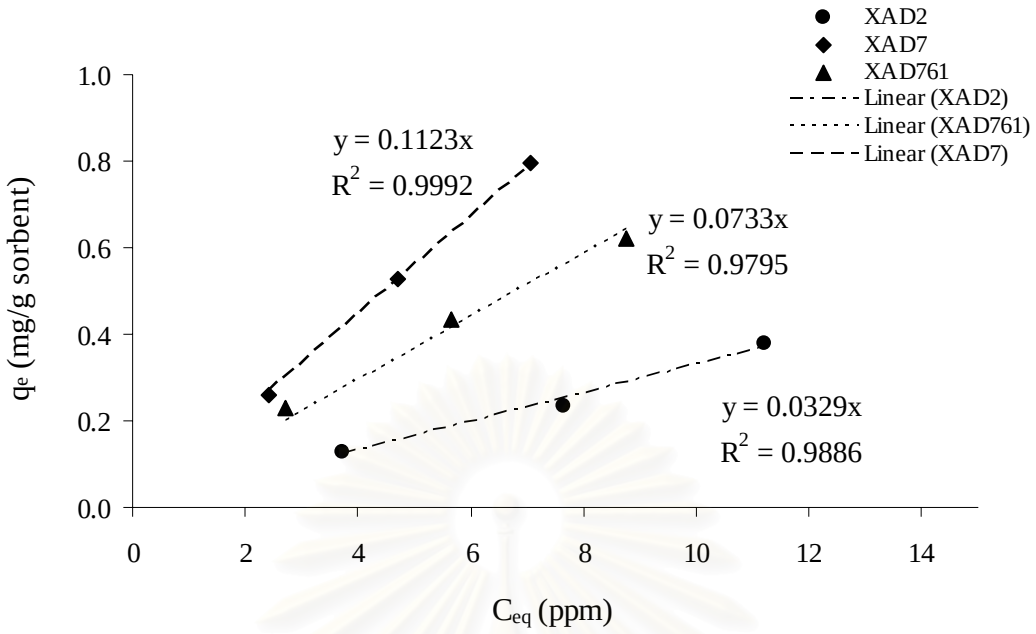


Figure 4.18: The linear sorption isotherm of acetaminophen onto polymeric sorbents

Figure 4.18 demonstrates the linear sorption isotherm of acetaminophen onto polymeric resins Amberlite XAD2, XAD7, and XAD761. In linear sorption isotherm, the slope of the plot, K_d is considered as the distribution or sorption coefficient. It can be seen from Table 4.2 that the XAD7 shows the highest sorption capacity according to the K_d value on the mass basis. Interestingly, the XAD761 shows the highest sorption capacity if the K_d value is normalized upon the specific surface area basis, followed by XAD 7 and XAD2, respectively, which is in agreement to the discussion previously mentioned.

Table 4.2: Summary of linear sorption coefficients and the normalized sorption coefficients by specific surface area of acetaminophen onto polymeric sorbents

Polymeric Resins	**Linear Isotherm**		
	K_d (L/g)	**K_d/SSA (L/m^2)**	**R^2**
XAD2	0.0329	9.97E-5	0.9886
XAD7	0.1123	2.50E-4	0.9992
XAD761	0.0733	6.21E-4	0.9795

The linear sorption isotherms of nalidixic acid are presented in Figure 4.19. The results are similar to that of the acetaminophen sorption where based on the mass, the distribution coefficient or K_d value of the XAD7 is highest among three resins. However, if the results are normalized upon the area basis, the XAD761 shows the greatest sorption capacity due to its highest polarity thus most influencing the sorption of nalidixic acid onto its surface.

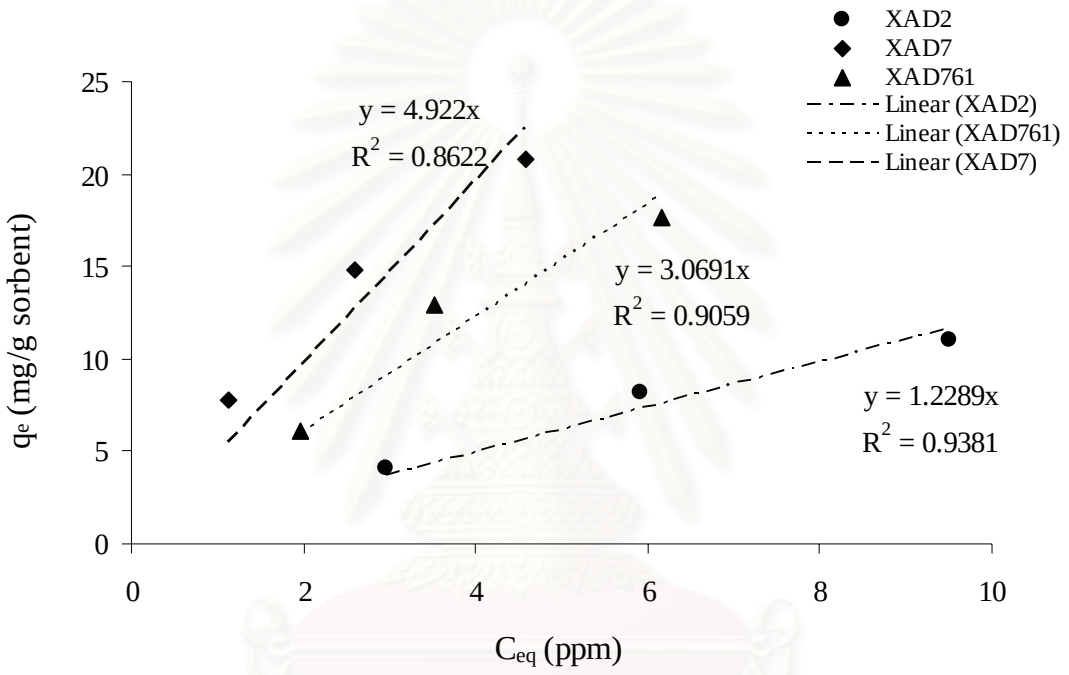


Figure 4.19: The linear sorption isotherm of nalidixic acid onto polymeric sorbents

Table 4.3: Summary of linear sorption coefficients and the normalized sorption coefficients by specific surface area of nalidixic acid onto polymeric sorbents

Polymeric Resins	Linear Isotherm		
	K_d (L/g)	K_d/SSA (L/m^2)	R^2
XAD2	1.2289	0.0037	0.9381
XAD7	4.9220	0.0109	0.8622
XAD761	3.0691	0.0260	0.9059

In addition, the sorption of acetaminophen and nalidixic acid onto activated carbon do not fit with linear adsorption isotherm since the initial concentrations in the sorption study are quite high (200-800 ppm) although the amount of adsorbent used is very little (0.02 g) due to the fact that the activated carbon has very high adsorption capacity.

4.3.4.2 Nonlinear Sorption Isotherm

As the linear sorption isotherms were experimentally determined for sorption at low concentrations where most of the adsorption sites were far from being occupied, the nonlinear sorption isotherms were introduced to reflect those situations in which the concentration of adsorbates (pharmaceuticals) are high as probably corresponded to the situation when there is an improper dump of expired or unused pharmaceutical into the sanitary or municipal waste receiver facilities. The nonlinear sorption isotherms of Langmuir and Freundlich were used to explain this case where the binding sites become filled and remaining sites are less attractive to the adsorbate molecules.

The higher concentrations of pharmaceuticals at 20 ppm and 50 ppm were investigated to observe the nonlinear isotherm of acetaminophen and nalidixic acid onto the polymeric adsorbents and the activated carbon. Table 4.4 shows the results of isotherm parameters for sorption of acetaminophen and nalidixic acid onto the polymeric resins, Amberlite XAD2, XAD7 and XAD 761. It can be summarized that the sorption of both acetaminophen and nalidixic acid are well fitted with the Langmuir adsorption isotherm according to the greater of the linear regression coefficient (R^2 value).

Table 4.4: The Linear, Langmuir and Freundlich isotherm parameters and correlation coefficients (R^2) of sorption of acetaminophen and nalidixic acid onto polymeric sorbents

Pharmaceuticals	Polymeric Resins	Linear isotherm		Langmuir isotherm			Freundlich isotherm		
		K_d (L/g)	R^2	K_L (L/mg)	R^2	Q (mg/g)	K_{fr} (mg/g sorbents) $(L/g)^N$	R^2	N
Acetaminophen	XAD2	0.017	0.1128	0.02472	0.9825	1.5399	0.06736	0.8788	0.6339
	XAD7	0.078	0.8945	0.00657	0.9960	16.9779	0.14243	0.9788	0.8290
	XAD761	0.0569	0.9539	0.02587	0.9990	3.4587	0.10375	0.9987	0.8184
Nalidixic Acid	XAD2	1.2185	0.9764	0.01801	0.9954	80.6452	1.5867	0.9907	0.8857
	XAD7	1.5668	-0.1713	0.16000	0.9972	51.0204	8.9475	0.9109	0.4923
	XAD761	1.8875	0.8648	0.02766	0.9774	123.4568	4.3501	0.9731	0.7399

The plot of 1/ q_e versus 1/C_{eq} yields a straight line for the Langmuir isotherm of acetaminophen and nalidixic acid as shown in Figure 4.20-4.21, respectively. The Langmuir adsorption isotherm indicates that the pharmaceuticals adsorb on the surface at one molecule coverage only or known as “monolayer” and thus the polymeric resins provide a limited area for sorption.

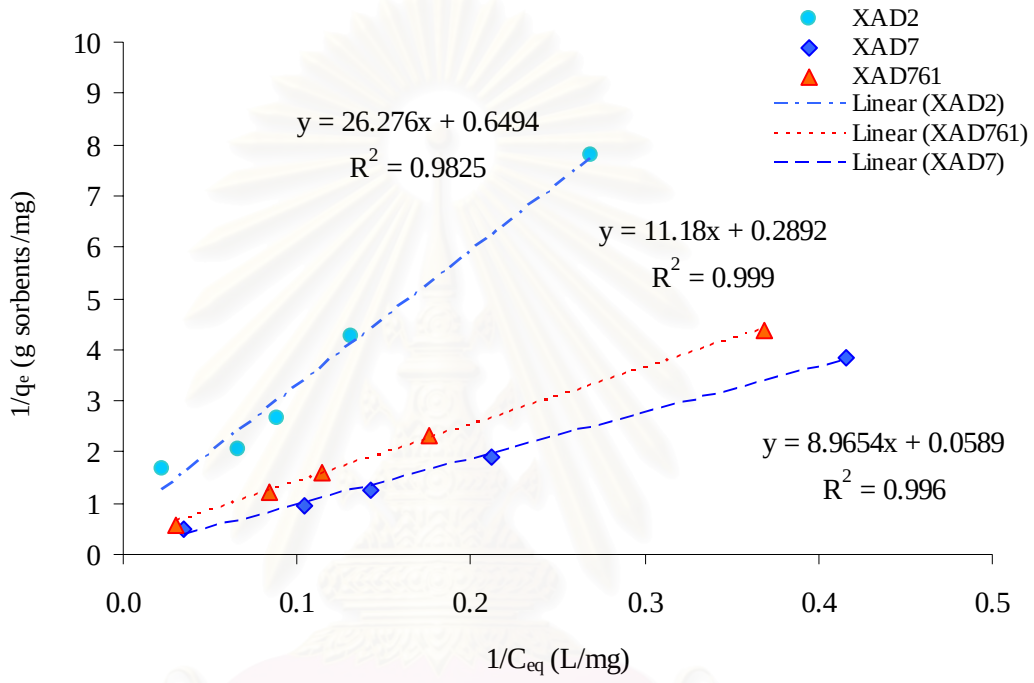


Figure 4.20: The Langmuir sorption isotherm of acetaminophen onto polymeric sorbents

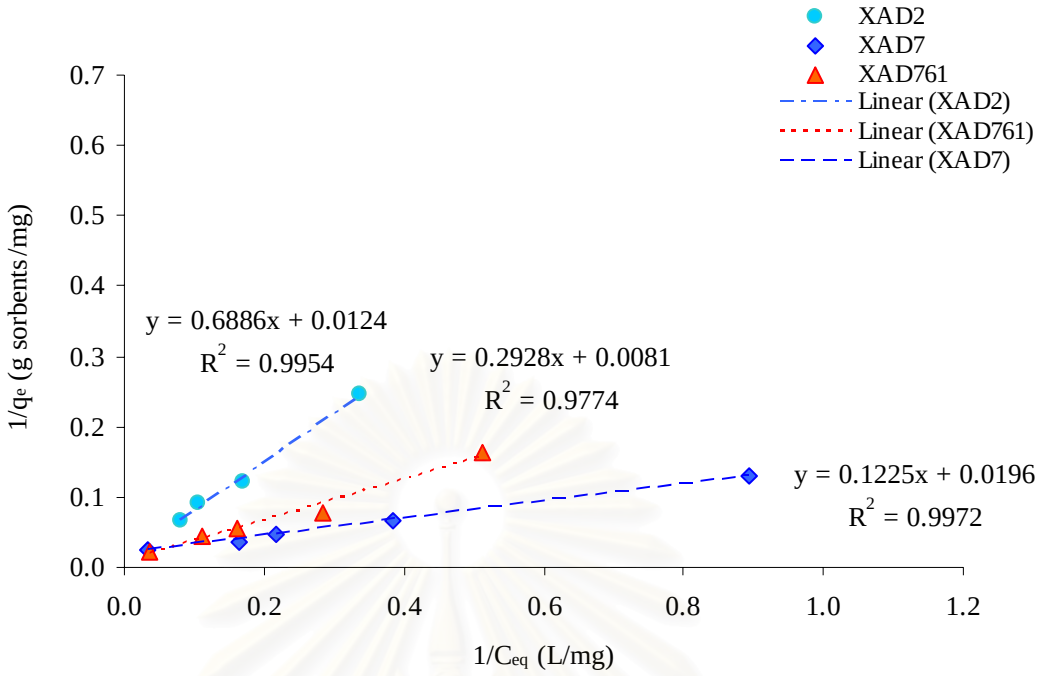


Figure 4.21: The Langmuir sorption isotherm of nalidixic acid onto polymeric sorbents

Table 4.5: The Langmuir isotherm constants, sorption coefficients, and normalized sorption coefficients by specific surface area of sorption of acetaminophen and nalidixic acid onto polymeric sorbents

Pharmaceuticals	Polymeric Resins	Langmuir isotherm		Sorption coefficient	
		K_L (L/mg)	Q (mg/g)	K_d (L/g)	K_d/SSA (L/m^2)
Acetaminophen	XAD2	0.02472	1.5399	0.03807	1.15E-04
	XAD7	0.00657	16.9779	0.11154	2.48E-04
	XAD761	0.02587	3.4587	0.08945	7.58E-04
Nalidixic Acid	XAD2	0.01801	80.6452	1.45222	0.0044
	XAD7	0.16000	51.0204	8.16327	0.0181
	XAD761	0.02766	123.4568	3.41530	0.0289

The sorption coefficient (K_d) can be calculated by two parameters namely the Langmuir isotherm constants (K_L), which is defined as the equilibrium constant of the sorption process; and the amount of solute adsorbed per unit weight of adsorbent required for monolayer capacity (Q). In general, the Q-value represents the maximum achievable surface concentration of specific pharmaceuticals onto particular resins. From the results we found that the Q-value varies according to type of pharmaceuticals and resins as shown in Table 4.5. However, it should be pointed out that the Q-values obtained from the nalidixic acid adsorption onto polymeric resin are obviously greater than those of acetaminophen adsorption because the nalidixic acid can greater adsorb onto the resins.

The calculated sorption coefficient K_d and normalized K_d/SSA value were indicates in Table 4.5. The results show that the normalized K_d are higher in nalidixic acid compared with acetaminophen. Also, XAD761 possesses the highest sorption capacity throughout these three resins for both pharmaceuticals. These results are well corresponded to discussion previously mentioned.

It could be seen from Table 4.6 that both sorption of acetaminophen and nalidixic acid onto activated carbon are well fitted with the Freundlich isotherm due to the heterogeneous nature of activated carbon. The results also revealed that the activated carbon provides enormous adsorption sites as compared to polymeric resins. Nonetheless, nalidixic acid also shows greater sorption capability than acetaminophen.

Table 4.6: The Linear, Langmuir and Freundlich isotherm parameters and correlation coefficients (R^2) of sorption of acetaminophen and nalidixic acid onto activated carbon

	Linear isotherm		Langmuir isotherm			Freundlich isotherm		
Pharmaceuticals	K_d (L/g)	R^2	K_L (L/mg)	R^2	Q (mg/g)	K_{fr} (mg/g activated carbon) $(L/g)^N$	R^2	N
Acetaminophen	0.179	-7.5635	0.07082	0.8984	303.030	105.4144	0.9982	0.1609
Nalidixic Acid	2.8005	-0.3937	0.03500	0.9305	476.191	78.5778	0.9737	0.3273

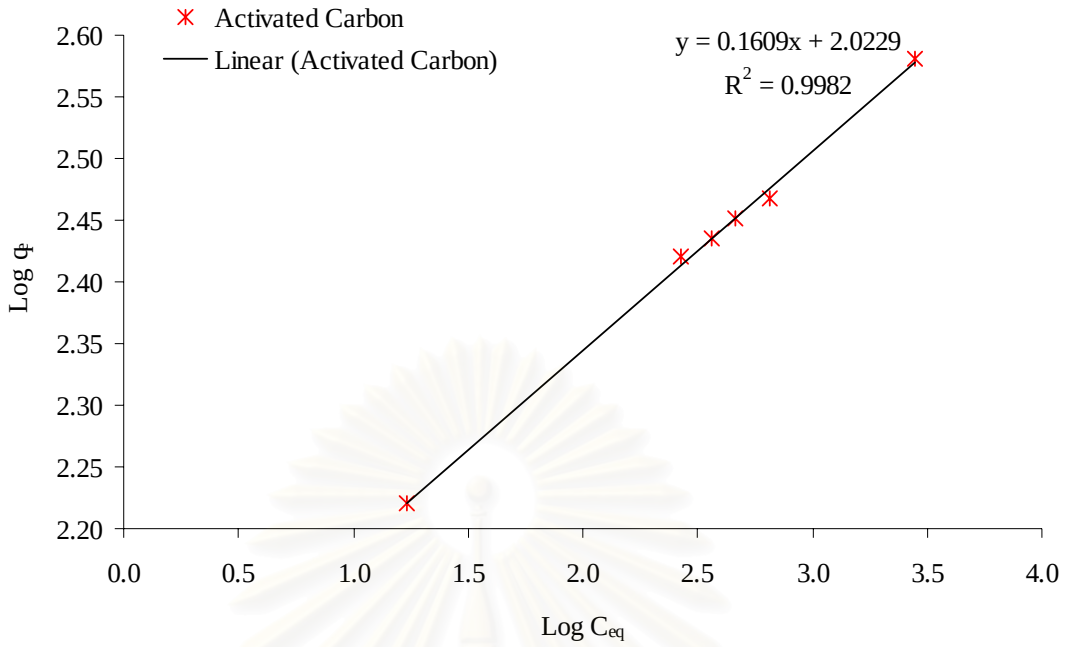


Figure 4.22: The Freundlich sorption isotherm of acetaminophen onto activated carbon

Figure 4.22 and Figure 4.23 showed the Freundlich sorption isotherm of acetaminophen and nalidixic acid onto activated carbon, respectively. The Freundlich isotherm assumes that there are multiple types of sorption sites acting in parallel, with each site type exhibiting a different sorption free energy and total site abundance (Schwarzenbach et al., 2003).

In this isotherm, N is the Freundlich exponent, which is an index of the diversity of free energies associated with the sorption of solute by multiple components of a heterogeneous adsorbent. In these cases, N<1, therefore the isotherms are concave downward and can be inferred that added adsorbates are bound with weaker and weaker free energies (Schwarzenbach et al., 2003).

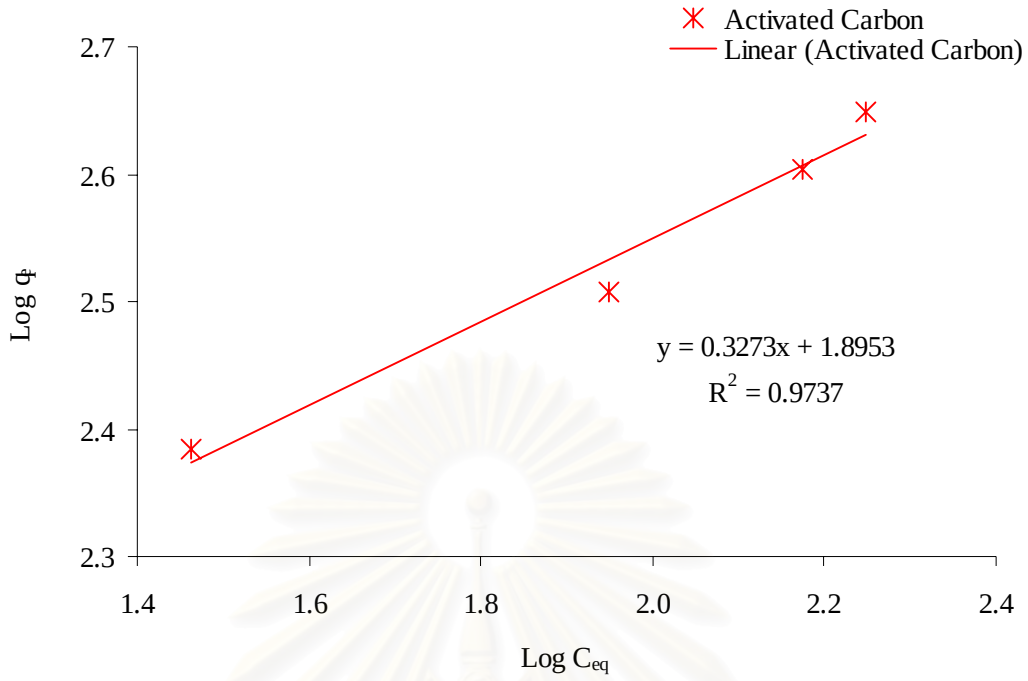


Figure 4.23: The Freundlich sorption isotherm of nalidixic acid onto activated carbon

It should be noted that there is a significant amount of methanol in the solution of nalidixic acid using in the study of sorption onto activated carbon since the studied concentration was very high. Therefore, the additional set of experiment was conducted to observe the effects of methanol in nalidixic acid solution by preparing two nalidixic acid solutions at the same concentration of 50 ppm. Although the studied nalidixic concentration was in the range of 150-400 ppm, these concentrations cannot be solely prepared by water since it exceeds the water solubility limit of nalidixic acid. One was prepared in water, whereas the other was made up by diluting with water from the stock solution of 1000 ppm of nalidixic acid prepared by methanol. Therefore, the latter solution was comprised of water and methanol. Figure 4.24 shows the differences in q_e value of sample diluted with different solvents. It was indicated that there is a negligible effect of the solvents on the sorption. Due to the fact that methanol is highly polar compound owing to its hydroxyl functional group and short alkyl chain; there is no interaction of methanol onto the surface of

activated carbon which is considerable as nonpolar surface. Thus, the competition between methanol and nalidixic acid is absent yielding no difference of sorption ability of nalidixic acid onto activated carbon.

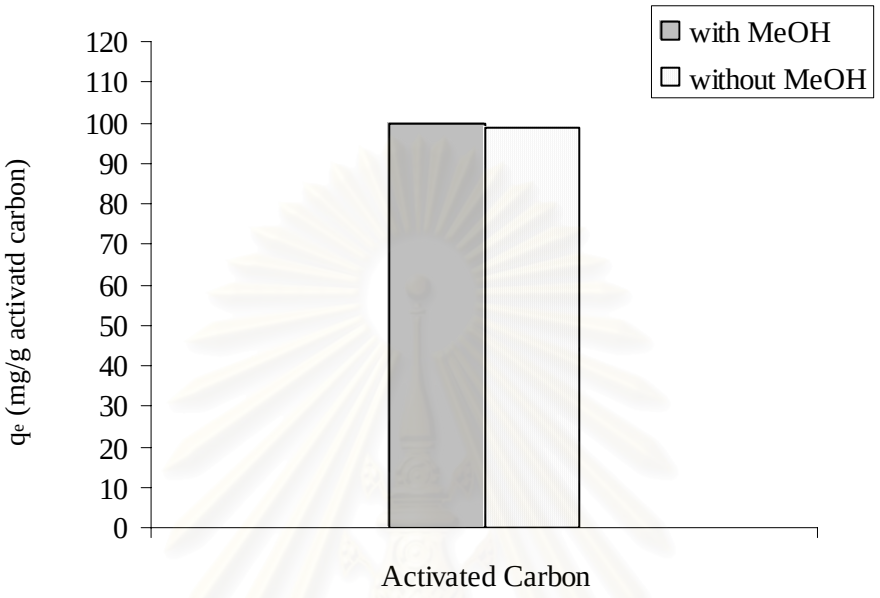


Figure 4.24: The effects of methanol in sorption of nalidixic acid onto activated carbon

4.4 Effect of pH on Acetaminophen Sorption

Sorption of acetaminophen onto all sorbents (Amberlite XAD2, XAD7, XAD761, and activated carbon) was conducted to investigate the influence of pH. As previously mentioned, there was no pH adjustment for acetaminophen but pH was adjusted to 5 for nalidixic acid. In order to represent on the same basis for both pharmaceuticals, the pH of acetaminophen was adjusted to 5. The sorption at pH 5 was compared with the sorption obtained at neutral pH (≈7) from the previous section.

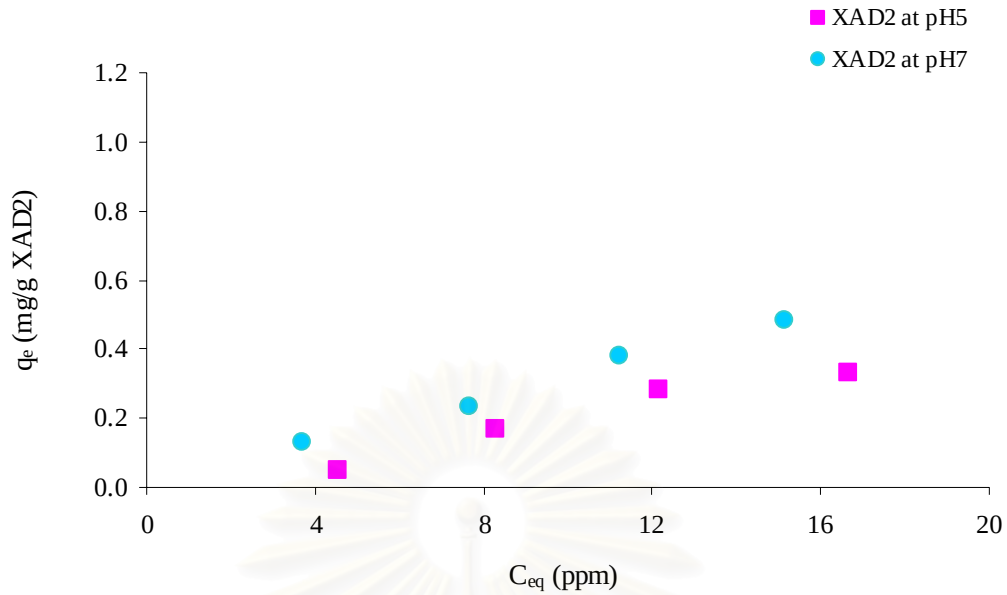


Figure 4.25: The sorption of acetaminophen onto Amberlite XAD2 at different pH

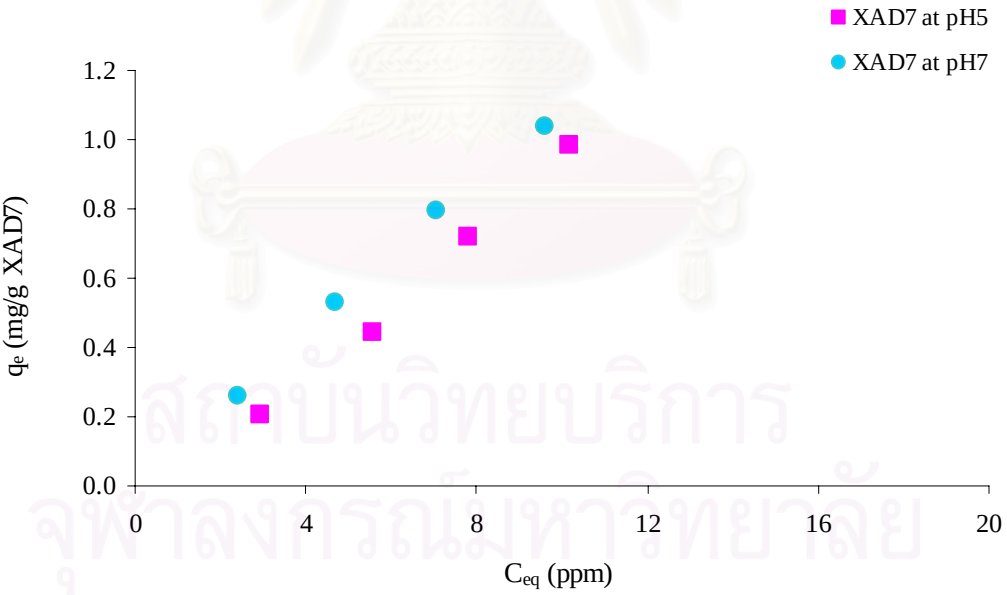


Figure 4.26: The sorption of acetaminophen onto Amberlite XAD7 at different pH

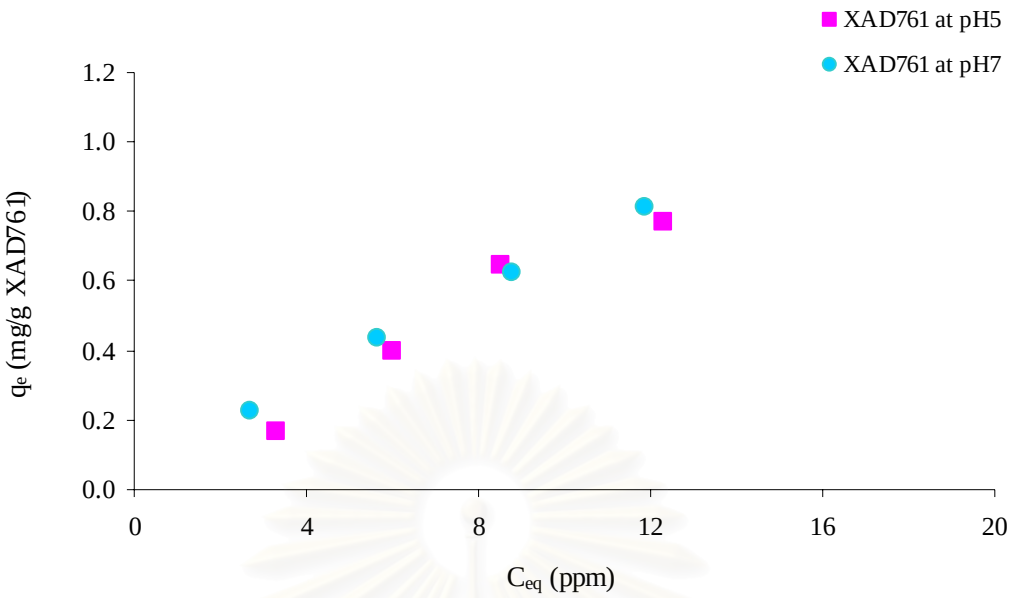


Figure 4.27: The sorption of acetaminophen onto Amberlite XAD761 at different pH

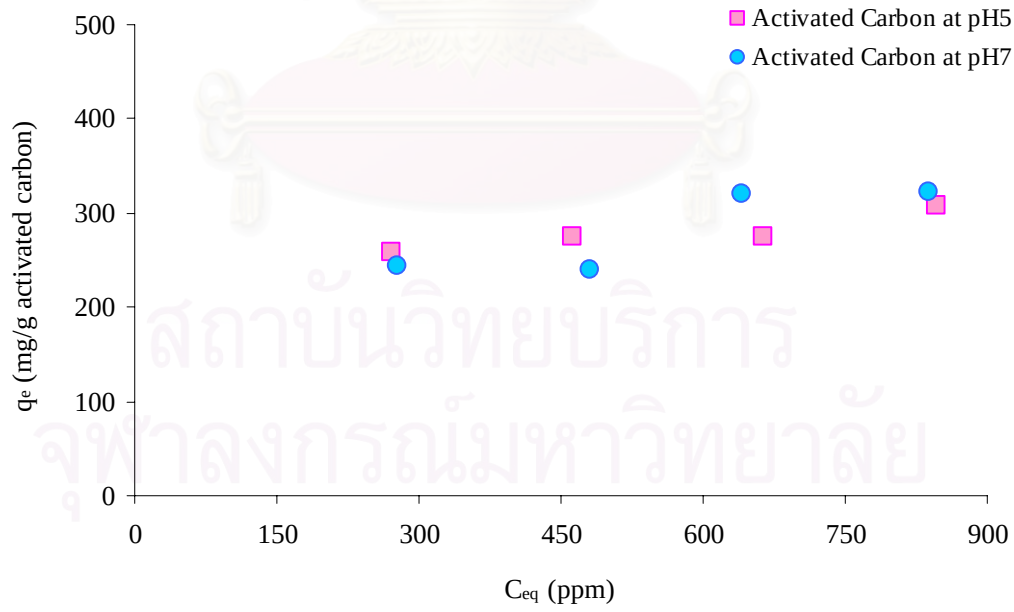


Figure 4.28: The sorption of acetaminophen onto activated carbon at different pH

Figure 4.25-4.28 shows no significant difference in sorption of acetaminophen onto all adsorbents studied here owing to the fact that pH at either 5 or 7 is lower than the pK_a of acetaminophen (pKa≈9.71), the molecule dissociation is theoretically absent and thus, the compound is in a neutral form. The ionized species in the solution mainly caused by the pH adjustment have nothing to do with these organic surfaces both polymeric resins and activated carbon since none of them contains surface charged. It could be concluded that an altering of pH in the solution of acetaminophen from 7 to 5 has negligible effect to the sorption onto the organic adsorbents.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The nonionic polymeric adsorbents: Amberlite XAD2, XAD7, and XAD761 and powdered activated carbon were used to represent the polar and nonpolar adsorbents, respectively. The pharmaceuticals studied were acetaminophen and nalidixic acid. The equilibrium sorption kinetic for acetaminophen and nalidixic acid with all adsorbents demonstrated that the adsorption process reaches the equilibrium within 24 hours. Both acetaminophen and nalidixic acid can adsorb onto all adsorbents with difference potential. Nalidixic acid shows higher sorption capability than acetaminophen onto both polymeric resins and activated carbon because nalidixic acid has lower water solubility and higher K_{ow} as compared to acetaminophen, therefore it tends to sorb onto the surface of adsorbents rather than dissolve in the bulk aqueous solution. The sorption of acetaminophen and nalidixic acid onto polymeric resins: Amberlite XAD2, XAD7, and XAD761 are well fitted with the Langmuir sorption isotherm. The specific surface area normalized sorption coefficients (K_d/SSA) are 1.15E-04, 2.48E-04, and 7.58E-04 L/m^2 for sorption of acetaminophen onto XAD2, XAD7, and XAD761, respectively. The sorption of nalidixic acid onto XAD2, XAD7, and XAD761 provides the normalized sorption coefficient or K_d/SSA of 0.0044, 0.0181, and 0.0289 L/m^2, respectively. For sorption of acetaminophen and nalidixic acid onto activated carbon, both sorptions follow the Freundlich isotherm with the equation of $q = 105.4144 \text{ (mg/g activated carbon) } (L/g)^N \times C_e^{0.1609}$ for acetaminophen and $q = 78.5778 \text{ (mg/g activated carbon) } (L/g)^N \times C_e^{0.3273}$ for nalidixic acid.

The interpretation from the adsorption studies could be concluded that the interaction caused by the affinity between polar moieties of pharmaceutical compounds and adsorbents plays an important role in the sorption of pharmaceuticals onto polymeric resins. On the other hand, the hydrophobic interaction governs the sorption of pharmaceuticals onto activated carbon as the hydrophobic part or nonpolar moiety of both acetaminophen and nalidixic acid partition onto the nonpolar surface of activated carbon. Furthermore, the degree of polarity of polymeric resins affects the sorption of pharmaceuticals onto its surfaces. In addition, the surface area is another main parameter affecting the amount of material adsorbed onto the surface. The sorption processes are induced according to the attraction or affinity between the adsorbents (Amberlite XAD2, XAD7, and XAD761, and activated carbon) and the adsorbates (pharmaceuticals).

In summary, the results thus imply that the pharmaceuticals can truly adsorb onto both polar and nonpolar surfaces due to their amphiphilic characteristic and the sorption behavior strongly depends on the molecular structure of pharmaceuticals and the surface properties of adsorbents. The pharmaceuticals with high water solubility tend to dissolve in aqueous phase and are capable of spread and transport with the groundwater whereas the pharmaceuticals with lower solubility tend to adsorb onto the organic materials and get retarded into the subsurface. The higher the sorption, the greater retardation is obtained with less mobility. In the aspects of application in wastewater treatment, activated carbon provides better sorption capacity than the polymeric resins. However, the choice of operation depends on the required lifetime of adsorbents as polymeric resins have longer life-span compared with activated carbon but the price is comparable. In the subsurface contamination scenario, an aquifer is composed of various components with inconsistent degree of polarity and

the amount of organic content, the pharmaceuticals will more or less adsorb onto these materials and hence, the movement can be definitely slow down by the adsorption process.

In conclusion, the transport of pharmaceuticals depends on both contaminant and surface properties. The sorption phenomena can be used to predict the pharmaceuticals migration in the subsurface and can be also used to design the appropriate wastewater treatment system according to the adsorption process. Furthermore, these findings are valuable fundamental knowledge supporting the idea of water reuse by installing an additional adsorption unit containing appropriate type of adsorbents to sorb the pharmaceuticals, thus eliminate the presence of pharmaceuticals in the drinking water.

5.2 Recommendations

The information on the fate and transport of pharmaceuticals and personal care products in Thailand are still lacked and no awareness on their risk to human and animal health is concerned. The study of actual situation in our country is required by monitoring the concentration of presented pharmaceuticals and personal care products in surface water, groundwater, tap water, drinking water, and influence/effluence streams of wastewater treatment facilities. A well planned pharmaceutical monitoring system should be concerned since there is a threat on human health according to the unknown effects on the pharmaceutical contamination in water resources especially at the rural areas in which the people use the water directly from the river or wells as their drinking water. So, the insight information on what pharmaceuticals truly cause the contamination will be gained and thus we can seek of an appropriate technique to remedy this problem later on. Moreover, this research was conducted in laboratory

scale, so the pilot scale experiment should be conducted to simulate the real application since there will be some other limitations not being concerned in laboratory scale such as clean-up cost and its economic aspect, the adsorbent recovery for reuse. Furthermore, it should be noted that this experiment was conducted using methanol as a solvent in preparing stock solution of nalidixic acid. Thus, there should be some concerns in applying water as a solvent when dealing with concentrations lower than the water solubility limit.

REFERENCES

Bedient, P. B., Rodgers A.C., Bouvette T.C., Tomson M. B., and Wang T. H. 1984. Ground-water quality at a creosote waste site. Groundwater 22, 318-329

Carballa, M., Omil, F., Lema, J. M., Llompart, M., Garcia-Jares, C., Rodriquez, I., Gomez, M., and Ternes, T. 2004. Behavior of pharmaceuticals, cosmetics and hormones in a sewage treatment plant. Water Research. 38:2918-2926.

Cheremisinoff, N. P. and Cheremisinoff, P. N. 1993. Carbon Adsorption for Pollution Control. The United States of America: PTR Prentice-Hall, Inc.

Daughton, C. G. and Jones-Lepp, T. 2001. Pharmaceuticals and personal care products in the environment: scientific and regulatory issues. Symposium Series 791, American Chemical Society, Washington D.C.

Dietrich, D. R., Webb, S. F., and Petry, T. 2002. Hot spot pollutants: pharmaceuticals in the environment. Toxicology Letters. 131:1-3

Faust, S. D. and Aly, O. M. 1998. Chemistry of Water Treatment. 2nd ed. The United States of America: Lewis Publisher.

Foye, W. O., Lemke, T. L., and Williams, D. A. 1995. Principles of Medicinal Chemistry. 4th ed. The United States of America: Williams and Wilkins.

Grathwohl, P. 1998. Diffusion in Natural Porous Media: Contaminant Transport, Sorption/Desorption and Dissolution Kinetics. The United States of America: Kluwer Academic Publishers.

Halling-Sorensen, B., Nielsen, S. N., Lanzky, P.F., Lutzhoft, H. C. H. and Jorgensen, S. E. 1998. Occurrence, fate and effects of pharmaceutical substances in the environment—A review. Chemosphere. 36: 357-394

Hansch, C., Sammes, P.G., Taylor, J.B. 1990. Comprehensive Medicinal Chemistry: The Rational Design, Mechanistic Study & Therapeutic Applications of Chemical Compounds. Volume 6, 1st ed. Great Britain: Pergamon Press plc.

Heberer, T. 2002a. Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: a review of recent research data. Toxicology Letters. 131:5-17

Heberer, T. 2002b. Tracking persistent pharmaceutical residues from municipal sewage to drinking water. Journal of Hydrology. 266: 175-189

Intravichit, J. 2003. Sorption of pharmaceutical compounds onto alumina, silica, and porapak**.** Master's Thesis. Inter-Departmental Program in Environmental Management. Graduate School. Chulalongkorn University.

Juang, R. and Shiau, J. 1999. Adsorption isotherms of phenols from water onto macroreticular resins. Journal of Hazardous Materials. B70: 171-183

Knox, R. C., Sabatini, D. A., and Canter, L. W. 1993. Subsurface Transport and Fate Processes. The United States of America: Lewis Publishers.

Kolpin, D. W., Furlong, E. T., Meyer, M. T., Thurman, E. M., Zaugg, S. D., Barber, L.B., and Buxton, H. T. 2002. Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999-2000: A national reconnaissance. Environmental Science and Technology. 36: 1202-1211.

Kummerer, K. 2001. Pharmaceuticals in the Environment: Sources, Fate, Effects and Risks. Germany: Springer-Verlag Berlin Heidelberg.

Lunn, G., Rhodes, S. W., Sansone, E. B., and Schmuff, N. R. 1994. Photolytic Destruction and Polymeric Resin Decontamination of Aqueous Solutions of Pharmaceuticals. Journal of Pharmaceutical Sciences. 83:1289-1293.

Mackay, D. M., Roberts, P.V., and Cherry J. A. 1985. Transport of organic contaminants in groundwater: Distribution and fate of chemicals in sand and gravel aquifers. Environmental Science and Technology. 19:384-392.

Myers, D. 1999. Surfaces, Interfaces, and Colloids: Principles and Applications. 2nd ed. The United States of America: Wiley-VCH.

Otero, M., Grande, C. A., and Rodrigues, A. E. 2004. Adsorption of salicylic acid onto polymeric adsorbents and activated charcoal. Reactive & Functional Polymers. 60:203-213.

Rohm and Haas Company: Product Information. Also available from: http://www.rohmhaas.com/ionexchange/Pharmaceuticals/AmberliteXAD_download.htm

Ruthven, D. M. 1984. Principles of Adsorption and Adsorption Processes. The United States of America: John Wiley & Sons.

Rytting, E., Lentz, K. A., Chen, X., Quian, F., and Venkatesh, S. 2005. Aqueous and cosolvent solubility data for drug-like organic compounds. The AAPS Journal. 7:E78-E105.

Schwarzenbach, R. P., Gschwend, P. M. and Imboden, D. M. 2003. Environmental Organic Chemistry. 2nd ed. The United States of America: John Wiley & Sons.

Sigma-aldrich Company: Product Data Sheet. Also available from: http://www.sigmaaldrich.com/sigma/product%20information%20sheet/xad7pis.pdf

Sontheimer, H. Translation of Reports on Special Problems of Water Technology, 9, Adsorption. 1976. APA-600/9-76-030. US.EPA Cited in Faust, S. D. and Aly, O. M. 1998. Chemistry of Water Treatment. 2nd ed. The United States of America: Lewis Publisher.

Streat, M. and Sweetland, L. A. 1998. Removal of pesticides from water using hypercrosslinked polymer phases: Part 4-Regeneration of spent adsorbents. Cited in Xu, Z., Zhang, Q., and Fang, H. H. P. 2003. Applications of porous resin sorbents in industrial wastewater and resource recovery. Critical Reviews in Environmental Science and Technology. 33(4): 363-389

Stumpf, M., Ternes, T. A., Wilken, R., Rodrigues, S. V., and Baumann, W. 1999. Polar drug residues in sewage and natural waters in the state of Rio de Janeiro, Brazil. The Science of the Total Environment. 225: 135-141.

The Dow Chemical Company. 2001. Dowex Optipore adsorbents: Fluidized bed properties of Dow polymeric adsorbents. Cited in Xu, Z., Zhang, Q., and Fang, H. H. P. 2003. Applications of porous resin sorbents in industrial wastewater and resource recovery. Critical Reviews in Environmental Science and Technology. 33(4): 363-389

Tolls, J. 2001. Sorption of veterinary pharmaceuticals in soils: A review. Environmental Science and Technology. 35: 3397-3406.

Trochimczuk, A. W., Streat, M., and Kolarz, B. N. 2001. Highly polar polymeric sorbents characterization and sorptive properties towards phenol and its derivatives. Reactive and Functional Polymers. 46: 259-271

Weber Jr., W. J., McGinley, P. M. and Katz, L. E. 1991. Sorption phenomena in subsurface systems: concepts, models, and effects on contaminant fate and transport. Water Research. 25:499-528.

Xu, Z., Zhang, Q., and Fang, H. H. P. 2003. Applications of porous resin sorbents in industrial wastewater and resource recovery. Critical Reviews in Environmental Science and Technology. 33(4): 363-389.

APPENDICES

APPENDIX A

Table A-1: Sorption Kinetic Data for Acetaminophen onto Amberlite XAD2

Initial Concentration: 10 ppm; Initial Sorbents Mass: 0.1 g

Time (h)	Absorbance			C_{eq} (mg/L)			Avg.	Stdev	%RSD	q_e (mg/g XAD2)			Avg.
	no.1	no.2	no.3	no. 1	no. 2	no. 3				no. 1	no. 2	no. 3	
6	0.538	0.536	0.536	9.56	9.52	9.52	9.53	0.02	0.22	0.09	0.10	0.10	0.09
12	0.578	0.575	0.569	9.46	9.41	9.31	9.39	0.08	0.80	0.11	0.12	0.14	0.12
24	0.584	0.579	0.584	9.56	9.48	9.56	9.53	0.05	0.50	0.09	0.10	0.09	0.09
36	0.57	0.565	0.576	9.33	9.25	9.43	9.33	0.09	0.97	0.13	0.15	0.11	0.13
48	0.556	0.558	0.558	9.03	9.06	9.06	9.05	0.02	0.21	0.19	0.19	0.19	0.19

Table A-2: Sorption Kinetic Data for Acetaminophen onto Amberlite XAD7

Initial Concentration: 10 ppm; Initial Sorbents Mass: 0.1 g

Time (h)	Absorbance			C_{eq} (mg/L)			Avg.	Stdev	%RSD	q_e (mg/g XAD7)			Avg.
	no.1	no.2	no.3	no. 1	no. 2	no. 3				no. 1	no. 2	no. 3	
6	0.389	0.386	0.386	6.91	6.86	6.86	6.87	0.03	0.45	0.62	0.63	0.63	0.63
12	0.408	0.402	0.381	7.25	7.14	6.77	7.05	0.25	3.57	0.55	0.57	0.65	0.59
24	0.385	0.384	0.382	6.84	6.82	6.79	6.81	0.03	0.40	0.63	0.64	0.64	0.64
36	0.353	0.361	0.354	6.27	6.41	6.29	6.32	0.08	1.22	0.75	0.72	0.74	0.74
48	0.381	0.382	0.360	6.77	6.79	6.39	6.65	0.22	3.32	0.65	0.64	0.72	0.67

Table A-3: Sorption Kinetic Data for Acetaminophen onto Amberlite XAD761

Initial Concentration: 10 ppm; Initial Sorbents Mass: 0.1 g

Time (h)	Absorbance			C_{eq} (mg/L)			Avg.	Stdev	%RSD	q_e (mg/g XAD761)			Avg.
	no.1	no.2	no.3	no. 1	no. 2	no. 3				no. 1	no. 2	no. 3	
6	0.540	0.539	0.536	8.77	8.75	8.70	8.74	0.03	0.39	0.25	0.25	0.26	0.25
12	0.514	0.525	0.519	8.41	8.59	8.49	8.50	0.09	1.06	0.32	0.28	0.30	0.30
24	0.501	0.499	0.498	8.13	8.10	8.08	8.11	0.02	0.31	0.37	0.38	0.38	0.38
36	0.53	0.525	0.532	8.67	8.59	8.71	8.66	0.06	0.68	0.27	0.28	0.26	0.27
48	0.528	0.512	0.525	8.57	8.31	8.52	8.47	0.14	1.63	0.29	0.34	0.30	0.31

Table A-4: Sorption Kinetic Data for Acetaminophen onto Activated Carbon

Initial Concentration: 100 ppm; Initial Sorbents Mass: 0.01 g

Time (h)	Absorbance			C_{eq} (mg/L)			Avg.	Stdev	%RSD	q_e (mg/g activated carbon)			Avg.
	no.1	no.2	no.3	no. 1	no. 2	no. 3				no. 1	no. 2	no. 3	
6	1.014	1.088	1.012	16.60	17.81	16.56	16.99	0.71	4.17	166.81	164.39	166.87	166.02
12	1.092	1.087	1.077	17.87	17.79	17.63	17.76	0.13	0.70	164.26	164.42	164.75	164.47
24	0.978	0.979	0.975	16.01	16.02	15.96	16.00	0.03	0.21	167.99	167.95	168.09	168.01
36	0.980	0.978	0.981	16.04	16.01	16.06	16.03	0.03	0.16	167.92	167.99	167.89	167.93
48	1.015	0.998	1.010	16.61	16.33	16.53	16.49	0.14	0.87	166.78	167.33	166.94	167.02

Table A-5: Sorption Kinetic Data for Nalidixic Acid onto Amberlite XAD2

Initial Concentration: 10 ppm; Initial Sorbents Mass: 0.1 g

Time (h)	Absorbance			C_{eq} (mg/L)			Avg.	Stdev	%RSD	q_e (mg/g XAD2)			Avg.
	no.1	no.2	no.3	no. 1	no. 2	no. 3				no. 1	no. 2	no. 3	
6	0.867	0.861	0.864	7.00	6.95	6.97	6.97	0.02	0.35	0.60	0.61	0.61	0.61
12	0.665	0.705	0.704	5.51	5.85	5.84	5.73	0.19	3.30	0.90	0.83	0.83	0.85
24	0.686	0.691	0.688	5.54	5.58	5.55	5.56	0.02	0.37	0.89	0.88	0.89	0.89
36	0.623	0.627	0.625	5.17	5.20	5.18	5.18	0.02	0.32	0.97	0.96	0.96	0.96
48	0.626	0.620	0.620	5.05	5.00	5.00	5.02	0.03	0.56	0.99	1.00	1.00	1.00

Table A-6: Sorption Kinetic Data for Nalidixic Acid onto Amberlite XAD7

Initial Concentration: 10 ppm; Initial Sorbents Mass: 0.1 g

Time (h)	Absorbance			C_{eq} (mg/L)			Avg.	Stdev	%RSD	q_e (mg/g XAD7)			Avg.
	no.1	no.2	no.3	no. 1	no. 2	no. 3				no. 1	no. 2	no. 3	
0.25	0.565	0.567	0.563	4.68	4.70	4.67	4.68	0.02	0.35	1.06	1.06	1.07	1.06
0.50	0.498	0.498	0.488	4.13	4.13	4.05	4.10	0.05	1.17	1.17	1.17	1.19	1.18
0.75	0.445	0.448	0.439	3.69	3.71	3.64	3.68	0.04	1.03	1.26	1.26	1.27	1.26
1	0.343	0.345	0.340	2.84	2.86	2.82	2.84	0.02	0.73	1.43	1.43	1.44	1.43
3	0.305	0.299	0.297	2.53	2.48	2.46	2.49	0.03	1.39	1.49	1.50	1.51	1.50
5	0.224	0.221	0.226	1.86	1.83	1.87	1.85	0.02	1.13	1.63	1.63	1.63	1.63
6	0.239	0.237	0.254	1.85	1.84	1.97	1.89	0.07	3.82	1.63	1.63	1.61	1.62
12	0.164	0.167	0.171	1.27	1.30	1.33	1.30	0.03	2.10	1.75	1.74	1.73	1.74
24	0.189	0.186	0.185	1.47	1.44	1.44	1.45	0.02	1.12	1.71	1.71	1.71	1.71
36	0.157	0.159	0.155	1.22	1.23	1.20	1.22	0.02	1.27	1.76	1.75	1.76	1.76
48	0.136	0.133	0.137	1.06	1.03	1.06	1.05	0.02	1.54	1.79	1.79	1.79	1.79

Table A-7: Sorption Kinetic Data for Nalidixic Acid onto Amberlite XAD761

Initial Concentration: 10 ppm; Initial Sorbents Mass: 0.1 g

Time (h)	Absorbance			C_{eq} (mg/L)			Avg.	Stdev	%RSD	q_e (mg/g XAD761)			Avg.
	no.1	no.2	no.3	no. 1	no. 2	no. 3				no. 1	no. 2	no. 3	
6	0.067	0.069	0.07	0.54	0.56	0.56	0.55	0.01	2.22	1.89	1.89	1.89	1.89
12	0.113	0.117	0.107	0.94	0.97	0.89	0.93	0.04	4.48	1.81	1.81	1.82	1.81
24	0.103	0.098	0.100	0.83	0.79	0.81	0.81	0.02	2.51	1.83	1.84	1.84	1.84
36	0.06	0.065	0.061	0.50	0.54	0.51	0.51	0.02	4.27	1.90	1.89	1.90	1.90
48	0.035	0.033	0.032	0.28	0.27	0.26	0.27	0.01	4.58	1.94	1.95	1.95	1.95

Table A-8: Sorption Kinetic Data for Nalidixic Acid onto activated carbon

Initial Concentration: 100 ppm; Initial Sorbents Mass: 0.01 g

Time (h)	Absorbance			C_{eq} (mg/L)			Avg.	Stdev	%RSD	q_e (mg/g activated carbon)			Avg.
	no.1	no.2	no.3	no. 1	no. 2	no. 3				no. 1	no. 2	no. 3	
6	0.186	0.19	0.187	1.54	1.58	1.55	1.56	0.02	1.11	196.92	196.85	196.90	196.89
12	0.189	0.188	0.191	1.57	1.56	1.58	1.57	0.01	0.81	196.87	196.88	196.83	196.86
24	0.155	0.167	0.164	1.29	1.38	1.36	1.34	0.05	3.85	197.43	197.23	197.28	197.31
36	0.186	0.183	0.179	1.54	1.52	1.48	1.51	0.03	1.92	196.92	196.97	197.03	196.97
48	0.17	0.176	0.18	1.41	1.46	1.49	1.45	0.04	2.87	197.18	197.08	197.01	197.09

APPENDIX B

Table B-1: Solid to Solution Ratio Data for Nalidixic Acid onto Activated Carbon

Initial Mass of adsorbent: 0.01 g

Initial conc. (mg/L)	Absorbance			C_{eq} (mg/L)			Avg.	Stdev	%RSD	q_e (mg/g activated carbon)			Avg.
	no.1	no.2	no.3	no. 1	no. 2	no. 3				no. 1	no. 2	no. 3	
5	0.021	0.021	0.023	0.16	0.16	0.17	0.17	0.01	4.88	9.67	9.68	9.65	9.67
10	0.021	0.024	0.025	0.16	0.18	0.19	0.18	0.01	7.84	19.67	19.64	19.62	19.64
15	0.023	0.027	0.024	0.17	0.21	0.19	0.19	0.02	9.35	29.65	29.58	29.63	29.62
20	0.022	0.029	0.030	0.17	0.22	0.23	0.21	0.04	17.01	39.67	39.56	39.53	39.59

Table B-2: Solid to Solution Ratio Data for Acetaminophen onto Amberlite XAD7

Initial Mass of adsorbent: 0.2 g

Initial conc. (mg/L)	Samples			C_{eq} (mg/L)			Avg.	Stdev	%RSD	q_e (mg/g XAD7)			Avg.
	abs1	abs2	abs3	no. 1	no. 2	no. 3				no. 1	no. 2	no. 3	
5	0.113	0.118	0.109	1.74	1.81	1.67	1.74	0.07	3.98	0.33	0.32	0.33	0.33
10	0.285	0.280	0.278	4.38	4.30	4.27	4.32	0.06	1.28	0.56	0.57	0.57	0.57
15	0.372	0.365	0.364	5.71	5.61	5.59	5.64	0.07	1.19	0.93	0.94	0.94	0.94
20	0.548	0.530	0.523	8.42	8.14	8.03	8.20	0.20	2.42	1.16	1.19	1.20	1.18

Table B-3: Solid to Solution Ratio Data for Nalidixic Acid onto Amberlite XAD7

Initial Mass of adsorbent: 0.01 g

Initial conc. (mg/L)	Samples			C_{eq} (mg/L)			Avg.	Stdev	%RSD	q_e (mg/g XAD2)			Avg.
	abs1	abs2	abs3	no. 1	no. 2	no. 3				no. 1	no. 2	no. 3	
5	0.589	0.579	0.577	4.57	4.49	4.48	4.51	0.05	1.11	0.86	1.02	1.05	0.97
10	0.575	0.570	0.592	8.92	8.84	9.19	8.98	0.18	1.99	2.16	2.31	1.63	2.03
15	0.840	0.859	0.867	13.03	13.33	13.45	13.27	0.22	1.62	3.93	3.34	3.10	3.46
20	1.152	1.162	1.173	17.87	18.03	18.20	18.03	0.16	0.90	4.25	3.94	3.60	3.93

APPENDIX C

Table C-1: Sorption Isotherm Data for Acetaminophen onto Amberlite XAD2

Initial Mass of adsorbent: 0.2 g

Initial conc. (mg/L)	Absorbance			C_{eq} (mg/L)			Avg.	Stdev	%RSD	q_e (mg/g XAD2)			Avg.	q_e(mg/m^2)	$1/C_{eq}$	$1/q_e$	$LogC_{eq}$	$Logq_e$
	no.1	no.2	no.3	no. 1	no. 2	no. 3				no. 1	no. 2	no. 3						
5	0.460	0.461	0.462	3.71	3.72	3.73	3.72	0.01	0.22	0.13	0.13	0.13	0.13	0.000389	0.27	7.80	0.57	-0.89
10	0.946	0.949	0.948	7.63	7.65	7.65	7.64	0.01	0.16	0.24	0.23	0.24	0.24	0.000714	0.13	4.24	0.88	-0.63
15	1.395	1.391	1.388	11.25	11.22	11.19	11.22	0.03	0.25	0.38	0.38	0.38	0.38	0.001145	0.09	2.65	1.05	-0.42
20	1.881	1.883	1.873	15.17	15.19	15.10	15.15	0.04	0.28	0.48	0.48	0.49	0.48	0.001469	0.07	2.06	1.18	-0.31
50*	0.273	0.270	0.276	44.03	43.55	44.52	44.03	0.48	1.10	0.60	0.65	0.55	0.60	0.001808	0.02	1.68	1.64	-0.22

*dilute 10x

Table C-2: Sorption Isotherm Data for Acetaminophen onto Amberlite XAD7

Initial Mass of adsorbent: 0.2 g

Initial conc. (mg/L)	Absorbance			C_{eq} (mg/L)			Avg.	Stdev	%RSD	q_e (mg/g XAD7)			Avg.	q_e(mg/m^2)	$1/C_{eq}$	$1/q_e$	$LogC_{eq}$	$Logq_e$
	no.1	no.2	no.3	no. 1	no. 2	no. 3				no. 1	no. 2	no. 3						
5	0.147	0.148	0.149	2.39	2.40	2.42	2.40	0.02	0.68	0.26	0.26	0.26	0.26	0.000577	0.42	3.85	0.38	-0.59
10	0.291	0.289	0.290	4.72	4.69	4.71	4.71	0.02	0.34	0.53	0.53	0.53	0.53	0.001176	0.21	1.89	0.67	-0.28
15	0.435	0.433	0.435	7.06	7.03	7.06	7.05	0.02	0.27	0.79	0.80	0.79	0.79	0.001766	0.14	1.26	0.85	-0.10
20	0.590	0.593	0.596	9.58	9.63	9.68	9.63	0.05	0.51	1.04	1.04	1.03	1.04	0.002305	0.10	0.96	0.98	0.02
50*	0.361	0.360	0.363	29.11	29.03	29.27	29.14	0.12	0.42	2.09	2.10	2.07	2.09	0.004636	0.03	0.48	1.46	0.32

*dilute 5x

Table C-3: Sorption Isotherm Data for Acetaminophen onto Amberlite XAD761

Initial Mass of adsorbent: 0.2 g

Initial conc. (mg/L)	Absorbance			C_{eq} (mg/L)			Avg.	Stdev	%RSD	q_e (mg/g XAD761)			Avg.	q_e(mg/m^2)	$1/C_{eq}$	$1/q_e$	$LogC_{eq}$	$Logq_e$
	no.1	no.2	no.3	no. 1	no. 2	no. 3				no. 1	no. 2	no. 3						
5	0.338	0.337	0.335	2.73	2.72	2.70	2.72	0.01	0.45	0.23	0.23	0.23	0.23	0.001936	0.37	4.38	0.43	-0.64
10	0.705	0.701	0.702	5.69	5.65	5.66	5.67	0.02	0.30	0.43	0.43	0.43	0.43	0.003672	0.18	2.31	0.75	-0.36
15	1.089	1.091	1.083	8.78	8.80	8.73	8.77	0.03	0.38	0.62	0.62	0.63	0.62	0.005278	0.11	1.61	0.94	-0.21
20	1.475	1.475	1.470	11.90	11.90	11.85	11.88	0.02	0.20	0.81	0.81	0.81	0.81	0.006880	0.08	1.23	1.07	-0.09
50*	0.212	0.213	0.211	32.57	32.72	32.41	32.57	0.15	0.47	1.74	1.73	1.76	1.74	0.014775	0.03	0.57	1.51	0.24

*dilute 10x

Table C-4: Sorption Isotherm Data for Acetaminophen onto Activated Carbon (Initial Mass of adsorbent: 0.02 g)

Initial conc. (mg/L)	Samples			C_{eq} (mg/L)			Avg.	Stdev	%RSD	q_e (mg/g activated carbon)			Avg.	q_e(mg/m^2)	$1/C_{eq}$	$1/q_e$	$LogC_{eq}$	$Logq_e$
	abs1	abs2	abs3	no. 1	no. 2	no. 3				no. 1	no. 2	no. 3						
5	0.017	0.010	0.023	0.253	0.146	0.346	0.248	0.10	40.25	9.493	9.708	9.309	9.50	0.0158	4.0268	0.1052	-0.605	0.978
10	0.015	0.016	0.027	0.223	0.238	0.415	0.292	0.11	36.56	19.555	19.524	19.171	19.42	0.0324	3.4263	0.0515	-0.535	1.288
15	0.021	0.023	0.022	0.323	0.346	0.338	0.335	0.01	3.50	29.355	29.309	29.324	29.33	0.0489	2.9817	0.0341	-0.474	1.467
20	0.027	0.025	0.023	0.415	0.384	0.353	0.384	0.03	8.00	39.171	39.232	39.293	39.23	0.0654	2.6040	0.0255	-0.416	1.594
100	1.038	1.035	1.036	16.99	16.94	16.96	16.96	0.03	0.15	166.02	166.12	166.09	166.08	0.2768	0.0590	0.0060	1.229	2.220
400*	0.823	0.817	0.820	269.39	267.43	268.41	268.41	0.98	0.37	261.21	265.14	263.18	263.18	0.4386	0.0037	0.0038	2.429	2.420
500*	1.101	1.116	1.118	360.39	365.30	365.96	363.88	3.04	0.84	279.21	269.39	268.09	272.23	0.4537	0.0027	0.0037	2.561	2.435
600**	1.122	1.120	1.121	459.08	458.27	458.67	458.67	0.41	0.09	281.83	283.47	282.65	282.65	0.4711	0.0022	0.0035	2.662	2.451
800***	1.003	0.993	0.998	656.63	650.08	653.36	653.36	3.27	0.50	286.74	299.84	293.29	293.29	0.4888	0.0015	0.0034	2.815	2.467
3000****	0.688	0.687	0.685	2815.06	2810.97	2802.78	2809.60	6.25	0.22	369.89	378.07	394.44	380.80	0.6347	0.0004	0.0026	3.449	2.581

*Dilute 20x, **25x, ***40x, and ****250x

Table C-5: Sorption Isotherm Data for Nalidixic Acid onto Amberlite XAD2

Initial Mass of adsorbent: 0.01 g

Initial conc. (mg/L)	Absorbance			C_{eq} (mg/L)			Avg.	Stdev	%RSD	q_e (mg/g XAD2)			Avg.	q_e(mg/m^2)	$1/C_{eq}$	$1/q_e$	$LogC_{eq}$	$Logq_e$
	no.1	no.2	no.3	no. 1	no. 2	no. 3				no. 1	no. 2	no. 3						
5	0.541	0.547	0.545	2.95	2.98	2.97	2.97	0.02	0.56	4.10	4.03	4.06	4.06	0.012315	0.34	0.25	0.47	0.61
10	1.078	1.079	1.095	5.88	5.88	5.97	5.91	0.05	0.88	8.24	8.23	8.06	8.18	0.024784	0.17	0.12	0.77	0.91
15	1.744	1.740	1.747	9.51	9.49	9.53	9.51	0.02	0.20	10.98	11.03	10.95	10.99	0.033288	0.11	0.09	0.98	1.04
20	2.288	2.289	2.280	12.48	12.48	12.43	12.46	0.03	0.22	15.05	15.04	15.14	15.07	0.045680	0.08	0.07	1.10	1.18

Table C-6: Sorption Isotherm Data for Nalidixic Acid onto Amberlite XAD7

Initial Mass of adsorbent: 0.01 g

Initial conc. (mg/L)	Samples			C_{eq} (mg/L)			Avg.	Stdev	%RSD	q_e (mg/g XAD7)			Avg.	q_e(mg/m^2)	$1/C_{eq}$	$1/q_e$	$LogC_{eq}$	$Logq_e$
	abs1	abs2	abs3	no. 1	no. 2	no. 3				no. 1	no. 2	no. 3						
5	0.205	0.203	0.208	1.12	1.11	1.13	1.12	0.01	1.23	7.76	7.79	7.73	7.76	0.017246	0.89	0.13	0.05	0.89
10	0.475	0.479	0.478	2.59	2.61	2.61	2.60	0.01	0.44	14.82	14.78	14.79	14.79	0.032877	0.38	0.07	0.42	1.17
15	0.831	0.843	0.844	4.53	4.60	4.60	4.58	0.04	0.86	20.94	20.81	20.80	20.85	0.046327	0.22	0.05	0.66	1.32
20	1.113	1.119	1.122	6.07	6.10	6.12	6.10	0.02	0.41	27.86	27.80	27.76	27.81	0.061796	0.16	0.04	0.79	1.44
50*	0.361	0.363	0.360	29.96	30.12	29.88	29.99	0.13	0.42	40.08	39.75	40.25	40.03	0.088950	0.03	0.02	1.48	1.60

*dilute 10x

Table C-7: Sorption Isotherm Data for Nalidixic Acid onto Amberlite XAD761

Initial Mass of adsorbent: 0.01 g

Initial conc. (mg/L)	Samples			C_{eq} (mg/L)			Avg.	Stdev	%RSD	q_e (mg/g XAD761)			Avg.	q_e(mg/m^2)	$1/C_{eq}$	$1/q_e$	$LogC_{eq}$	$Logq_e$
	abs1	abs2	abs3	no. 1	no. 2	no. 3				no. 1	no. 2	no. 3						
5	0.242	0.245	0.246	1.94	1.96	1.97	1.96	0.02	0.85	6.12	6.08	6.06	6.09	0.051589	0.51	0.16	0.29	0.78
10	0.647	0.648	0.639	3.53	3.53	3.48	3.52	0.03	0.77	12.94	12.93	13.03	12.97	0.109914	0.28	0.08	0.55	1.11
15	1.138	1.134	1.122	6.21	6.18	6.12	6.17	0.05	0.74	17.59	17.63	17.76	17.66	0.149684	0.16	0.06	0.79	1.25
20	1.625	1.645	1.638	8.86	8.97	8.93	8.92	0.06	0.62	22.28	22.06	22.14	22.16	0.187790	0.11	0.05	0.95	1.35
50*	0.339	0.332	0.333	27.14	26.58	26.66	26.79	0.30	1.13	45.72	46.84	46.68	46.41	0.393309	0.04	0.02	1.43	1.67

*dilute 10x

Table C-8: Sorption Isotherm Data for Nalidixic Acid onto Activated Carbon

Initial Mass of adsorbent: 0.02 g

Initial conc. (mg/L)	Samples			C_{eq} (mg/L)			Avg.	Stdev	%RSD	q_e (mg/g activated carbon)			Avg.	q_e(mg/m^2)	$1/C_{eq}$	$1/q_e$	$LogC_{eq}$	$Logq_e$
	abs1	abs2	abs3	no. 1	no. 2	no. 3				no. 1	no. 2	no. 3						
5	0.021	0.021	0.023	0.163	0.159	0.175	0.166	0.008	4.879	9.674	9.682	9.651	9.669	0.0161	6.0422	0.1034	-0.781	0.985
10	0.021	0.024	0.025	0.163	0.182	0.190	0.178	0.014	7.838	19.674	19.635	19.620	19.643	0.0327	5.6043	0.0509	-0.749	1.293
15	0.023	0.027	0.024	0.175	0.209	0.186	0.190	0.018	9.352	29.651	29.581	29.628	29.620	0.0494	5.2612	0.0338	-0.721	1.472
20	0.027	0.029	0.030	0.209	0.221	0.233	0.221	0.012	5.263	39.581	39.558	39.535	39.558	0.0659	4.5228	0.0253	-0.655	1.597
150*	0.699	0.703	0.696	28.98	29.15	28.86	28.99	0.15	0.50	242.04	241.71	242.29	242.01	0.4034	0.0345	0.0041	1.462	2.384
250**	0.535	0.534	0.540	88.72	88.56	89.55	88.94	0.53	0.60	322.55	322.89	320.90	322.11	0.5369	0.0112	0.0031	1.949	2.508
350**	0.900	0.902	0.898	149.25	149.59	148.92	149.25	0.33	0.22	401.49	400.83	402.16	401.49	0.6692	0.0067	0.0025	2.174	2.604
400**	1.068	1.067	1.065	177.11	176.95	176.62	176.89	0.25	0.14	445.77	446.10	446.77	446.21	0.7437	0.0057	0.0022	2.248	2.650

*Dilute 5x, and **20x

APPENDIX D

Table D-1: Sorption Isotherm Data for Acetaminophen at pH5 onto Amberlite XAD2 (Initial Mass of adsorbent: 0.2 g)

Initial conc. (mg/L)	Samples			C_{eq} (mg/L)			Avg.	Stdev	%RSD	q_e (mg/g XAD2)			Avg.
	abs1	abs2	abs3	no. 1	no. 2	no. 3				no. 1	no. 2	no. 3	
5	0.298	0.295	0.293	4.58	4.53	4.50	4.54	0.04	0.85	0.04	0.05	0.05	0.05
10	0.538	0.542	0.539	8.26	8.33	8.28	8.29	0.03	0.39	0.17	0.17	0.17	0.17
15	0.787	0.791	0.798	12.09	12.15	12.26	12.17	0.09	0.70	0.29	0.28	0.27	0.28
20	1.089	1.089	1.076	16.73	16.73	16.53	16.66	0.12	0.69	0.33	0.33	0.35	0.33

Table D-2: Sorption Isotherm Data for Acetaminophen at pH5 onto Amberlite XAD7 (Initial Mass of adsorbent: 0.2 g)

Initial conc. (mg/L)	Samples			C_{eq} (mg/L)			Avg.	Stdev	%RSD	q_e (mg/g XAD2)			Avg.
	abs1	abs2	abs3	no. 1	no. 2	no. 3				no. 1	no. 2	no. 3	
5	0.190	0.192	0.189	2.92	2.95	2.90	2.92	0.02	0.80	0.21	0.21	0.21	0.21
10	0.363	0.368	0.359	5.58	5.65	5.51	5.58	0.07	1.24	0.44	0.43	0.45	0.44
15	0.509	0.510	0.506	7.82	7.83	7.77	7.81	0.03	0.41	0.72	0.72	0.72	0.72
20	0.663	0.662	0.658	10.18	10.17	10.11	10.15	0.04	0.40	0.98	0.98	0.99	0.98

Table D-3: Sorption Isotherm Data for Acetaminophen at pH5 onto Amberlite XAD761 (Initial Mass of adsorbent: 0.2 g)

Initial conc. (mg/L)	Samples			C_{eq} (mg/L)			Avg.	Stdev	%RSD	q_e (mg/g XAD2)			Avg.
	abs1	abs2	abs3	no. 1	no. 2	no. 3				no. 1	no. 2	no. 3	
5	0.211	0.219	0.219	3.24	3.36	3.36	3.32	0.07	2.14	0.18	0.16	0.16	0.17
10	0.390	0.397	0.388	5.99	6.10	5.96	6.02	0.07	1.21	0.40	0.39	0.40	0.40
15	0.554	0.549	0.562	8.51	8.43	8.63	8.53	0.10	1.18	0.65	0.66	0.64	0.65
20	0.797	0.803	0.801	12.24	12.33	12.30	12.29	0.05	0.38	0.78	0.77	0.77	0.77

Table D-4: Sorption Isotherm Data for Acetaminophen at pH5 onto Activated Carbon (Initial Mass of adsorbent: 0.01 g)

Initial conc. (mg/L)	Samples			C_{eq} (mg/L)			Avg.	Stdev	%RSD	q_e (mg/g activated carbon)			Avg.
	abs1	abs2	abs3	no. 1	no. 2	no. 3				no. 1	no. 2	no. 3	
400**	0.442	0.440	0.440	271.58	270.35	270.35	270.76	0.71	0.26	256.84	259.29	259.29	258.47
600**	0.757	0.753	0.748	465.13	462.67	459.60	462.47	2.77	0.60	269.74	274.65	280.80	275.06
800**	1.078	1.079	1.080	662.37	662.98	663.59	662.98	0.61	0.09	275.27	274.04	272.81	274.04
1000**	1.373	1.379	1.380	843.63	847.31	847.93	846.29	2.33	0.27	312.75	305.38	304.15	307.42

**Dilute 40x

Biography

Name: Miss Umarat Suntisukaseam

Date of Birth: March 20, 1984

Nationality: Thai

Education:

2000-2003 Bachelor of Science in Environmental Technology, Department of Environmental Technology, Sirindhorn International Institute of Technology, Thammasat University, Patumthani, Thailand.