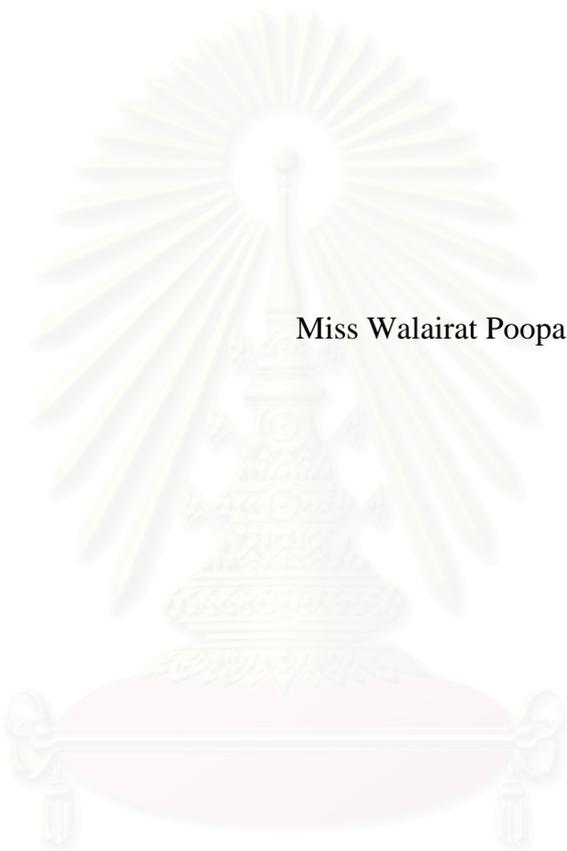EFFECT OF HYDROPHOBICITY OF AMPHIPHILE MOLECULE ON ADSORPTION
BEHAVIOR ONTO VARIOUS ADSORBENTS AND ITS INTERFACE CHARACTERISTICS

Miss Walairat Poopa

A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Science in Environmental Management (Inter-Department)

Chulalongkorn University

Academic Year 2004

ISBN 974-53-1704-7

ผลของคุณสมบัติความไม่ชอบน้ำของโมเลกุลแอมฟิไฟล์ต่อพฤติกรรมการดูดติดผิว
บนตัวดูดซับชนิดต่างๆ และคุณสมบัติที่ผิวร่วม

นางสาววลัยรัตน์ ปูผ้า

Thesis Title   Effect of Hydrophobicity of Amphiphile Molecule on Adsorption Behavior onto Various Adsorbents and Its Interface Characteristics

By   Miss Walairat Poopa

Field of Study   Environmental Management

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วลัยรัตน์ ปูผ้า: ผลของคุณสมบัติความไม่ชอบน้ำของโมเลกุลแอมฟิไฟล์ต่อพฤติกรรมการดูดติดผิวบนตัวดูดซับชนิดต่างๆ และคุณสมบัติที่ผิวร่วม (Effect of Hydrophobicity of Amphiphile Molecule on Adsorption Behavior onto Various Adsorbents and Its Interface Characteristics) อ. ที่ปรึกษา: ดร. ปัญจพร เวชยันต์วิวัฒน์, อ. ที่ปรึกษาร่วม: Prof. Dr. David A. Sabatini 71 หน้า ISBN 974-53-1704-7

การปนเปื้อนของสารประกอบจำพวกยาในน้ำใต้ดินเป็นปัญหาสำคัญที่อาจส่งผลต่อสิ่งมีชีวิตและสิ่งแวดล้อม ซึ่งโครงสร้างของสารประกอบยาเป็นโมเลกุลจำพวกแอมฟิไฟล์ ประกอบไปด้วยส่วนที่ชอบน้ำ และไม่ชอบน้ำในโมเลกุลเดียวกัน การศึกษานี้ได้ทำการศึกษาสารประกอบที่มีโครงสร้างลักษณะเดียวกับสารประกอบยา โดยทำการศึกษาพฤติกรรมการดูดติดผิวของโมเลกุลแอลกอฮอล์ (แปรผันคุณสมบัติความไม่ชอบน้ำ) บนพื้นผิวของตัวกลางต่างๆ ประกอบด้วยอะลูมินา ซิลิกา ผงถ่านกัมมันต์ และ AMBERLITE XAD 761 ที่อุณหภูมิ 25 องศาเซลเซียส ผลการศึกษาโมเลกุลแอลกอฮอล์ไม่แสดงผลการดูดติดผิวของอะลูมินา และซิลิกา เนื่องจากหมู่ฟังก์ชันของแอลกอฮอล์ไม่แตกตัว แต่สามารถแสดงผลการดูดติดผิวบนผิวของผงถ่านกัมมันต์ และ AMBERLITE XAD 761 โดยเมื่อเพิ่มคุณสมบัติความไม่ชอบน้ำ (เพิ่มความยาวของหมู่อะคิว) ค่าคงที่ของการดูดติดผิวจะเพิ่มขึ้น โดยลักษณะการดูดติดผิวของผงถ่านกัมมันต์เป็น Langmuir isotherm โดยค่าสัมประสิทธิ์การดูดติดผิวซึ่งหารโดยพื้นที่ผิวของ บิวทานอล เพนทานอล เฮกซานอล เฮปทานอล และ ออกทานอล เท่ากับ 1.98, 7.27, 29.70, 81.70 และ 794.00 มิลลิลิตรต่อตารางเมตร ขณะที่ลักษณะการดูดติดผิวของ AMBERLITE XAD 761 สามารถแสดงเป็น Freundlich isotherm ของ บิวทานอล เฮกซานอล และ ออกทานอล ได้ดังนี้ $q = 0.9738$ (g/g XAD 761) $(L/g)^N$ x $C_e^{0.5052}$; $q = 1.2201$ (g/g XAD 761) $(L/g)^N$ x $C_e^{1.3269}$; และ $q = 0.4288$ (g/g XAD 761) $(L/g)^N$ x $C_e^{1.5911}$ โดยปฏิกิริยาระหว่างผิวของผงถ่านกัมมันต์(พื้นผิวไม่มีขั้ว) และโมเลกุลแอมฟิไฟล์เป็นปฏิกิริยาความไม่ชอบน้ำ ขณะที่ปฏิกิริยาบนผิวของ AMBERLITE XAD 761 เป็นปฏิกิริยาความไม่ชอบน้ำ และปฏิกิริยาเฉพาะของหมู่ฟังก์ชันของแอลกอฮอล์ นอกจากนี้ได้ทำการศึกษาคุณสมบัติอื่นๆ ประกอบด้วยแรงตึงผิวระหว่างอากาศกับของเหลว แรงตึงผิวระหว่างของเหลว และมุมสัมผัส เพื่ออธิบายพฤติกรรมการดูดติดผิวของสารประกอบที่มีโครงสร้างโมเลกุลแบบแอมฟิไฟล์ โดยสามารถอธิบายได้ว่าการแปรผันคุณสมบัติความไม่ชอบน้ำมีผลต่อแรงตึงผิวระหว่างอากาศกับของเหลว โดยเมื่อเพิ่มคุณสมบัติความไม่ชอบน้ำ ค่าแรงตึงผิวระหว่างอากาศกับของเหลว จะเพิ่มขึ้น ซึ่งเป็นไปในลักษณะเดียวกับแรงตึงผิวระหว่างสารประกอบแอลกอฮอล์บริสุทธิ์กับน้ำ แต่ไม่มีผลต่อมุมสัมผัส จากผลการศึกษาสรุปได้ว่า ค่าแรงตึงผิวระหว่างอากาศกับของเหลวและค่าแรงตึงผิวระหว่างของเหลวมีความสัมพันธ์ต่อพฤติกรรมการดูดติดผิวของโมเลกุลแอมฟิไฟล์ กับพื้นผิวผงถ่านกัมมันต์ได้

สาขาวิชาการจัดการสิ่งแวดล้อม	ลายมือชื่อนิสิต………………………………..
ปีการศึกษา 2547	ลายมือชื่ออาจารย์ที่ปรึกษา………………………
	ลายมือชื่ออาจารย์ที่ปรึกษาร่วม…………………

4689480020: MAJOR ENVIRONMENTAL MANAGEMENT

KEY WORD: ADSORPTION/ PHARMACEUTICAL/ AMPHIPHILE MOLECULE/ SURFACE TENSION/ INTERFACIAL TENSION/ CONTACT ANGLE

WALAIRAT POOPA: EFFECT OF HYDROPHOBICITY OF AMPHIPHILE MOLECULE ON ADSORPTION BEHAVIOR ONTO VARIOUS ADSORBENTS AND ITS INTERFACE CHARACTERISTICS. THESIS ADVISOR: PUNJAPORN WESCHAYANWIWAT, Ph.D. THESIS CO-ADVISOR: PROF. DAVID A. SABATINI, Ph.D. 71 PP. ISBN 974-53-1704-7

Pharmaceutical contaminations in surface water and groundwater are the environmental emerged problems. Most of pharmaceuticals are amphiphile molecules that contain both polar and non-polar parts within the molecules. To understand the fundamental process of adsorption of these amphiphile molecules, a homologous series of alcohols with varied alkyl chain length from butanol to octanol was used as representatives of these molecules in which the degree of hydrophobicity was systematically varied. The adsorption behavior was studied in term of adsorption isotherm at $25^{o}C$ on each pure media, i.e., alumina, silica, powder activated carbon and AMBERLITE XAD 761. In addition, the surface tension of the alcohol solution at the air/liquid interface, the interfacial tension at water/alcohol interface and the contact angle of alcohol solution on surfaces were studied to in order to correlate with the adsorption behavior. The results showed that the alcohols adsorb onto powder activated carbon surface and AMBERLITE XAD 761 but not onto alumina and silica surfaces. On powder activated carbon, the adsorptions follow the Langmuir adsorption isotherm. The adsorption coefficients which were normalized by specific surface area are 1.98, 7.27, 29.70, 81.70 and 794.00 mL/m^2 for butanol, pentanol, hexanol, heptanol, and octanol, respectively. On AMBERLITE XAD 761, the adsorption isotherms were expressed by the Freundlich adsorption isotherm by these following equations: $q = 0.9738$ (g/g XAD 761) $(L/g)^N$ x $C_e^{0.5052}$; $q = 1.2201$ (g/g XAD 761) $(L/g)^N$ x $C_e^{1.3269}$; and $q = 0.4288$ (g/g XAD 761) $(L/g)^N$ x $C_e^{1.5911}$ for butanol, hexanol, and octanol, respectively. As the degree of hydrophobicity increases (or longer the chain length of alcohols), the adsorption onto activated carbon and AMBERLITE XAD 761 surfaces as well as the surface tension and the interfacial tension increase. Therefore, the degree of hydrophobicity affects the adsorption onto organic surfaces, the surface tension and the interfacial tension but no significant effect is found in the contact angle. The adsorption of amphiphile molecules onto powder activated carbon (non-polar surface) is hydrophobic interaction while onto AMBERLITE XAD 761 (hydrophilic surface) are both hydrophobic interaction of alkyl chain and hydrophilic (specific) interaction of hydroxyl functional group onto hydrophilic surfaces. Moreover, the surface tension and interfacial tension of amphiphile molecules (alcohol molecules) correlate to the adsorption behavior onto nonpolar surface (powder activated carbon).

Field of study Environmental management   Student's signature………………….

Academic year 2004   Advisor's signature…………………

     Co-Advisor's signature……………..

ACKNOWLEDGEMENTS

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NOMENCLATURES

q = mass of chemical sorbed/ mass of adsorbent (mmol/g of adsorbent)

K_p = linear partition coefficient (L/g of adsorbent)

C_e = solute concentration at equilibrium (mmol/L)

K_d = adsorption coefficient (dimensionless)

K_{fr} = Freundlich partition coefficient (L/g of adsorbent)^N

N = Freundlich exponent coefficient

K_L = Langmuir constant (L/mol)

a = mass of adsorbate required to saturate a unit mass of adsorbent

(mmol/g adsorbent)

f_{oc} = organic carbon content

K_{oc} = organic carbon normalized sorption coefficient

K_{ow} = octanol-water partition coefficient (dimensionless)

S_w = water solubility (mg/L)

θ = contact angle

PZC = point of zero charge

SSA = specific surface area (m^2/g)

ST = surface tension (mN/m)

C = solution concentration (mg/L)

ST(pure) = Surface tension of pure alcohols (mN/m)

IFT(pure) = Interfacial tension of pure alcohols (mN/m)

CHAPTER I

INTRODUCTION

1.1 Pharmaceuticals in the Environment

Pharmaceuticals are used for human and animal therapy, husbandry, agriculture and aquaculture. The global consumption of pharmaceuticals both in human pharmaceuticals and veterinary pharmaceuticals rapidly increase every year. The new pharmaceutical products escalate introduction to the marketplace. Consequently, the large arrays of pharmaceuticals are increased. Recently, the potential adverse human and ecological health effects of pharmaceuticals released into the environment have been increasingly concerned. They have continually and ubiquitously been released into the environment in numerous quantities from the pharmaceutical manufacturers, excretion from humans and animals mainly in form of urines and feces, and unused and expired drugs disposal not only into the domestic sewage system but also in the landfills (Daughton and Ternes, 1999). In addition, they can be runoff from agricultural fields irrigated with treated water (Pedersen, Yeager and Suffer, 2003). It has been reported that some pharmaceuticals can not be completely eliminated in the sewage treatment plants (STWs) (Daughton and Ternes, 1999). The recent studies have illustrated that a variety of pharmaceuticals can be detected in Canada, U.S. and many countries in Europe (Smeby, 2000; Kolpin et al, 2002; Andreozzi, Raffaele and Nicklas, 2003; Boyd et al, 2003). In surface water and groundwater, pharmaceuticals can be detected in the concentration range from ng/L to µg/L (Sawyer, McCarty and Parkin, 2003).

Pharmaceuticals are known as highly biologically active compounds, which are designed to affect the target organisms on the specific metabolic pathways.

However they can possibly have the unknown effects on the non-target as well if they are released into the environment. In addition, they may have a long-term detrimental effect on the environment at low concentration due to the combined effect, either antagonistic or synergistic (Halling-Sorensen et al, 1998; Daughton and Ternes, 1999). Moreover, several species found to be persistent in the environment. Most of pharmaceuticals can metabolite to conjugate compounds that increase the risk of exposure and can convert back to the origin compounds resulting in greater toxicity (Daughton and Ternes, 1999).

1.2 Research Motivation

Little is known about the extent of environmental occurrence, transport, fate, exposure and impact of pharmaceuticals on the environment (Daughton and Ternes, 1999). Furthermore, related literatures are rare and highly fragmented, especially about the adsorption, fate and transport of pharmaceuticals in the groundwater. Therefore, it is difficult to integrate all knowledge and information to the current environmental situation. In general, the pharmaceuticals are non-polar substances containing many polar functional groups leading to high water solubility (Gringauz, 1997). The mobility and sorption of these molecules in the environment lead to the risk of human and environment for exposure. The role of solute-soil interaction of these amphiphilic compounds on the sorption process is not well studied unlike the sorption of neutral organic compounds. The sorption behavior of neutral organic compounds in the subsurface can be estimated by a few parameters namely the organic carbon content (f_{oc}), which is a function of adsorbent, and the organic carbon normalized sorption coefficient (K_{oc}), which is the ability of organic adsorbent to adsorb the neutral adsorbate that depends on type of adsorbate (Chiou, 2002).

However, there are literatures reported that the sorption behavior of the amphiphile molecules cannot be correctly predicted using this method. Therefore, the purposes of this research firstly to systematically study the adsorption of the amphiphillic molecules onto the various media by means of adsorption isotherms. A series of alcohols with different alkyl chain length were used as the representatives of pharmaceutical molecules contained hydroxyl functional group in which the degree of hydrophobicity was varied. The various types of pure media, which posses different properties were used as adsorbents. Secondly, investigate the correlations among adsorption coefficient and some interfacial properties of these amphiphile molecules. If there are correlations, the interfacial properties of the amphiphile molecules can be used to predict the adsorption behavior of these molecules in the subsurface without simulating the adsorption studies which are rather complex.

1.2.1 Objectives

The main purpose of this study was to investigate the effect of hydrophobicity of the amphiphile alcohol molecules varied from butanol to octanol on adsorption onto these following pure adsorbents: alumina, silica, powder activated carbon and AMBERLITE XAD 761, which are positive charge surface, negative charge surface, non-polar surface and phenolic adsorbent resin, respectively. In addition, the effect of hydrophobicity of alcohol molecules on some interfacial properties i.e., surface tension, interfacial tension and contact angle was studied. Three specific objectives were as follows:

1. To study the adsorption behavior of amphiphile molecules by mean of adsorption isotherms using a homologous series of alcohols with varied alkyl

chain length on alumina, silica, activated carbon and AMBERLITE XAD 761 surfaces.

2. To investigate the surface tension of the alcohol solution at the air/liquid interface, the interfacial tension at water/alcohol interface and the contact angle of alcohol solution on alumina, silica, activated carbon and AMBERLITE XAD 761 surfaces.

3. To determine the correlations among surface tension, interfacial tension, contact angle and adsorption coefficient.

1.2.2 Hypotheses

1. The degree of hydrophobicity of amphiphile molecules has an effect on adsorption onto hydrocarbon surfaces.

2. The interactions between functional group of amphiphile molecules and surfaces play important roles on adsorption.

3. There are correlations among surface tension, interfacial tension, contact angle and adsorption coefficient.

1.2.3 Scopes of the study

All experiments were carried out as batch operation in laboratory scale at 25°C.

1. The adsorption behavior of alcohols including butanol, pentanol, hexanol, heptanol and octanol onto alumina, silica, activated carbon and AMBERLITE XAD 761 surfaces were studied. The adsorption isotherms and adsorption coefficient were investigated.

2. The properties at the interface of alcohols which are surface tension, interfacial tension and contact angle were determined using tensiometer.

3. The relationships among surface tension, interfacial tension, contact angle and adsorption coefficient were correlated as empirical equations.

1.3 Advantages of the study

The fate and transport of pharmaceuticals on subsurface is still unclear. Moreover, there are thousands classes of pharmaceuticals. This research studies the adsorption of the alcohol molecules to describe the adsorption of the pharmaceuticals contained hydroxyl functional group. Physicochemical properties are the main adsorption factors. The effect of hydrophobicity of alcohol molecules is studied by varied the alkyl chain length. Therefore, the result will describe the adsorption of pharmaceuticals contained hydroxyl functional group by varied the hydrophobicity.

Furthermore, the amphiphile molecules affect the interface properties (i.e., surface tension, interfacial tension and contact angle). This research also studies the interface properties and their relationship among the adsorption. The correlation will used for adsorption estimation. The result of this work will provide new perception and new quantitative tools for evaluation the pharmaceuticals adsorption onto different properties media.

CHAPTER II

BACKGROUND AND LITERATURE REVIEWS

2.1 Background

The fate, transport and adsorption behavior of chemicals on the subsurface are generally governed by two main factors, which are the physicochemical properties of chemical and the nature of aquifer or media in the subsurface (Sawyer, et al., 2003). The physicochemical properties of chemical concerned in this study i.e., solubility, hydrophobicity and polarity are corresponded to its molecule structure while nature of aquifer depends on type of aquifer and its physical properties i.e., polarity or charges on surface, porosity, hydraulic conductivity and etc.

2.1.1 Pharmaceuticals

Pharmaceuticals are defined as chemicals used for treatment or prevention of illness, synthetic hormones and veterinary health care. They are also found in personal care products such as fragrances, sunscreen agents and preservatives (Sawyer, et al., 2003). The structure can be ranged from simple to very complex. In addition, pharmaceuticals are highly active substances that contain a wide variety of functional groups e.g. $-COOH$, $-OH$, $-SO_3$ and $-NH_3$ (Daughton and Ternes, 1999; Tolls, 2001). The structure of these compounds is amphiphilic, which exhibits polar and apolar characteristics resulting in the dual behavior. However, pharmaceuticals possess high hydrophobicity that is an important property for molecules to transport to its site of action generally lipid membrane cells effectively. (Connell, 1997; Gringauz, 1997; Sawyer et al., 2003)

2.1.2 Alcohols

Alcohols are compounds that have hydroxyl groups bonded to carbon atoms and can be considered as hydroxyl alkyl compounds (McMurry, 2000; Sawyer et al., 2003). These compounds occur widely in nature and have many industrial and pharmaceutical applications.

The short chain alcohols are completely soluble in aqueous medium due to its relatively high polarity caused by the hydroxyl group. When the molecular size increases, the hydrophobicity also increases causing the water solubility to be decreased.

Alcohols are weakly basic and weakly acidic. As weak bases, they can reversibly be protonated by strong acid to yield oxonium ion, ROH_2^+. As weak acids, they dissociate to a slight extent in dilute aqueous solution that is shown in reaction below (Connell, 1997; McMurry, 2000).

As weak bases:

$$ROH \;\; + \;\; H^+ \;\; \rightarrow \;\; ROH_2^+$$

As weak acids:

$$ROH \;\; + \;\; H_2O \;\; \rightarrow \;\; RO^- \;\; + \;\; H_3O^+$$
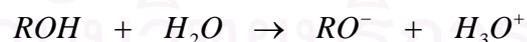
2.1.3 Adsorbents

2.1.3.1 Charged mineral surfaces

Inorganic subsurface soil is the weathered and fragmented outer layer of the earth's crust. The majority elements of earth's crust are silica, alumina and iron. These elements are in form of metal oxides (e.g. SiO_4, Al_2O_3, FeO and Fe_2O_3) (Driscoll, 1996). The hydroxyl groups cover the surfaces when surfaces are wetted by

water. The proton-exchange reactions can occur by these hydroxyl moieties which is similar to dissolved acids:

$$\equiv M - OH_2^+ \quad \leftrightarrow \quad \equiv M - OH \quad + \quad H^+$$

$$\equiv M - OH \quad \leftrightarrow \quad \equiv M - O^- \quad + \quad H^+$$
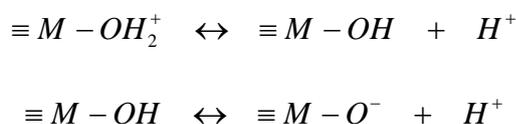
where $\equiv M$ refers as atom like Al and Si in the particle surface.

The surface's charge is controlled by the amount of $\equiv M - OH_2^+$ and $\equiv M - O^-$ species on the solid surface. At pH of point of zero charge, pH_{pzc}, these two species present in equal concentrations which show the zero net charge:

$$\left[\equiv M - OH_2^+\right] \quad = \quad \left[\equiv M - O^-\right] \qquad at \quad pH_{pzc}$$

At solution pH below the pH_{pzc}, the surface is a positively surface charged, $\left[\equiv M - OH_2^+\right] > \left[\equiv M - O^-\right]$. Conversely, at pH above the pH_{pzc}, the surface exhibits a net negative charge, $\left[\equiv M - OH_2^+\right] < \left[\equiv M - O^-\right]$ (Schwarzenbach, Gschwend and Imboden, 2003).

For alumina ($pH_{pzc} \sim 9.5$), the surface is a positively surface charged at neutral pH (pH 7) since $\left[\equiv Al - OH_2^+\right]$ is dominant at the surface. On silica ($pH_{pzc} \sim 2$), the surface is a negatively surface charged at pH 7 since $\left[\equiv Si - O^-\right]$ is dominant at the surface (Kosmulski, 2002).

2.1.3.2 Activated carbon

Activated carbon is a widely used adsorbent because of high efficiency to adsorb a broad range of different types of adsorbates. The activated carbon has high degree of porosity and extensive surface areas. The surfaces consist of two different

types. The basal plane areas are the bulk part. This part is largely uniform nonpolar surfaces that encourage hydrophobic and physical adsorptions. The heterogeneous edges of carbon planes in which carbon-oxygen functional groups formed are the smaller part. Many interactions can occur with these functional groups including electrostatic, hydrogen bonding, and chemisorption interaction. These interactions enhance the adsorption at very low adsorbate concentration (Slejko, 1985).

2.1.3.3 AMBERLITE XAD 761

XAD 761 is a granular form of the highly porous phenolic adsorbent resin. It has large active surface and pore size distribution. The phenolic hydroxyl and methylol groups of the surfaces account for hydrophilic properties. In general, the well adsorbates, which are adsorbed by XAD 761, are high molecular weight water soluble organic compounds containing highly polar substitutes, while nonpolar compounds and neutral salts do not adsorb. The adsorption of polar substances increases with increasing the molecular weight on homologous series of molecules. Acids are more effectively adsorbed than base where aromatic compounds have more affinity than aliphatic compounds. When acids and bases are least ionized, they tend to be most completely adsorbed (Rohm and Haas co., 2004).

2.1.4 Adsorption Phenomenon

Adsorption is one of the most important chemical processes in groundwater determining the quantity of contaminants retained on the aquifer materials. Therefore, it dramatically affects the fate and transport of contaminants in the environment. Adsorption can be defined as a surface phenomenon by which the concentration of a chemical species (adsorbate) from its solution or a vapor phase tends to accumulate on surfaces or pores of a solid (adsorbent) (Chiou, 2002). Although adsorption

process is the combination process, it can be classified into three general types including physical, chemical and exchange adsorption depended on the structural properties of the adsorbate and adsorbent of interest (Sawyer et al., 2003).

The Physical adsorption occurs by London-van der Waals forces between molecules. This force is weak and reversible. When concentration of adsorbate decreases, the material can be desorbed. The chemical adsorption (chemisorption) is a process in which there is a chemical bonding formed between adsorbent and adsorbate. This force is much stronger than physical adsorption. Also, chemical adsorption is seldom reversible. The exchange adsorption occurs by electrical attraction between molecules. The ions of adsorbate can concentrate at the oppositely charged surface as a result of the electrostatic attraction (Sparks, 1995; Chiou, 2002; Sawyer et al., 2003).

2.1.4.1 Adsorption Isotherm

Adsorption isotherm is an equilibrium distribution of a chemical between the adsorbate concentration in solution (mass/volume) and its adsorbed concentration at surface (mass adsorbate/mass adsorbent) applied at a constant temperature (Sparks, 1995).

Adsorption isotherm can be classified into four types (L, S, C and H) as shown in figure 2.1. An L-type isotherm describes the high affinity adsorption between adsorbate and adsorbent at low concentration but the adsorption decreases as the concentration is further increased. The S-type describes the low affinity adsorption at low concentration, because of adsorbate-adsorbate interaction on adsorbent. When the ligand saturation is reached, the adsorption precedes which increases affinity adsorption at higher concentration. The C-type describes a partition mechanism without any specific bonding between the adsorbate and adsorbent. The interaction is

generally a hydrophobic adsorbate partition with hydrophobic adsorbent. The H-type describes a strong adsorbate-adsorbent interaction which occurs by chemisorption interactions. This type is an extreme case of the L-type (Sparks, 1995; Evangelou, 1998).

There are many types of adsorption isotherm depending on the composition of adsorbent and the properties of adsorbate (Schwarzenbach et al., 2003).
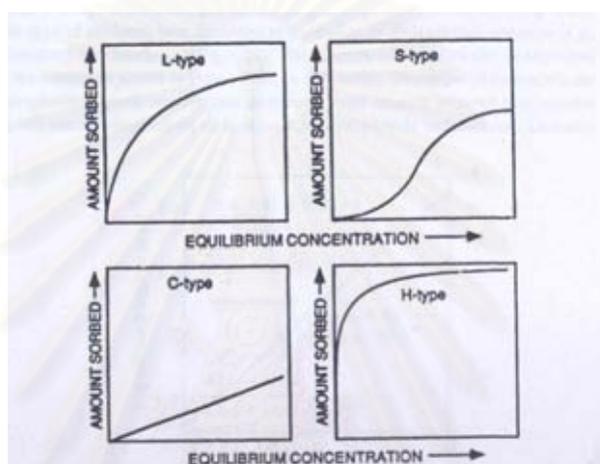
Figure 2.1 Classification of type of adsorption isotherm

The very common adsorption isotherms used in the adsorption processes are the linear adsorption isotherm, the Freundlich isotherm and the Langmuir isotherm (Sparks, 1995).

(a) Linear Adsorption Isotherm

The linear adsorption isotherm lies on the assumption that the same affinity of the adsorption is occurred over the concentration range. This model is suitable for low adsorbate concentration where the saturate ion condition of adsorption sites is far away (Schwarzenbach et al., 2003). The model is described by equation (2.1).

$$q = K_p \cdot C_e \qquad (2.1)$$

where

    q   = mass of chemical sorbed/mass of adsorbent (g/g of adsorbent)

    K_p = linear partition coefficient (L/g of adsorbent)

    C_e = solute concentration at equilibrium (g/L)

The adsorption coefficient (K_d) of linear adsorption isotherm is the linear partition coefficient (K_p)

(b) Freundlich Adsorption Isotherm

The Freundlich model is a mathematical approach for fitting the experimental data of adjustable parameter to account for the variation in adsorption heat on an energetic heterogeneity of surface with the concentration of adsorbate (Chiou, 2002; Schwarzenbach et al., 2003). The relationship can be described by equation (2.2) (Knox, Sabatini and Canter, 1993).

$$q = K_{fr} \cdot C_e{}^N \qquad (2.2)$$

where

    q   = mass of chemical sorbed/mass of adsorbent (g/g of adsorbent)

    K_{fr} = Freundlich partition coefficient (g/g of adsorbent) $(L/g)^N$

    C_e = solute concentration at equilibrium (g/L)

    N   = Freundlich exponent coefficient

The Freundlich isotherm lies on the assumption that there are multiple types of adsorption sites acting in parallel and there are interactions between adsorbate molecules. The difference adsorption free energy and total site abundance are displayed in each site type. The exponent is an indicative of the diversity of free energies. When N = 1, the isotherm is linear and the free energy is constant over the

concentration range; when N < 1, the isotherm can be deduced the weaker adsorption and weaker free energies; when N > 1, the isotherm can be deduced that more adsorbates are adsorbed in which the free energies for further adsorption is enhanced. In summary, higher N means higher adsorption. The Freundlich equation can be linearized as shown in equation (2.3) (Schwarzenbach et al., 2003).

$$\log q = \log K_{fr} + N \log C_e \qquad (2.3)$$

The adsorption coefficient (K_d) of Freundlich isotherm varied with adsorbate concentration as shown in equation (2.4) (Schwarzenbach et al., 2003).

$$K_d = K_{fr} \cdot C_e^{N-1} \qquad (2.4)$$

(c) Langmuir Adsorption Isotherm

Langmuir isotherm is based on the theoretical principle that the active site on the adsorption process is limited (Chiou, 2002). The assumption concepts of this isotherm are the adsorption process is monolayer (each molecule occupies one sorption site) and the affinity of each site for adsorbate is the same with no interaction between adsorbate molecules (Knox, et al., 1993). The expression of this isotherm can be described by equation (2.5)

$$q = \frac{aK_L \cdot C_e}{1 + K_L \cdot C_e} \qquad (2.5)$$

where

    q   = mass of chemical sorbed/mass of adsorbent (g/g of adsorbent)

    K_L = Langmuir constant (L/g)

    C_e = solute concentration at equilibrium (g/L)

    a   = mass of adsorbate required to saturate a unit mass of

            adsorbent   (g/g adsorbent)

This model can be inferred by linear regression as equation (2.6);

$$\frac{1}{q} = \frac{1}{aK_L} \cdot \frac{1}{C_e} + \frac{1}{a} \qquad\qquad (2.6)$$

The adsorption coefficient (K_d) of Langmuir isotherm as shown in equation (2.7) (Schwarzenbach et al., 2003).

$$K_d = K_L \cdot a \qquad\qquad (2.7)$$

2.1.4.2 Adsorption of Neutral Organic Compounds

For neutral organic compounds, the hydrophobic partitioning plays an important role in adsorption process. The adsorption coefficient (K_d) depends on the organic carbon content (f_{oc}) of adsorbent and the ability of organic material to adsorb the neutral organic compounds which can be defined as an organic carbon normalized sorption coefficient (K_{oc}). The K_{oc} values can be estimated from their physicochemical properties, such as octanol-water partition coefficient (K_{ow}) or water solubility (S_w). In general, the water solubility of organic compounds decrease with increasing the hydrophobicity. The adsorption increases because of the accumulation

at the interface of hydrophobic organic substances and non-polar organic surface. The adsorbent existed in the subsurface environment generally exhibits very low organic carbon contents leading to a poor adsorption of organic solutes or adsorbates. Therefore, the mineral surfaces may be the only adsorption sites in the subsurface but the neutral organic compounds exhibit a weak tendency to adsorb into the mineral surfaces (Chiou, 2002; Schwarzenbach et al., 2003).

2.1.4.3 Adsorption of amphiphillic organic compounds

The nonlinear adsorption isotherms of amphiphilic organic adsorbates interacting with natural solids are found (Chiou and Kile, 1998; Schwarzenbach et al., 2003). The interaction between adsorbate and adsorbent which have oppositely charged is an electrostatic attraction while that of similarly charged is an electrostatic repulsion. The adsorption behavior is varies by pH because it governs both the charge on mineral surfaces and the ionized form of amphiphile molecules (Schwarzenbach et al., 2003). This interaction was found in many observations, such as the adsorption of fluorescent dyes onto mineral media (Kasnavia, Vu de and Sabatini, 1999; Sabatini, 2000) and the adsorption of anionic pesticides onto mineral media (Clausen, Fabricius and Madsen, 2001).

The hydrophobic portions of amphiphile molecule influence their adsorption. An interesting phenomenon observed by Sanemesa, Nakahara and Zheng (2003) is that the uptake of n-alkane and n-alcohol onto ion-exchange resins is found to be roughly proportional to the relative hydrophobicity (K_{ow}). This result showed the hydrophobicity interaction. Cowan and White (1958) observed the adsorption of a series of alkyl ammonium ions to the same Na-montmorillonite that showed the isotherm slope was steeper with increasing the alkyl chain length (Cowan and White, 1958 cited in Schwarzenbach et al., 2003). An increase in hydrophobicity of alkyl

groups enhances the tendency of the adsorbate to be collected near the surface and results in supporting the electrostatic forces since the hydrophobic portion repulses the bulk water and prefers to move into the near surface (Somasundaran et al., 1984 cited in Schwarzenbach et al., 2003). As demonstrated by Clausen et al (2001), the more polarity of pesticides, the less adsorption was observed.

Due to the combined interaction, the adsorption is rather complex. In addition, the estimation on adsorption behavior of these amphiphile molecules is more difficult than those of neutral organic compounds. Adsorption coefficient of neutral organic compounds can be estimated from a few key parameters namely f_{oc} and K_{oc}. However, the sorption of amphiphile molecules cannot be explained by these variations (Tolls, 2001).

2.1.5 Surface Tension

Surface tension is the force between air/liquid interface. At the interface, the liquid molecules have fewer neighbor molecules than the molecules in the interior. So, the imbalance forces occur on the surface molecules pulling toward the bulk liquid and out into the vapor phase tending to decrease the interface area (Hiemenz and Rajagopalan, 1997; Myers, 1999).

The molecule orientation at the interface is a function of the surface tension. For an aqueous solution of n-alcohols, the surface tension results when the hydroxyl group immerses into the water and the alkyl group pointing out toward the air as shown in figure 2.2 (Myers, 1999). The vibration spectra indicate the orientation of n-alcohols (C_1-C_8) at the liquid/vapor interface that the hydroxyl group orients at such interface whiles the alkyl group pointing away from the liquid (Stanners et al., 1995). This is also in agreement with the concepts of the orientation of surfactant

amphiphilic molecules that contain both hydrophobic and hydrophilic groups similar to the alcohol molecules.
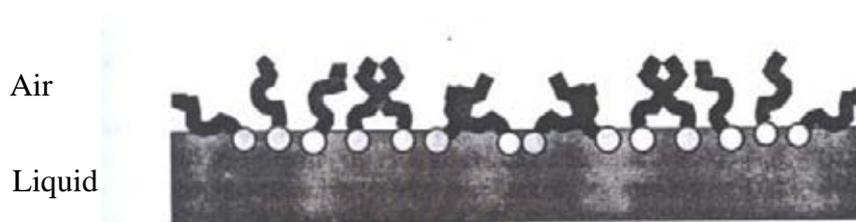
Figure 2.2 The orientation of amphiphile molecules at surface and interface

2.1.6 Interfacial Tension

The basic concept used to describe the surface tension as mentioned previously can be applied to the interfacial tension. Interfacial tension is defined as the forces between two immiscible phases, i.e. two immiscible liquids, liquid/solid and solid/vapor. It is a parameter used to measure the interfacial free energy per unit area. In subsurface, the interfacial tension can be used to describe the movement of contaminants through the porous media (Myers, 1999; Montgomery, 2000; Birdi, 2003).

In general, the surface tension of water at air/water interface is always higher than the interfacial tension between liquid/water interface. In addition, the characteristics of the interfacial tension between the members of homologous series of substance and water will slightly change as a function of the molecular weight. The interfacial tension will lie between the two surface tensions if the two liquid are highly immiscible (e.g., water-alkane). The interfacial tension will be lower than the lower of the two surface tensions, where the two liquid are significant miscible (e.g., water-octanol) (Myer, 1999).

2.1.7 Contact Angle

Contact angle (θ) is defined as the angle formed by the interaction of three phases (e.g., solid/liquid/vapor junction). This parameter can be used to consider the wetting characteristic of liquid on the solid. In case that the liquid completely wets the solid, the contact angle is zero since liquid spreads as a uniform film (figure 2.3a). If a finite contact angle between 0 and 90° ($0 > \theta > 90^{\circ}$) is formed, the system would be partially wetting (figure 2.3b). If the liquid cannot wet the solid, the contact angle is 90° (figure 2.3c). The size of contact angle can be used to explain the feature of the interaction of liquid on solid (Myers, 1999).

(a)   (b)   (c)
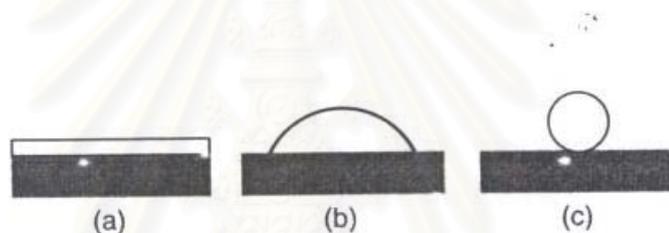
Figure 2.3 A liquid drop on a solid surface

2.2 Literature Reviews

2.2.1 Pharmaceuticals in the Aquatic Environment

Tolls (2001) reviewed the sorption of veterinary pharmaceuticals on soils. He concluded that the partition coefficient (Kd) is underestimated if it is predicted by the values of Koc and Kow. This indicates that there are another processes governed the sorption of veterinary pharmaceuticals besides the hydrophobicity partitioning, which is a main process influenced the sorption of neutral organic compounds.

Ying et al. (2002) reviewed the occurrence and fate of hormone steroid in the environment. The steroids of environmental concern are mainly estrogen and contraceptives due to their endocrine disruption potential. Also, the hormone steroid generation in waste of livestock is occurred by using steroid drug in cattle as well as livestock. Hormone steroid can be detected at various levels in the environment including wastewater, animal waste, surface water and groundwater. The fate and behavior in different environmental media have been still unclear.

2.2.2 Sorption on a Solid Surface

Clausen et al. (2001) studied the adsorption of pesticides in the mineral surfaces. Pesticides were composed of three anionic pesticides: mecoprop [(*RS*)-2-(4-chloro-2-methyl-phenoxy)propionic acid], 2,4-D (2,4-dichlorophenoxyacetic acid) and bentazone [3-isopropyl-1*H*-2,1,3-benzothiadiazin-4-(*3H*)-one 2,2-dioxide] and two nonionic pesticides: atrazine (6-chloro-N^2-ethyl-N^4-isopropyl-1,3,5-triazine-2,4-diamine) and isoproturon [3-(4-isopropyl-phenyl)-1,1-dimethylurea)]. The mineral surfaces represent an aquifer media that included quartz, calcite, kaolinite and α-alumina. The result showed the adsorption of anionic pesticides is an electrostatic interaction between the anionic part of the molecule and the positive site of the surface (calcite, α-alumina and quartz (pH 2.4)). Moreover, the interaction depends on the dissociation, the strength of anionic part and the polarity of compound. At the studied pH, the adsorption depends on the dissociation of the compound. The stronger of anionic part, the greater electrostatic interactions are observed. The difference in the polarity causes the difference in the adsorption. Less adsorption is observed if the compound has higher polarity. The adsorption of nonionic pesticides is only found on kaolinite. The adsorption of atrazine is greater than isoproturon owing to less water

solubility. The more water solubility, the less adsorption is found. It may indicate that the adsorption occurs at the Si-oxide part of the kaolinite because no adsorption on α-alumina is observed.

Intravichit (2003) studied the sorption of three pharmaceuticals; acetaminophen, nalidixic acid and 17-α-ethynylestradiol onto pure aquifer media; alumina, silica and porapak. Acetaminophen that has high water solubility prefers to soluble in water phase. Nalidixic acid exhibits ionized carboxylic group. The ionized form sorbed to positively charge of alumina surface by the electrostatic interaction. The 17-α-ethynylestradiol exhibits predominantly neutral form which consists of two hydroxyl groups. There are no sorptions onto both charged alumina and silica surfaces. The sorption onto porapak is significant because it exhibits the most hydrophobic molecule.

Kasnavia et al. (1999) studied the effect of fluorescent dye, which is commonly used in groundwater tracing studies, and media properties on dye sorption. Alumina and silica were used as the net positively and negatively charged mineral surfaces, respectively. The n-octanol represented a neutral organic phase. The studied ionic functional groups (e.g. COO^- and SO_3^- groups) can interact with oppositely charged surface site due to the electrostatic interaction and relatively independent to the hydrophobic interaction. However, the hydrophobic interaction can also exhibit depending on pH since it governs the changing of net charge of surface and neutralization of anionic dye functional groups. The result showed that sorption depends on the type and location (e.g. para- and meta-) of dye functional group, the minerals present in the media, and the environment conditions. They suggested that the sorption of other organic compounds that have pH dependent functional group such as pesticides and surfactants would also be a function of these conditions.

Palmer et al. (1992) studied the sorption of hydrophobic organic compounds and amphiphile nonionic surfactants onto subsurface materials utilizing four neutral organic chemicals (NOCs): atrazine, diuron, o-xylene and p-xylene and four nonionic surfactants of alkylphenolpolyoxyethoxylate (NISs): Igepal CA620, CO620, CO630 and CO660 with two subsurface materials: alluvial sand and sandstone. The result showed that the nature of organic matter (maturity) can affect the sorption of amphiphillic compounds whereas it does not impact the sorption of NOCs. The NISs sorbed on the mineral surfaces of the media are not adequate to account for the hydrophobic partitioning. Decreasing sorption of NISs is observed with decreasing hydrophobicity (increasing oxyethylene groups) as based on the hydrophobic theory. Also, the interaction between the mineral surfaces and the polar moiety of surfactants increases with increasing oxyethylene groups.

Sabatini and Austin (1991) studied the characteristics of rhodamine WT and fluorescien as adsorbing groundwater tracers. The studies showed the use of these dyes is observed to delimit the appearance of two pesticides (atrazine and alachor). The batch studies presented that the adsorption cannot be predicted by empirical relationships based on K_{ow} and f_{oc}. The breakthrough curve indicated that the adsorptive mechanism of the fluorescent dyes differ from the adsorptive mechanism of most pesticides.

Sabatini (2000) studied the sorption of two fluorescent dyes (fluorescein and sulforhodamine B) with natural aquifer media (negatively charged sandstone and positively charged limestone). This equilibrium sorption is dominated by electrostatic interactions. The ionic functional groups interact with oppositely charged surface site. Sorption kinetic rates decrease with increasing particle size, which is consistent with

diffusion limited intraparticle sorption. These results showed the importance of both equilibrium and kinetics of dye sorption in designing and interpreting tracer studies.

Sanemasa et al. (2003) reported the uptake of alkanes (C_5-C_9) and alcohols (C_4-C_7) by ion-exchange resins in aqueous solution. Ion-exchange resins were composed of strong acid cation exchange resins and strong base anion exchange resins. The amount of uptake is propotional to the equilibrium concentration of solute. The study found the uptake of anion exchange resin is greater than the cation exchange resin. The hydrophobicity is found to be roughly proportional to the uptake of n-alkane and n-alcohol for both ion-exchange resins. The result showed the hydrophobic interaction plays an important role in the uptake of solute by both ion-exchange resins.

2.2.3 Adsorbent and Adsorbate Properties

Kosmulski (2002) reported that alumina and silica surfaces exhibit amphoteric, pH-dependent surface charging. The point of zero charge (PZC) of alumina falls at pH about 9 in the absence of strongly adsorbing species. At pH above the PZC, alumina shows negatively charged resulting in the tendency to adsorb cations. At below PZC, it shows positively charged resulting in the tendency to adsorb anions. The PZC of silica falls at pH about 2. Silica shows negatively surface charged at pH above PZC. This creates favorable electrostatic conditions for cation adsorption, while the ability to adsorb anions is limited at neutral pH. The density of the surface charge depends on the pH and ionic strength.

Stanners et al. (1995) studied polar ordering of n-alcohols (C_1-C_8) at the liquid/vapor interface. The vibration spectra were acquired by the CH and OH stretching region using infrared-visible sum-frequency generation. The spectra

showed the orientation of all alcohols are polar (hydroxyl group) oriented at the liquid/vapor interface and the alkyl group pointing out to the vapor phase. For alcohols containing more than five carbon atoms, i.e. hexanol, heptanol and octanol, the presence of trans-gauche defects in the alkyl chain can be found by the spectra.

CHAPTER III

METHODOLOGY

3.1 Materials

3.1.1 Adsorbents

Adsorbents used in this study were pure materials including alumina (PZC~9), silica (PZC~2), powder activated carbon (nonpolar surface) and AMBERLITE XAD 761 (hydrophilic surface). The aluminum oxide medium (alumina) has a specific surface area of 155 m^2/g with the mesh size of 150. The silica gel (silica) has a specific surface area of 480 m^2/g with the mesh size of 35-60. The powder activated carbon has specific surface area of 600 m^2/g with the mesh size of 100-325. These media were purchased from Aldrich Chemical Co and used as received. AMBERLITE XAD 761 is a highly porous phenolic polymer, which have phenol-formaldehyde polycondensate as a crosslinking agent. The AMBERLITE XAD 761 has a reported surface area of 150-250 m^2/g. The AMBERLITE XAD 761 preparation was firstly sieving with the mesh size of 20-70 followed by washing with the ultra pure water and finally drying in the hot air. Table 3.1 lists the properties of adsorbent materials in this study.

Table 3.1 Adsorbents properties

Chemical Form	PZC	Specific Surface Area (SSA) (m^2/g)	Mesh Size	References
Al_2O_3	9.5±0.5	155	150	(a)
SiO_2 (gel)	2-4	480	35-60	(a)
Activated carbon	N/A	600	100-325	(a)
AMBERLITE XAD 761	N/A	150-250	20-70	(b)

References:
(a) Aldrich Chemical Co.
(b) Rohm and Haas Co. (2004)
N/A : not available

3.1.2 Alcohol Compounds

Five alcohol compounds were used in this study; 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol and 1-octanol. The alcohols have purity higher than 99.5%. These chemicals were purchased from Merck KGaA, Germany. All the chemicals were used without further purification. Table 3.2 lists properties of these alcohols. Ultra pure water was used throughout the experiments.

Table 3.2 Alcohol properties

Alcohol Name	1-Butanol	1-Pentanol	1-Hexanol	1-Heptanol	1-Octanol
Carbon atoms	4	5	6	7	8
Formula	C_4H_9OH	$C_5H_{11}OH$	$C_6H_{13}OH$	$C_7H_{15}OH$	$C_8H_{17}OH$
CAS Number	71-36-3	71-41-0	111-27-3	111-70-6	111-87-5
Mol weight (g)	74.12	88.15	102.17	116.20	130.22
Melting point (^{o}C)	-79.9	-78.5	-51.6	-34.6	-16.0
Boiling point (^{o}C)	117.0	137.9	157.2	175.0	194.5
Log K_{ow}	0.88 (a)	1.56 (a)	2.03 (a)	2.72 (a)	3.00 (b)
Water Solubility at 25°C (mg/L)	9.0×10^4	2.7×10^4	6.0×10^3	1.8×10^3	5.4×10^2

Reference: Speight, 2003

(a): Sanemasa et al., 2003

(b): International Programme on Chemical Safety (2002)

3.2 Experimental Methods

The experiment was divided into two phases; adsorption study and interfacial properties study (surface tension, interfacial tension and contact angle).

3.2.1 Adsorption Studies

The adsorption studies were divided into two parts. The first part was the preliminary study aimed to find the solid to solution ratio and equilibrium time for adsorption. The second part was the determination of adsorption isotherms.

3.2.1.1 Preliminary Study

Firstly, the solid to solution ratio study was conducted to evaluate the appropriate mass of adsorbent to volume of solution. Alumina was placed into a 22 mL headspace vial by varying the weight. Then, each alcohol solution at varied concentration was added into the vial until almost volume of the vial has occupied to avoid the headspace loss. The samples were shaken at constant temperature of 25 $^{\circ}$C for 5 days. The samples were then centrifuged at 3,000 rpm for 15 min to separate the suspended particles. The supernatant was separated and analyzed for the alcohol concentration. The appropriate solid to solution ratio was determined if a substantial reduction in the concentration of alcohol caused by adsorption process was clearly observed. All above procedures were repeated for silica, activated carbon and AMBERLITE XAD 761, respectively.

The required time for adsorption process to reach the equilibrium was then investigated. For each alcohol, the systems of identical solid to solution ratio were prepared in which the solid to solution ratio of 1:44 g/mL were used for alumina and silica. The solid to solution ratio of 1:2200 g/mL and 1:220 g/mL were used for activated carbon and AMBERLITE XAD 761, respectively. The prepared samples were preceded by the same method mentioned previously. The supernatant solutions were withdrawn to analyze the alcohol concentration. The equilibrium time was defined as the minimum time in which the concentration of alcohol in supernatant solution has no further change.

<u>3.2.1.2 Adsorption Isotherm Study</u>

The study of adsorption isotherm was carried out at equilibrium condition using a constant solid to solution ratio as mentioned previously for each adsorbent. It is noted that the volume of solution used was equal to the volume of vial, which is 22 mL.

The solution at varied initial alcohol concentrations were placed into the vial and shaken for 60 hours (as evaluated from the preliminary study). Then, the samples were centrifuged at 3,000 rpm for 15 min. The equilibrium alcohol concentrations in the supernatant were collected and analyzed. The pH of the suspension was measured by pH meter (sension^{TM} model 51935-00). The adsorption isotherm was plotted for each alcohol. The adsorbed mass can be calculated by mass balance.

The rubber septa coated with Teflon were used to cap these vials to make sure that there is no leakage. In each experiment, triplicates were done and blank solutions were used for correction of background interferences.

3.2.2 Surface Tension, Interfacial Tension and Contact Angle Studies

Surface tension, interfacial tension and contact angle studies were conducted to determine the interfacial properties of each alcohol by using tensiometer. Both pure alcohols and alcohol solution prepared at desired concentrations were used depending on the studied interfacial property at constant temperature of 25 ^{o}C. For the surface tension measurement, the pure alcohol/air and solution of alcohol/air interface were evaluated. For the interfacial tension measurement, the pure alcohol/water and solution of alcohol/water interfaces were evaluated. For the contact angle measurement, three pure media; alumina, silica and activated carbon, and the pure alcohol and solution of alcohol were determined.

3.3 Correlation study

The correlations among adsorption, surface tension, interfacial tension and contact angle were studied.

3.4 Analytical Instruments

The concentrations of each alcohol were determined by Gas Chromatography (Perkin Elmer; Model Clarus 500 GC) with a flame ionized detector (FID); column: Elite-Wax with 30 m. x 0.32 mm. ID, 0.25 µm. film thickness; carrier gas: helium at 20 mL/min. equipped with headspace auto sampler (Perkin Elmer; Model TurboMatrix 40).

The surface tension, interfacial tension and contact angle were measured by tensiometer (DataPhysics; Model DCAT 11). The surface tension and interfacial tension measurements were done by using the Wilhelmy plate while the contact angle measurement was followed the Washburn method.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Adsorption Isotherm Studies

Adsorption isotherms were studied in order to investigate the adsorption behavior between alcohols and adsorbents with varying the degree of hydrophobicity by vary the alkyl chain of alcohol. The adsorption isotherms were conducted in batch experiments using five n-alcohols; 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol and 1-octanol and four adsorbents; alumina, silica, powder activated carbon and AMBERLITE XAD 761.

4.1.1 Adsorption isotherm for n-alcohols onto alumina

There is no adsorption of n-alcohols onto alumina surface. The experiments were conducted at pH about 6 to 7. At pH 7, alumina, which has PZC of ~9, possesses a net positive charge. Since alcohols are weak acid ($pK_a = 16$), the alcohols exhibit predominantly at neutral form at the studied pH. Intravichit (2003) found that there is no sorption of 17-α-ethynylestradiol which consists of two hydroxyl groups and exhibits neutral form because of the high pK_a. This was in agreement with the results obtained in this study, where no adsorption is found. Since the weak acid has less degree of the dissociation, the ionized form of alcohols is not strong enough to have an electrostatic interaction with a positive charge of alumina.

4.1.2 Adsorption isotherm for n-alcohols onto silica

At neutral pH, alcohols exhibit weak acid properties and behave predominantly like neutral organics as explained previously. Silica, having PZC of ~3 has a net negative charge at neutral pH. No adsorption can be observed which is consistent with the sorption of 17-α-ethynylestradiol onto silica as studied by Intravichit (2003).

In summary, the high pK_a of these alcohols leads to no adsorption at all on the charged mineral media since the alcohol dissociation seldom occurs. It generally behaves like neutral molecule. Therefore, the adsorption of these molecules onto uncharged organic surfaces was further investigated using hydrophobic activated carbon and hydrophilic AMBERLITE XAD 761 surfaces.

4.1.3 Adsorption isotherm for n-alcohols onto powder activated carbon

The adsorption data on powder activated carbon were analyzed by mean of Linear, Langmuir and Freundlich adsorption isotherm as shown in table 4.1. It is clear that the Langmuir isotherm shows the best fit among these three isotherms. Because the powder activated carbon surface exhibit largely uniform nonpolar surfaces, the hydrophobic portion of alcohol molecule tends to adsorb via hydrophobic partitioning interaction as a monolayer on the surface of activated carbon as referred to the Langmuir adsorption isotherm. In addition, there is no interaction between adsorbate molecules.

Table 4.1 Summary results of Linear, Langmuir and Freundlich isotherm parameters and correlation coefficient (R^2)

Alcohols	Linear isotherm		Langmuir isotherm			Freundlich isotherm		
	K_d (L/g)	R^2	K_L (L/mol)	R^2	a (mmol/g)	K_{fr} (g/g activated carbon) $(L/g)^N$	R^2	N
Butanol	0.4509	0.6844	751.19	0.8560	1.5795	0.6831	0.7049	0.4580
Pentanol	0.9296	0.3669	2222.17	0.9272	1.9643	1.3023	0.8095	0.2739
Hexanol	1.4166	0.3373	9609.63	0.9536	1.8549	1.6638	0.8545	0.2383
Heptanol	1.9435	0.0533	26730.39	0.9590	1.8339	1.8298	0.6951	0.1594
Octanol	3.0623	0.6472	229285.71	0.9958	2.0768	2.2713	0.7848	0.1194

A plot of $1/C_e$ vs. $1/q$ yielded a straight line as shown in figure 4.1-4.5. The Langmuir constant (K_L), maximum alcohol to adsorb onto the powder activated carbon (a), and the adsorption coefficient (K_d) are shown in table 4.2.

y = 0.8428x + 0.6331
R^2 = 0.8560
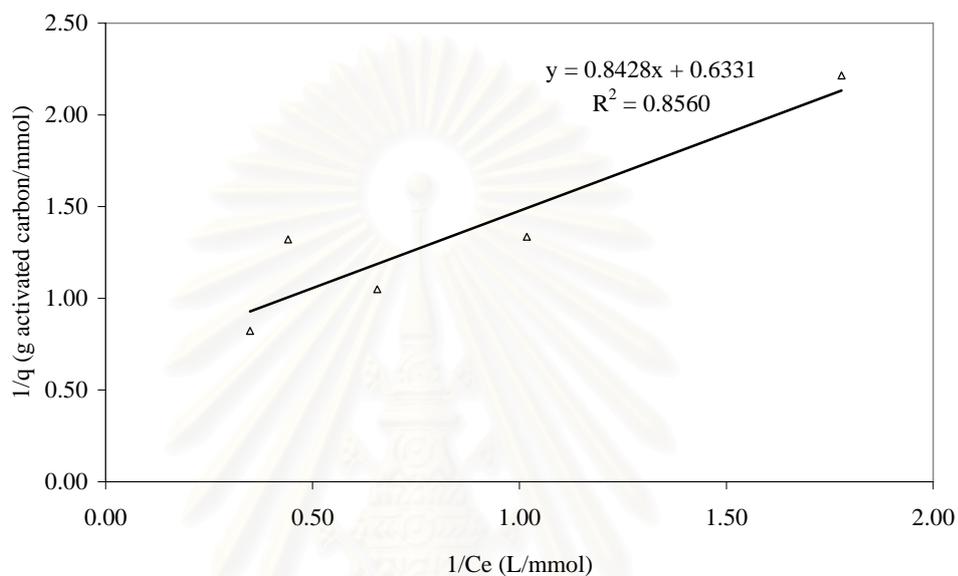
Figure 4.1 The Langmuir adsorption isotherm of butanol onto activated carbon surface

y = 0.2291x + 0.5091
R^2 = 0.9272
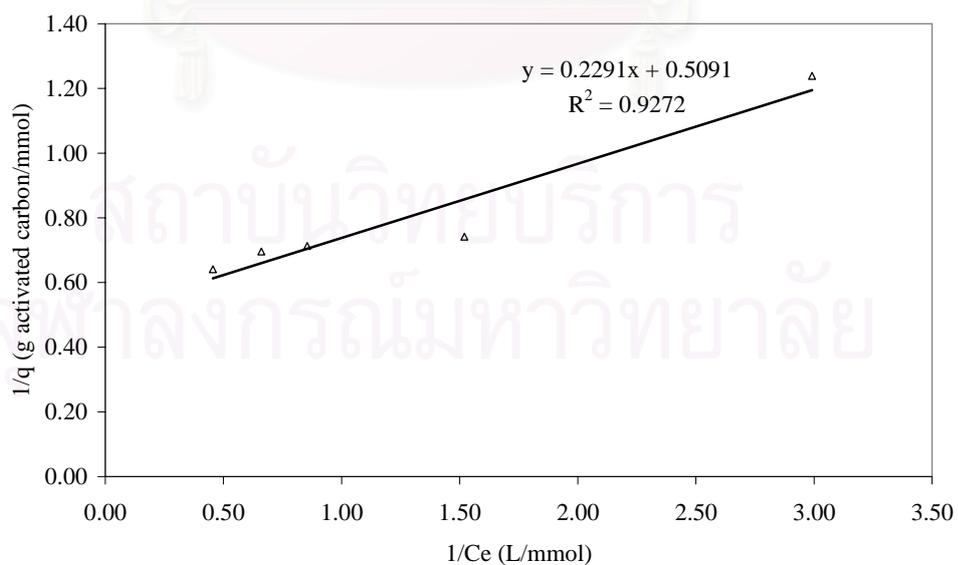
Figure 4.2 The Langmuir adsorption isotherm of pentanol onto activated carbon surface
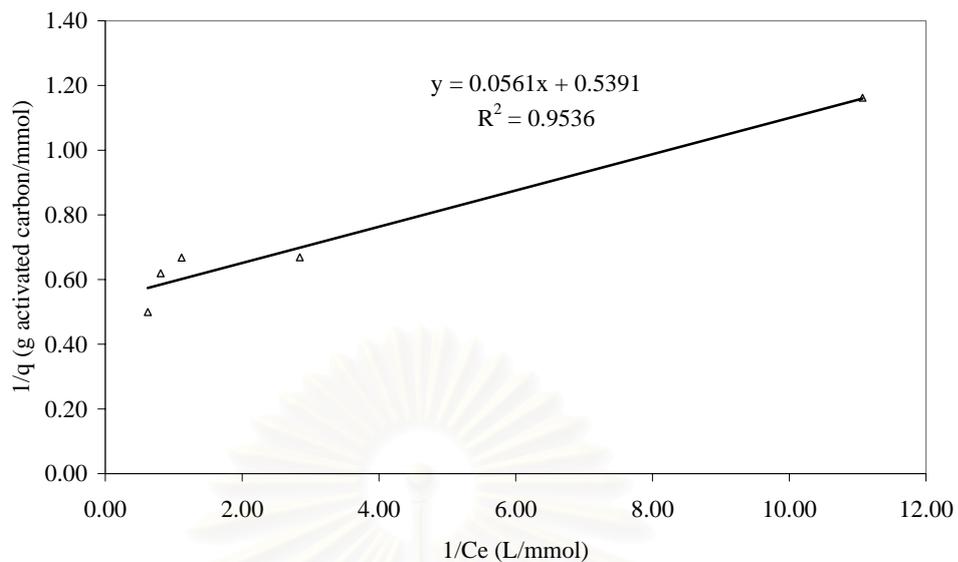
Figure 4.3 The Langmuir adsorption isotherm of hexanol onto activated carbon surface
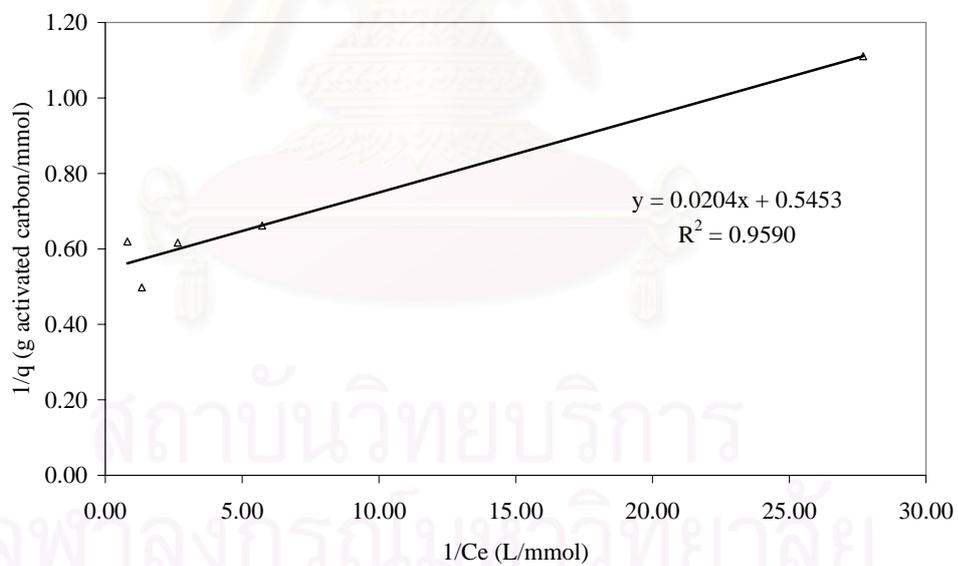
Figure 4.4 The Langmuir adsorption isotherm of heptanol onto activated carbon surface
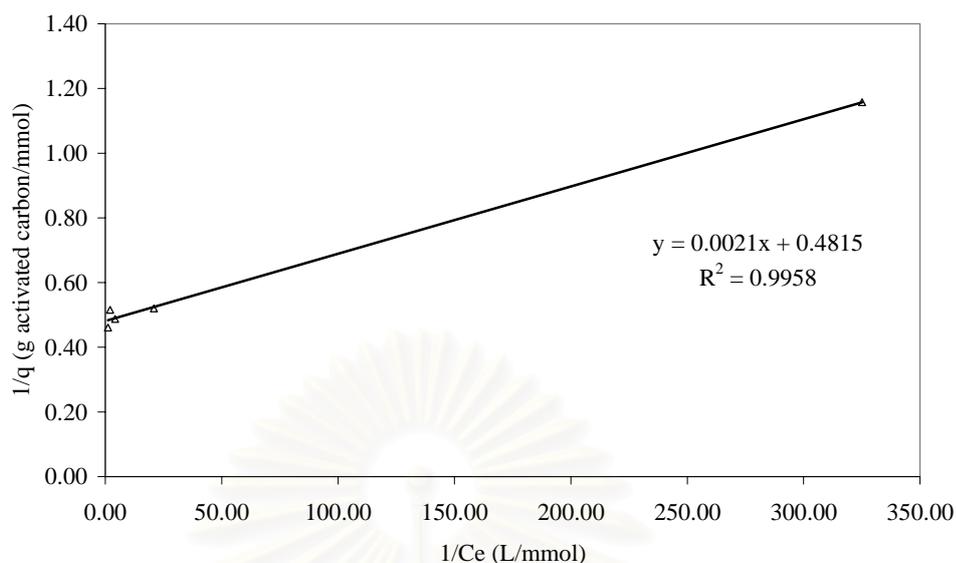
Figure 4.5 The Langmuir adsorption isotherm of octanol onto activated carbon surface

Table 4.2 Summarized results of Langmuir adsorption isotherm parameters, the adsorption coefficient and the normalized adsorption coefficients by specific surface area

Alcohols	Langmuir isotherm		Adsorption coefficient	
	K_L (L/mol)	a (mmol/g)	K_d (L/kg)	K_d/SSA (L/m^2)
Butanol	751.19	1.5795	1186.52	1.98E-03
Pentanol	2222.17	1.9643	4364.91	7.27E-03
Hexanol	9609.63	1.8549	17825.31	2.97E-02
Heptanol	26730.39	1.8339	49019.61	8.17E-02
Octanol	229285.71	2.0768	476190.48	7.94E-01

Effect of hydrophobicity of n-alcohol for adsorption onto powder activated carbon

It is noticed that when the number of carbon in the alcohol chain length increased, the adsorption onto powder activated carbon also increases. In several investigations of varied hydrophobicity or water solubility of compounds on adsorption, the higher hydrophobicity or the less of water solubility of compound, the greater adsorption is found because of the hydrophobic interaction (Palmer et al., 1992; Clausen et al., 2001; Intravichit, 2003; Sanemasa et. al., 2003). From figure 4.6, the relation between the octanol-water partition coefficient (K_{ow}), which has been taken as an indication of a relative hydrophobicity of alcohols, and the adsorption coefficient which were normalized by specific surface area (K_d/SSA) was plotted. The linear relation was found between log K_{ow} and log K_d/SSA as shown in figure 4.6. The correlation between these two parameters can be explained by this equation with $R^2 = 0.9382$.

$$\log K_d / SSA = 1.1239 \log K_{ow} - 3.8020 \qquad (4.1)$$

This result indicated that the hydrophobicity of compounds affects the adsorption onto non-polar activated carbon surface. Thus, the hydrophobic interaction plays an important role in the adsorption of alcohols onto activated carbon.
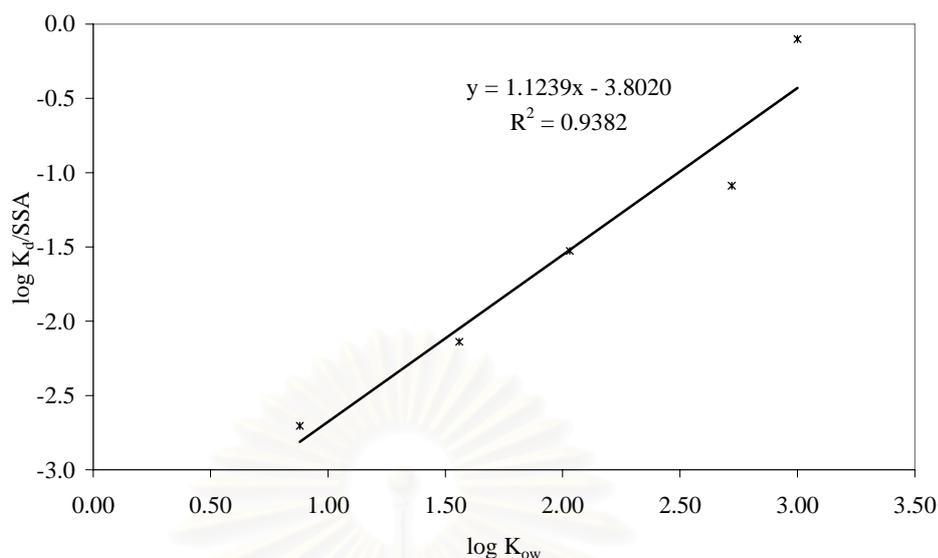
Figure 4.6 Relation between the octanol-water partition coefficient (K_{ow}) and the normalized adsorption coefficient by specific surface area (K_d/SSA)

4.1.4 Adsorption isotherm for n-alcohols onto AMBERLITE XAD 761

The results for adsorption of three n-alcohols; butanol, hexanol and octanol, onto AMBERLITE XAD 761 were analyzed by mean of Linear, Langmuir and Freundlich adsorption isotherms as shown in table 4.3. The Freundlich isotherm shows the best fit. The adsorption isotherms indicate that there are more than one adsorption layer with the interaction among adsorbate molecules.

Table 4.3 Summary results of Linear, Langmuir and Freundlich isotherm parameters and correlation coefficient (R^2)

Alcohols	Linear isotherm		Langmuir isotherm			Freundlich isotherm		
	K_d (L/g)	R^2	K_L (L/mol)	R^2	a (mmol/g)	K_{fr} (g/g XAD 761) $(L/g)^N$	R^2	N
Butanol	0.03	0.7419	0.02	0.7939	1.5618	0.9738	0.8894	0.5052
Hexanol	0.11	0.9465	785.99	0.9541	0.2714	1.2201	0.9703	1.3269
Octanol	0.80	0.8935	6385.78	0.9799	0.3650	0.4288	0.9972	1.5911

A plot of log Ce vs. log q yielded a straight line as shown in figure 4.7-4.9. Summarized results including the Freundlich constant (K_{fr}), the exponent coefficient (N) and correlation coefficient (R^2) are given in table 4.3.
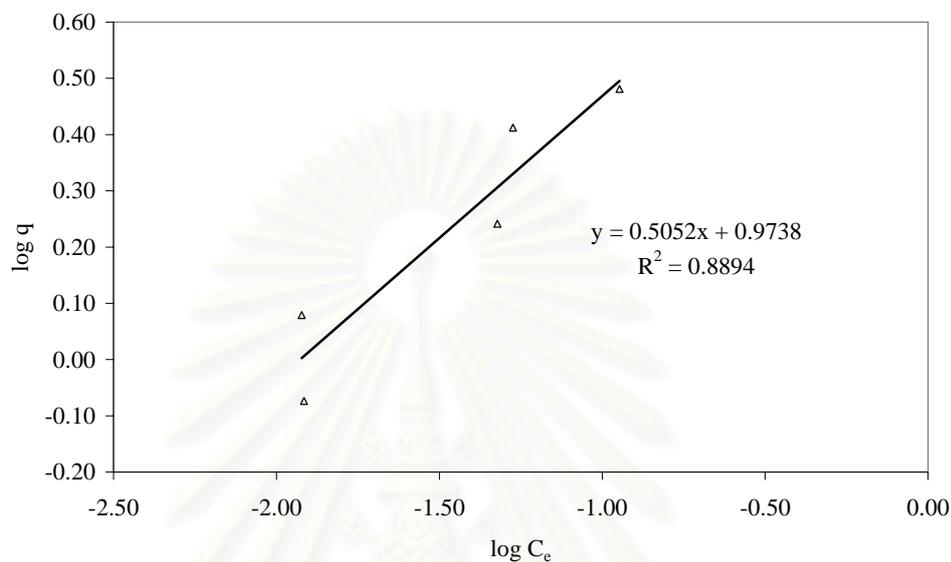
Figure 4.7 The Freundlich adsorption isotherm of butanol onto AMBERLITE XAD 761
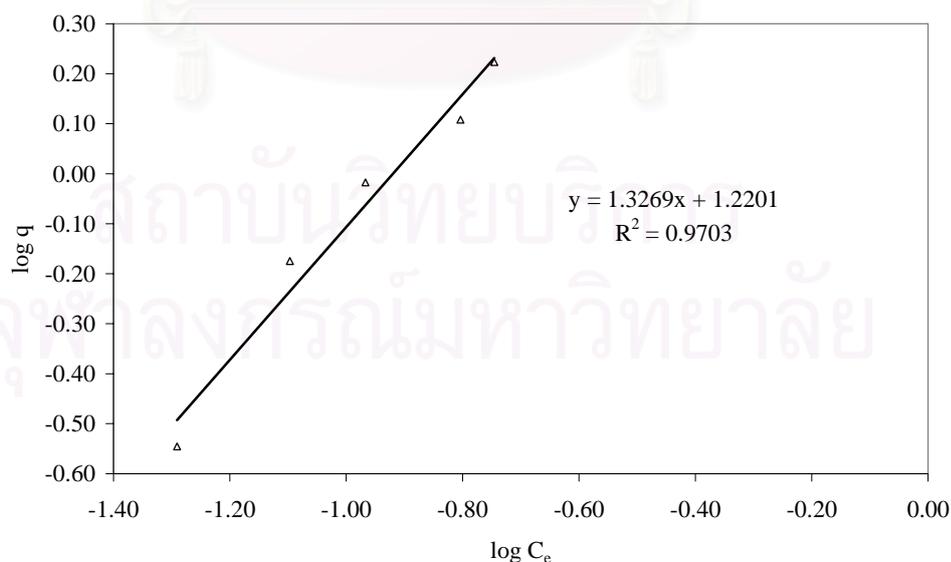
Figure 4.8 The Freundlich adsorption isotherm of hexanol onto AMBERLITE XAD 761
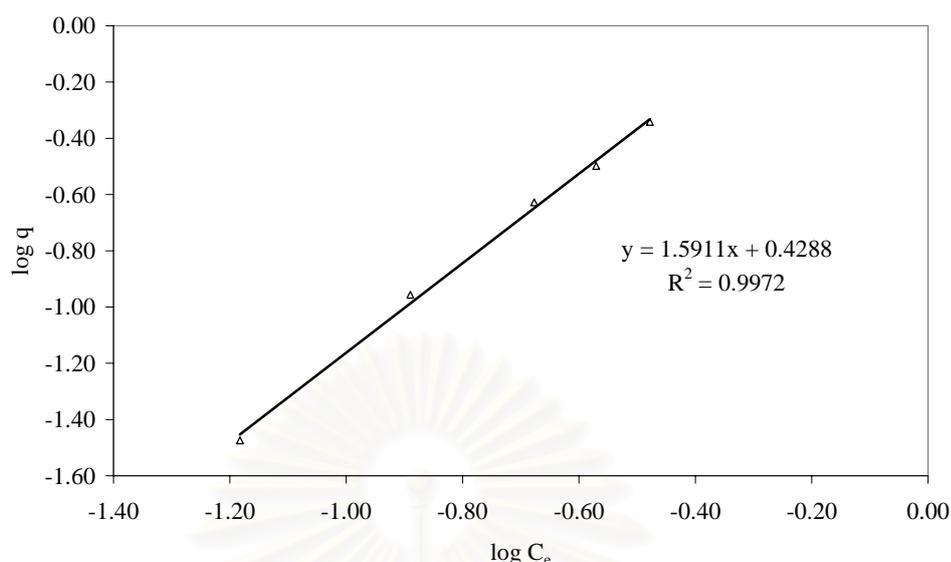
Figure 4.9 The Freundlich adsorption isotherm of octanol onto AMBERLITE XAD 761

Effect of hydrophobicity of n-alcohol for adsorption onto AMBERLITE XAD 761

The comparison of Freundlich adsorption coefficient (K_{fr}) is quite difficult because of the varying exponent coefficient (N). Adsorption isotherms are shown in figure 4.10. The degree of adsorption tends to increase with increasing the number of carbons in the alcohol chain length as shown in table 4.3 and figure 4.10. The result was consistent to many investigations on the effect of varied hydrophobicity of adsorbate on the adsorption (Palmer et al., 1992; Clausen et al., 2001; Intravichit, 2003; Sanemasa et. al., 2003).

Since AMBERLITE XAD 761 is porous phenolic polymer, it is classified as hydrophilic surface as compared to the nonpolar activated carbon. The hydrophilic (specific) interaction between hydroxyl moiety of alcohol and AMBERLITE XAD 761 phenolic surface occurs in the adsorption process. The adsorption of alcohol

molecules on the AMBERLITE XAD 761 surface (first layer) is not resulted by the hydrophobic interaction since the adsorption of nonpolar molecules is not favorable onto this surface (Rohm and Haas Co., 2004). However, not only hydrophilic interaction occurs in the adsorption process but also the hydrophobic interaction between alcohol molecules themselves. If only hydrophilic interaction is dominant, the butanol which has the highest relative hydrophilicity among alcohols studied here will show the greatest adsorption. From the results, it was shown that the octanol on the other hand has the highest adsorbed amount per gram of AMBERLITE XAD 761 (q). This can be explained by the solvent motivated mechanism in which the repulsion of the hydrophobic molecules from water promotes the adsorption. It corresponds to the results that the adsorption of alcohol onto AMBERLITE XAD 761 surface followed the Freundlich isotherm in which the multilayer adsorption occurring. Thus, the hydrophobic interaction between alkyl chains of alcohol molecules results in the multilayer adsorption excluding the first layer on the surface where the hydrophilic interaction is dominant.
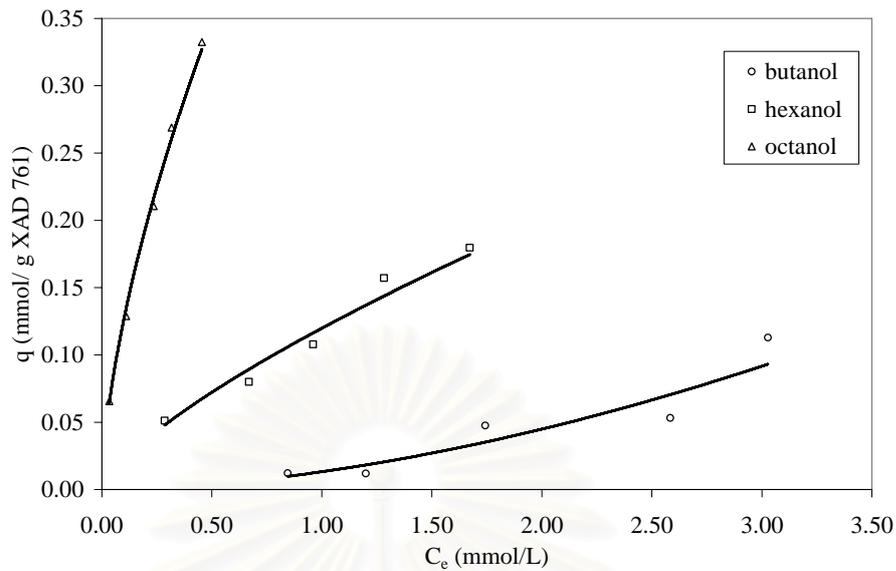
Figure 4.10 Adsorption isotherms of alcohols onto AMBERLITE XAD 761 surface

4.2 Surface Tension, Interfacial Tension, and Contact Angle Studies.

Effect of hydrophobicity of n-alcohol on surface tension, interfacial tension and contact angle

The surface tension decreases with increasing the concentration of alcohol solutions because of the orientation of alcohols (Stanners et al., 1995) as shown in figure 4.11 but no significant effect is found on the interfacial tension and the contact angle. Figure 4.12 shows the correlation between alcohol concentration and the surface tension. The linear correlation with $R^2 = 0.8522$ can be explained by this equation.

$$ST = -75.229 \cdot C/_{Sw} + 67.581 \qquad (4.2)$$

where

ST   = surface tension (mN/m)

C   = solution concentration (mg/L)

S_w = water solubility (mg/L)
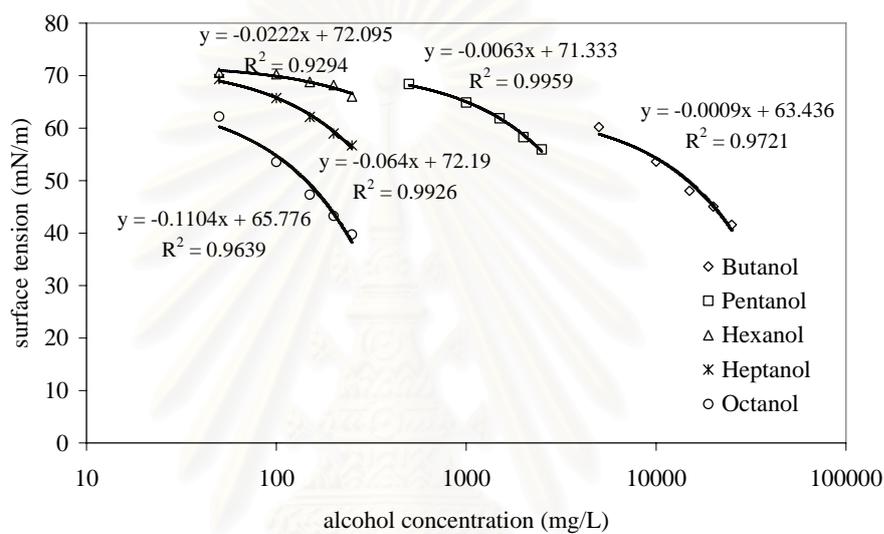
Figure 4.11 The relation between the alcohols concentration and the surface tension
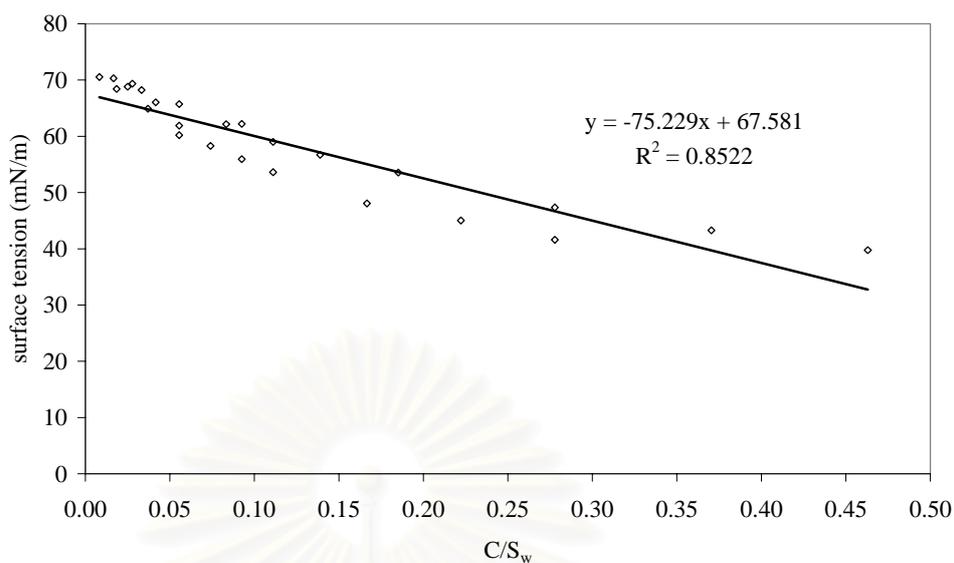
Figure 4.12 The correlation between alcohol concentration and surface tension

The equation (4.2) was normalized in order to make it applicable to any alcohols regardless to their hydrophobicity. When the alcohol concentration increases, the surface tension tends to decrease.

Table 4.4 Surface tension and interfacial tension of pure alcohols

Alcohols	Surface Tension (mN/m)	Interfacial Tension* (mN/m)
1-butanol	24.1	1.8
1-pentanol	25.1	4.4
1-hexanol	25.7	6.8
1-heptanol	26.5	7.7
1-octanol	27.0	8.5

* Adopted from Birdi, K. S., 2003 (12)

The surface tension and the interfacial tension of pure alcohols were illustrated in Table 4.4. The result showed that the degree of hydrophobicity of alcohol molecules slightly raises the surface tension. Nevertheless, the interfacial tension obviously increases upon the degree of hydrophobicity of alcohol molecules due to an increase in the dissimilarity between alcohol/water interfaces. The correlation between the degree of hydrophobicity using K_{ow} as a representative and the surface tension and the interfacial tension were shown in figure 4.13 and 4.14, respectively. In addition, the contact angles of alcohols on the surfaces do not change with the degree of hydrophobicity.
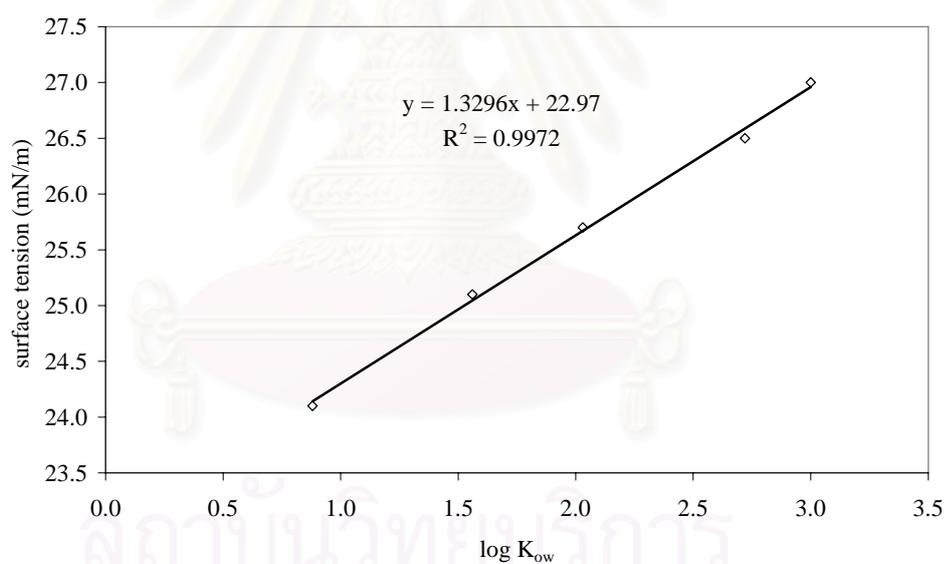
Figure 4.13 The correlation between the degree of hydrophobicity and the surface tension
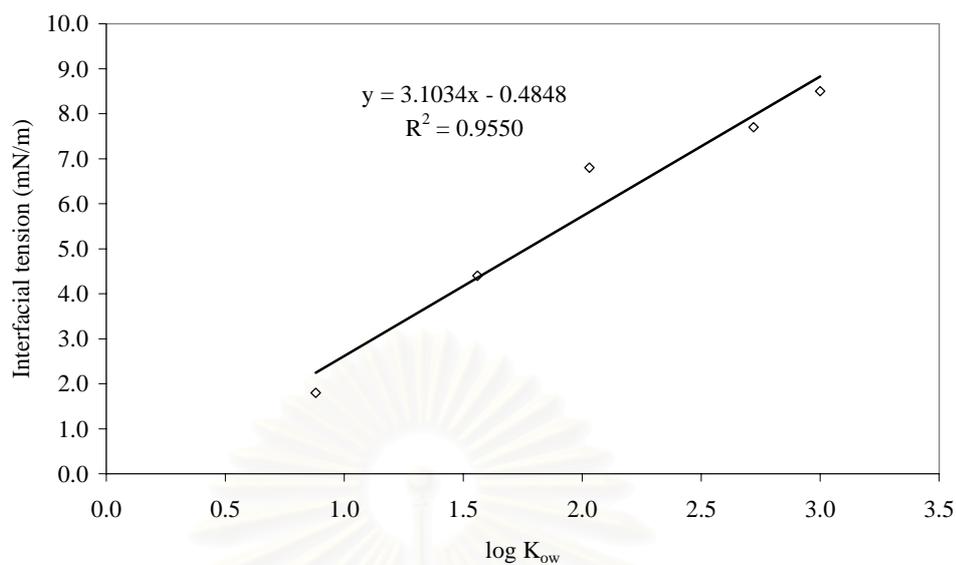
Figure 4.14 The correlation between the degree of hydrophobicity and the interfacial tension

The linear correlation equations of surface tension with $R^2 = 0.9972$ and interfacial tension with $R^2 = 0.9550$ can be expressed by equation (4.3) and (4.5), respectively.

$$ST(pure) = 1.3296 \log K_{ow} + 22.97 \qquad (4.3)$$

$$IFT(pure) = 3.1034 \log K_{ow} - 0.4848 \qquad (4.4)$$

where

ST (pure)   = Surface tension of pure alcohols (mN/m)

IFT (pure)   = Interfacial tension of pure alcohols (mN/m)

4.3 The Correlation between Adsorption and Surface Tension and Interfacial Tension

The correlation between the adsorption coefficient which was normalized by specific surface area (K_d/SSA) onto powder activated carbon and the surface tension and interfacial tension of pure alcohols were shown in figure 4.15 and 4.16, respectively.
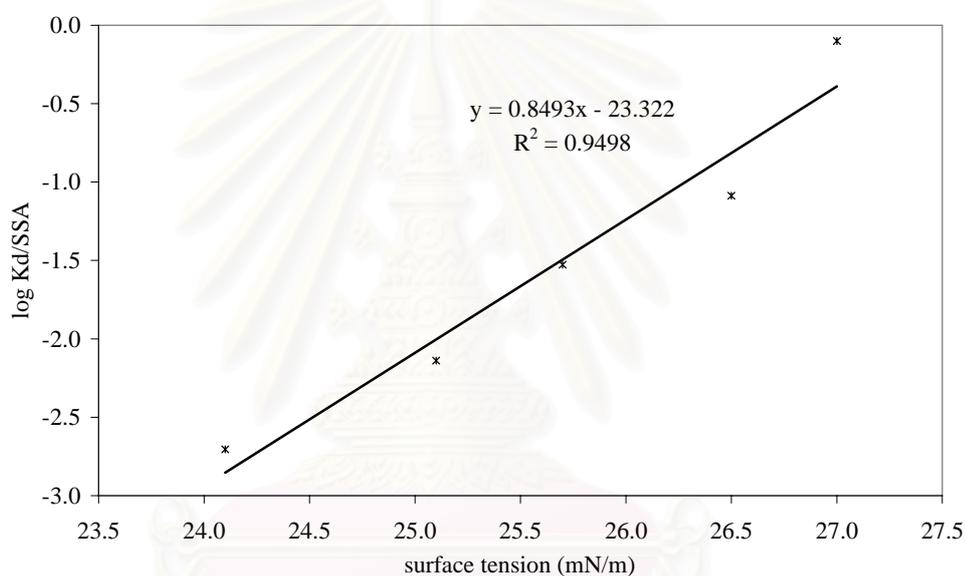
Figure 4.15 The correlation between surface tension and logarithm of the normalized adsorption coefficient by specific surface area (log K_d/SSA)
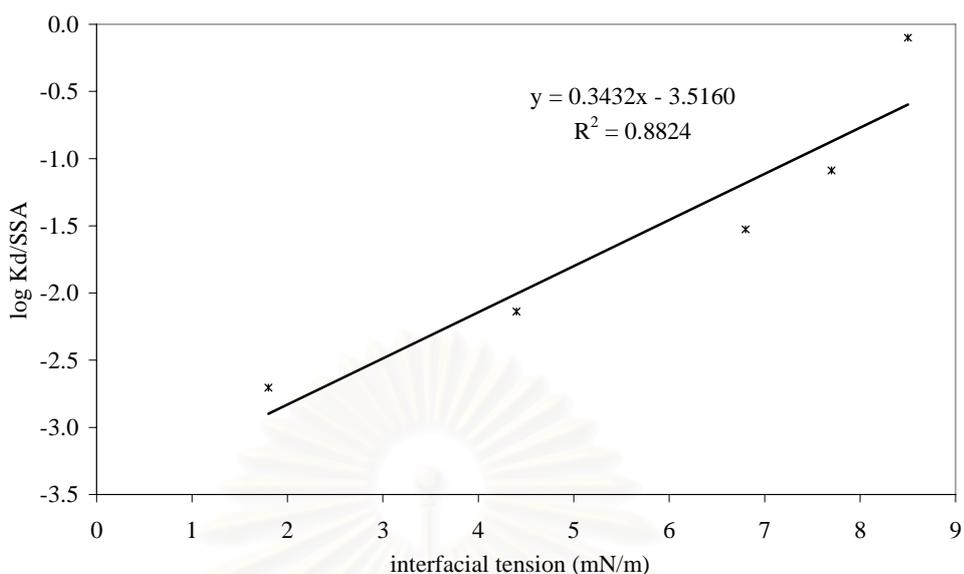
Figure 4.15 The correlation between interfacial tension and logarithm of the normalized adsorption coefficient by specific surface area (log K_d/SSA)

The linear correlation equations of the adsorption coefficient and surface tension with $R^2 = 0.9498$ and interfacial tension with $R^2 = 0.8824$ can be expressed by equation (4.5) and (4.6), respectively. These equations can be applied only to alcohol molecules as the adsorbate and powder activated carbon as the adsorbent.

$$\log K_d / SSA = 0.8493 \cdot ST(pure) - 23.3220 \qquad (4.5)$$

$$\log K_d / SSA = 0.3423 \cdot IFT(pure) - 3.5160 \qquad (4.6)$$

These two equations can be used to estimate the adsorption behavior of the amphiphile alcohol molecules onto activated carbon surface by mean of adsorption coefficient. Instead of conducting adsorption study in the laboratory, these equations

can be applied by only measuring the surface or interfacial tension of pure alcohol which is quite straight forward experiment. Then the adsorption coefficient can be directly estimated. However, these equations are limited to alcohol molecules as the adsorbate and activated carbon as the adsorbent only.

The correlation between adsorption onto AMBERLITE XAD 761 and the surface tension and interfacial tension of pure alcohols cannot be explained by the empirical equations since the adsorption coefficient (K_d) cannot be readily evaluated owing to the exponent coefficient (N) difference. However, the relationship can be roughly predicted in the sense that the adsorption increases with increasing surface tension and interfacial tension.
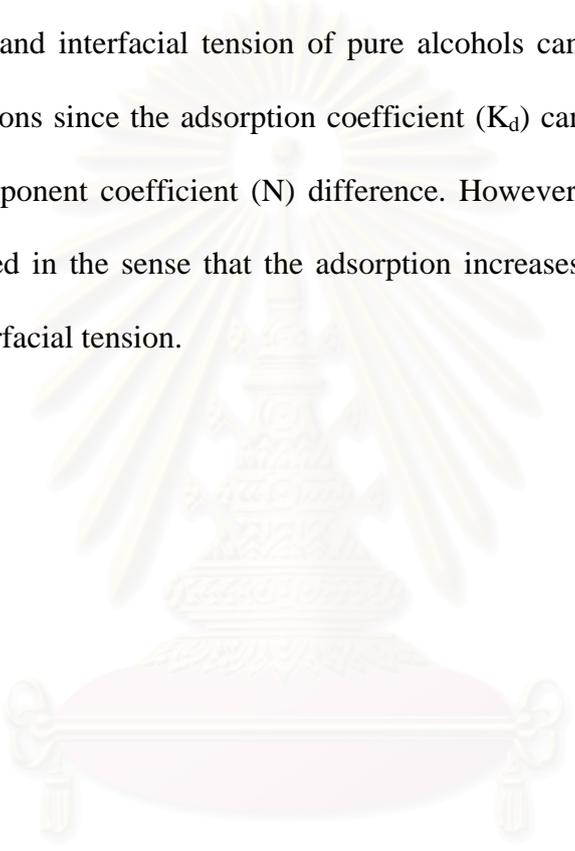
CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Alcohols adsorb onto powder activated carbon and AMBERLITE XAD 761 while showing no significant adsorption onto alumina and silica. On powder activated carbon, the adsorptions are Langmuir adsorption isotherm. The adsorption coefficients which were normalized by specific surface area are 1.98, 7.27, 29.70, 81.70 and 794.00 mL/m^2 for butanol, pentanol, hexanol, heptanol, and octanol, respectively. On AMBERLITE XAD 761, the adsorptions follow Freundlich adsorption isotherm by these following equations: $q = 0.9738$ (g/g XAD 761) (L/g)^N x $C_e^{0.5052}$; $q = 1.2201$ (g/g XAD 761) (L/g)^N x $C_e^{1.3269}$; and $q = 0.4288$ (g/g XAD 761) (L/g)^N x $C_e^{1.5911}$ for butanol, hexanol, and octanol, respectively. In conclusion, the hydrophobic interaction plays an important role in adsorption. For alumina and silica, there is no adsorption of alcohols. This indicates that there are no electrostatic interactions since alcohols have weak degree of dissociation and still exhibit neutral form.

In conclusion, the degree of hydrophobicity of alcohols affects the adsorption onto the organic surfaces. The magnitude of the adsorption depends on the properties of adsorbate (e.g., the molecular structure, the functional group, the degree of dissociation and the hydrophobicity of molecule) and the adsorbent properties (e.g., the surface characteristics including charged, surface area, surface homogeneity, etc.).

Some aspects related to fate and transport of amphiphile molecule on the environment can be revealed via the adsorption results obtained from this study. The results of adsorption onto alumina and silica, which represent the natural media, can

be concluded that the pharmaceutical molecules containing the hydroxyl functional group do not adsorb onto these subsurface media. This indicates that the pharmaceutical molecules which have the functional group similar to alcohols can spread on the environment through the groundwater with no adsorption if the subsurface composes of mineral media with no organic content.

For the adsorption onto powder activated carbon and AMBERLITE XAD 761, the adsorptions depend on the surface properties and the structure of molecules. These media represent soil containing organic matter. It is a heterogeneous mixture of different materials such as residues from microbial degradation of higher plants and carbonaceous particles from incomplete combustion of plant materials. The organic matter is the most important parameter governing the adsorption and thus the fate and transport of the pollutant in soils and sediments. The results showed that the adsorption increases with increasing the degree of hydrophobicity of alcohols. So, the pharmaceutical molecules with high degree of hydrophobicity prefer to adsorb onto this organic soil, while the lower ones prefer to spread on the environment.

In summary, the fate and transport of pharmaceutical pollutant depends on both contaminant and surface properties. The adsorption is one of parameters used to predict the contaminant migration. The lower the adsorption, the greater movement occurs since the contaminant is less retarded. The findings of this study on the adsorption can be used to predict the migration of pollutant plume in the subsurface, in which the proper management for remediation can be determined afterward.

The degree of hydrophobicity of amphiphile molecules affects the interfacial properties only on the surface tension and the interfacial tension but not on the contact angle. The surface tension and interfacial tension of pure alcohols increase with

increasing the hydrophobicity. Moreover, the surface tension decreases with increasing the concentration of alcohol solutions but no significant effect is found on the interfacial tension.

The adsorption of alcohols onto non-polar surface (powder activated carbon) correlates to some interfacial properties (i.e., surface tension and interfacial tension). This finding is of importance because it is the fundamental knowledge for understanding the relation between adsorption of amphiphile molecule and the interfacial properties. The correlation can be applied to estimate the adsorption behavior via the interfacial properties under certain limitations that the amphiphile molecules must have similar properties to alcohols and the adsorbents should possess the nonpolar characteristic alike the activated carbon.

5.2 Recommendations

Because the fate and transport of pharmaceuticals are poorly understood, the study in this topic is necessary. For future research works, the study of various amphiphile molecules with different classes is required to investigate the behavior of these molecules in the subsurface. The correlation among the adsorption and the interface properties of other amphiphile molecules besides alcohols should be conducted to reduce the factors for the adsorption estimation. Moreover, the study of the actual pharmaceuticals and the real natural soil should be conducted to evaluate the fate and transport of pharmaceuticals in the real situation.

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APPENDICES

Table A-1 the adsorption data for butanol on alumina, ratio 1:44

Initial conc. (mg/L)	C_{eq} (mg/L)			Avg.	%RSD	C_{blank}(mg/L)			Avg.	%RSD	Ads. Conc. (mg/L)			q (mg/g alumina)			Avg.
	no. 1	no. 2	no. 3			no. 1	no. 2	no. 3			no. 1	no. 2	no. 3	no. 1	no. 2	no. 3	
50	53.80	53.26	58.10	55.05	4.82	58.21	58.88	58.54	58.54	0.57	4.74	5.29	0.44	0.21	0.23	0.02	0.15
100	115.12	115.30	97.25	109.22	9.49	114.28	110.20	109.49	111.32	2.32	-3.80	-3.98	14.07	-0.17	-0.18	0.62	0.09
150	158.91	139.81	155.92	151.54	6.78	160.98	169.06	165.02	165.02	2.45	6.11	25.21	9.10	0.27	1.11	0.40	0.59
200	212.15	208.59	211.10	210.62	0.87	213.89	210.07	208.44	210.80	1.28	-1.35	2.21	-0.30	-0.06	0.10	-0.01	0.01
250	274.73	282.01	264.96	273.90	3.12	280.74	277.91	273.96	277.54	1.23	2.81	-4.48	12.58	0.12	-0.20	0.55	0.16

Table A-2 the adsorption data for pentanol on alumina, ratio 1:44

Initial conc. (mg/L)	C_{eq} (mg/L)			Avg.	%RSD	C_{blank}(mg/L)			Avg.	%RSD	Ads. Conc. (mg/L)			q (mg/g alumina)			Avg.
	no. 1	no. 2	no. 3			no. 1	no. 2	no. 3			no. 1	no. 2	no. 3	no. 1	no. 2	no. 3	
50	49.96	47.67	49.35	48.99	2.42	50.81	56.22	55.35	54.13	5.37	4.17	6.46	4.78	0.18	0.28	0.21	0.22
100	100.24	101.35	105.12	102.24	2.50	103.80	111.55	103.32	106.22	4.35	5.98	4.87	1.10	0.26	0.21	0.05	0.18
150	154.01	156.39	154.54	154.98	0.81	145.06	142.22	139.98	142.42	1.79	-11.59	-13.97	-12.12	-0.51	-0.62	-0.53	-0.55
200	185.58	187.90	189.56	187.68	1.07	201.88	198.13	180.87	193.63	5.79	8.05	5.73	4.07	0.35	0.25	0.18	0.26
250	253.90	231.15	220.16	235.07	7.32	222.04	226.30	219.35	222.56	1.57	-31.34	-8.59	2.40	-1.38	-0.38	0.11	-0.55

Table A-3 the adsorption data for hexanol on alumina, ratio 1:44

Initial conc. (mg/L)	C_{eq} (mg/L) no. 1	no. 2	no. 3	Avg.	%RSD	C_{blank}(mg/L) no. 1	no. 2	no. 3	Avg.	%RSD	Ads. Conc. (mg/L) no. 1	no. 2	no. 3	q (mg/g alumina) no. 1	no. 2	no. 3	Avg.
50	63.61	63.55	56.88	61.35	6.31	57.59	58.28	61.31	59.06	3.35	-4.55	-4.49	2.18	-0.20	-0.20	0.10	-0.10
100	126.07	123.65	123.10	124.27	1.27	112.51	123.30	129.33	121.71	7.00	-4.36	-1.94	-1.39	-0.19	-0.08	-0.06	-0.11
150	175.03	162.10	162.72	166.62	4.38	167.02	166.74	168.42	167.39	0.54	-7.64	5.29	4.67	-0.34	0.23	0.21	0.03
200	232.65	215.67	215.28	221.20	4.48	211.08	218.48	224.21	217.92	3.02	-14.73	2.25	2.64	-0.64	0.10	0.12	-0.14
250	252.92	303.99	281.23	279.38	9.16	261.48	305.29	304.55	290.44	8.64	37.52	-13.55	9.21	1.64	-0.59	0.40	0.49

Table A-4 the adsorption data for heptanol on alumina, ratio 1:44

Initial conc. (mg/L)	C_{eq} (mg/L) no. 1	no. 2	no. 3	Avg.	%RSD	C_{blank}(mg/L) no. 1	no. 2	no. 3	Avg.	%RSD	Ads. Conc. (mg/L) no. 1	no. 2	no. 3	q (mg/g alumina) no. 1	no. 2	no. 3	Avg.
50	52.84	56.57	46.69	52.03	9.59	51.73	53.99	55.66	53.79	3.67	0.95	-2.78	7.10	0.04	-0.12	0.31	0.08
100	98.19	102.30	98.92	99.80	2.20	99.70	106.21	105.05	103.65	3.35	5.46	1.35	4.73	0.24	0.06	0.21	0.17
150	149.97	150.57	146.08	148.87	1.64	158.91	162.80	163.44	161.72	1.52	11.75	11.15	15.64	0.51	0.49	0.69	0.56
200	186.24	201.86	205.53	197.88	5.18	226.06	194.09	205.63	208.59	7.76	22.35	6.73	3.06	0.98	0.30	0.13	0.47
250	213.41	213.94	213.60	213.65	0.13	270.78	228.62	275.01	258.14	9.94	44.73	44.20	44.54	1.97	1.94	1.96	1.95

Table A-5 the adsorption data for octanol on alumina, ratio 1:44

Initial conc. (mg/L)	C_{eq} (mg/L)			Avg.	%RSD	C_{blank}(mg/L)			Avg.	%RSD	Ads. Conc. (mg/L)			q (mg/g alumina)			Avg.
	no. 1	no. 2	no. 3			no. 1	no. 2	no. 3			no. 1	no. 2	no. 3	no. 1	no. 2	no. 3	
50	38.35	36.02	37.61	37.32	3.19	45.28	39.53	34.21	39.67	13.95	1.33	3.66	2.07	0.06	0.16	0.09	0.10
100	84.51	82.33	83.15	83.33	1.32	85.93	87.04	86.74	86.57	0.66	2.06	4.24	3.42	0.09	0.19	0.15	0.14
150	106.67	117.56	114.64	112.95	4.99	128.81	125.02	148.65	134.16	9.46	27.49	16.60	19.52	1.21	0.72	0.86	0.93
200	150.66	162.47	158.01	157.05	3.80	160.22	154.35	161.66	158.75	2.44	8.09	-3.72	0.73	0.36	-0.16	0.03	0.07
250	202.92	200.68	202.27	201.96	0.57	217.64	226.79	203.65	216.03	5.39	13.11	15.34	13.76	0.57	0.67	0.60	0.61

APPENDIX B

Table B-1 the adsorption data for butanol on silica, ratio 1:44

Initial conc. (mg/L)	C_{eq} (mg/L)			Avg.	%RSD	C_{blank} (mg/L)			Avg.	%RSD	Ads. Conc. (mg/L)			q (mg/g silica)			Avg.
	no. 1	no. 2	no. 3			no. 1	no. 2	no. 3			no. 1	no. 2	no. 3	no. 1	no. 2	no. 3	
50	56.75	55.99	58.75	57.16	2.50	58.21	58.88	58.00	58.36	0.79	1.62	2.38	-0.39	0.07	0.10	-0.02	0.05
100	107.60	111.90	111.89	110.46	2.25	114.28	110.20	109.49	111.32	2.32	3.72	-0.58	-0.57	0.16	-0.03	-0.02	0.04
150	163.58	162.95	160.84	162.45	0.88	160.98	169.06	165.68	165.24	2.46	1.66	2.29	4.40	0.07	0.10	0.19	0.12
200	201.38	200.98	198.99	200.45	0.64	198.44	207.44	203.56	203.15	2.22	1.76	2.17	4.16	0.08	0.09	0.18	0.12
250	276.29	275.38	274.98	275.55	0.24	280.74	273.96	276.97	277.23	1.22	0.94	1.84	2.24	0.04	0.08	0.10	0.07

Table B-2 the adsorption data for pentanol on silica, ratio 1:44

Initial conc. (mg/L)	C_{eq} (mg/L)			Avg.	%RSD	C_{blank} (mg/L)			Avg.	%RSD	Ads. Conc. (mg/L)			q (mg/g silica)			Avg.
	no. 1	no. 2	no. 3			no. 1	no. 2	no. 3			no. 1	no. 2	no. 3	no. 1	no. 2	no. 3	
50	56.17	54.51	50.66	53.78	5.26	50.81	56.22	55.35	54.13	5.37	-2.04	-0.38	3.47	-0.09	-0.02	0.15	0.02
100	89.82	94.34	84.30	89.49	5.62	103.80	111.55	103.32	106.22	4.35	16.40	11.88	21.92	0.72	0.52	0.96	0.73
150	124.17	148.85	129.37	134.13	9.70	145.06	142.22	139.98	142.42	1.79	18.25	-6.43	13.05	0.80	-0.28	0.57	0.36
200	189.94	181.63	184.80	185.46	2.26	201.88	198.13	180.87	193.63	5.79	3.69	12.00	8.83	0.16	0.52	0.39	0.36
250	220.57	223.69	219.16	221.14	1.05	222.04	226.30	219.35	222.56	1.57	1.99	-1.13	3.40	0.09	-0.05	0.15	0.06

Table B-3 the adsorption data for hexanol on silica, ratio 1:44

Initial conc. (mg/L)	C_{eq} (mg/L)			Avg.	%RSD	C_{blank} (mg/L)			Avg.	%RSD	Ads. Conc. (mg/L)			q (mg/g silica)			Avg.
	no. 1	no. 2	no. 3			no. 1	no. 2	no. 3			no. 1	no. 2	no. 3	no. 1	no. 2	no. 3	
50	68.19	61.24	56.08	61.84	9.83	57.59	58.28	61.31	59.06	3.35	-9.13	-2.18	2.98	-0.40	-0.10	0.13	-0.12
100	106.80	100.81	107.13	104.91	3.39	112.51	123.30	129.33	121.71	7.00	14.91	20.90	14.58	0.66	0.91	0.64	0.74
150	170.58	163.80	160.29	164.89	3.17	167.02	166.74	168.42	167.39	0.54	-3.19	3.59	7.10	-0.14	0.16	0.31	0.11
200	221.28	193.66	228.58	214.51	8.59	211.08	218.48	224.21	217.92	3.02	-3.36	24.26	-10.66	-0.15	1.05	-0.46	0.15
250	264.15	307.59	276.05	282.60	7.94	261.48	305.29	304.55	290.44	8.64	26.29	-17.15	14.39	1.14	-0.75	0.63	0.34

Table B-4 the adsorption data for heptanol on silica, ratio 1:44

Initial conc. (mg/L)	C_{eq} (mg/L)			Avg.	%RSD	C_{blank} (mg/L)			Avg.	%RSD	Ads. Conc. (mg/L)			q (mg/g silica)			Avg.
	no. 1	no. 2	no. 3			no. 1	no. 2	no. 3			no. 1	no. 2	no. 3	no. 1	no. 2	no. 3	
50	51.23	50.90	52.87	51.67	2.04	51.73	53.99	55.66	53.79	3.67	2.56	2.90	0.92	0.11	0.13	0.04	0.09
100	97.47	102.63	101.63	100.58	2.72	99.70	106.21	105.05	103.65	3.35	6.18	1.02	2.02	0.27	0.05	0.09	0.13
150	130.76	127.41	152.42	136.86	9.92	158.91	161.00	163.44	161.12	1.41	30.36	33.71	8.70	1.33	1.47	0.38	1.06
200	200.81	196.95	213.22	203.66	4.17	226.06	194.09	205.63	208.59	7.76	7.78	11.64	-4.63	0.34	0.51	-0.20	0.22
250	251.43	234.65	262.49	249.52	5.62	270.78	228.62	275.01	258.14	9.94	6.71	23.49	-4.35	0.29	1.03	-0.19	0.38

Table B-5 the adsorption data for octanol on silica, ratio 1:44

Initial conc. (mg/L)	C_{eq} (mg/L)			Avg.	%RSD	C_{blank}(mg/L)			Avg.	%RSD	Ads. Conc. (mg/L)			q (mg/g silica)			Avg.
	no. 1	no. 2	no. 3			no. 1	no. 2	no. 3			no. 1	no. 2	no. 3	no. 1	no. 2	no. 3	
50	40.42	37.62	39.90	39.31	3.79	45.28	39.53	34.21	39.67	13.95	-0.74	2.06	-0.22	-0.03	0.09	-0.01	0.02
100	86.44	81.58	82.21	83.41	3.17	85.93	87.04	86.74	86.57	0.66	0.13	4.99	4.36	0.01	0.22	0.19	0.14
150	115.65	115.57	126.27	119.17	5.16	128.81	125.02	148.65	134.16	9.46	18.51	18.59	7.89	0.81	0.81	0.35	0.66
200	159.83	159.81	159.89	159.84	0.03	160.22	154.35	161.66	158.75	2.44	-1.08	-1.07	-1.15	-0.05	-0.05	-0.05	-0.05
250	189.62	203.32	206.37	199.77	4.47	217.64	226.79	203.65	216.03	5.39	26.40	12.70	9.65	1.15	0.55	0.42	0.71

APPENDIX C

Table C-1 the adsorption data for butanol on powder activated carbon, ratio 1:2200

Initial conc. (mg/L)	C_{eq} (mg/L)			Avg.	%RSD	C_{blank}(mg/L)			Avg.	%RSD	Ads. Conc. (mg/L)			q (mg/g activated carbon)			Avg.
	no. 1	no. 2	no. 3			no. 1	no. 2	no. 3			no. 1	no. 2	no. 3	no. 1	no. 2	no. 3	
50	42.85	38.54	43.64	41.68	6.59	56.87	59.01	57.94	57.94	1.84	15.09	19.40	14.30	33.87	38.46	28.10	33.47
100	71.08	74.55	-	72.81	3.36	101.34	97.33	101.24	99.97	2.29	28.89	25.43	-	56.75	54.31	-	55.53
150	113.23	115.62	109.93	112.93	2.53	137.32	154.89	149.72	147.31	6.13	34.08	31.69	37.38	65.78	62.24	83.91	70.64
200	170.09	166.13	167.89	168.04	1.18	195.74	195.46	190.47	193.89	1.53	23.80	27.76	26.00	52.89	60.46	55.00	56.12
250	216.25	201.75	218.74	212.25	4.32	244.92	243.87	288.82	259.21	9.90	42.95	57.46	40.47	78.75	109.91	81.67	90.11

Table C-2 the adsorption data for pentanol on powder activated carbon, ratio 1:2200

Initial conc. (mg/L)	C_{eq} (mg/L)			Avg.	%RSD	C_{blank}(mg/L)			Avg.	%RSD	Ads. Conc. (mg/L)			q (mg/g activated carbon)			Avg.
	no. 1	no. 2	no. 3			no. 1	no. 2	no. 3			no. 1	no. 2	no. 3	no. 1	no. 2	no. 3	
50	29.85	30.51	28.05	29.47	4.32	60.05	59.86	60.19	60.04	0.28	30.18	29.53	31.98	62.64	78.27	72.54	71.15
100	57.12	59.23	57.64	58.00	1.90	110.05	105.63	108.51	108.06	2.08	50.94	48.83	50.42	127.35	119.36	109.84	118.85
150	105.38	104.42	99.62	103.14	2.99	155.28	146.05	156.64	152.65	3.78	47.27	48.24	53.03	114.28	119.24	137.26	123.59
200	137.36	134.37	128.66	133.46	3.31	171.88	196.79	201.14	189.93	8.31	52.58	55.56	61.28	124.38	127.32	128.39	126.70
250	180.13	190.60	210.70	193.81	8.02	265.46	257.51	241.83	254.93	4.72	74.81	64.33	44.23	164.57	136.08	111.86	137.50

Table C-3 the adsorption data for hexanol on powder activated carbon, ratio 1:2200

Initial conc. (mg/L)	C_{eq} (mg/L)			Avg.	%RSD	C_{blank}(mg/L)			Avg.	%RSD	Ads. Conc. (mg/L)			q (mg/g activated carbon)			Avg.
	no. 1	no. 2	no. 3			no. 1	no. 2	no. 3			no. 1	no. 2	no. 3	no. 1	no. 2	no. 3	
50	9.80	-	8.65	9.23	8.79	51.20	52.02	49.96	51.06	2.03	41.26	-	42.40	82.51	-	93.29	87.90
100	37.71	34.68	35.43	35.94	4.39	99.90	103.23	112.24	105.12	6.07	67.41	70.44	69.69	148.31	151.93	158.07	152.77
150	87.32	87.73	99.91	91.65	7.81	141.33	166.37	162.18	156.63	8.56	69.31	68.90	56.71	160.51	151.58	146.79	152.96
200	122.04	129.10	128.02	126.39	3.01	219.20	199.01	192.76	203.66	6.79	81.61	74.56	75.64	179.55	164.03	151.28	164.95
250	174.48	157.62	161.38	164.49	5.38	257.02	248.28	263.68	256.33	3.01	81.84	98.71	94.95	180.06	208.81	224.61	204.49

Table C-4 the adsorption data for heptanol on powder activated carbon, ratio 1:2200

Initial conc. (mg/L)	C_{eq} (mg/L)			Avg.	%RSD	C_{blank}(mg/L)			Avg.	%RSD	Ads. Conc. (mg/L)			q (mg/g activated carbon)			Avg.
	no. 1	no. 2	no. 3			no. 1	no. 2	no. 3			no. 1	no. 2	no. 3	no. 1	no. 2	no. 3	
50	4.19	-	4.19	4.19	0.03	49.91	50.83	45.90	48.88	5.36	44.68	-	44.68	106.85	-	102.40	104.63
100	-	19.97	20.57	20.27	2.10	85.60	94.84	99.42	93.29	7.55	-	73.32	72.72	-	175.34	175.81	175.57
150	44.78	45.23	41.98	44.00	4.00	139.61	137.18	128.58	135.12	4.29	90.34	89.89	93.14	185.74	186.57	193.31	188.54
200	91.78	83.48	86.64	87.30	4.80	196.35	196.63	198.85	197.28	0.69	105.50	113.80	110.64	232.10	229.69	238.63	233.47
250	152.96	-	134.89	143.93	8.88	216.06	237.92	249.46	234.48	7.23	81.52	-	99.59	164.54	-	210.68	187.61

Table C-5 the adsorption data for octanol on powder activated carbon, ratio 1:2200

Initial conc. (mg/L)	C_{eq} (mg/L)			Avg.	%RSD	C_{blank}(mg/L)			Avg.	%RSD	Ads. Conc. (mg/L)			q (mg/g activated carbon)			Avg.
	no. 1	no. 2	no. 3			no. 1	no. 2	no. 3			no. 1	no. 2	no. 3	no. 1	no. 2	no. 3	
50	0.38	0.42	-	0.40	7.24	45.89	49.85	-	47.87	5.84	47.49	47.45	-	107.71	117.29	-	112.50
100	6.37	6.12	6.24	6.25	1.99	112.51	112.50	113.56	112.86	0.54	106.49	106.74	106.62	254.64	249.81	246.90	250.45
150	-	30.07	31.90	30.99	4.18	149.21	144.73	133.76	142.57	5.58	-	112.49	110.66	-	274.99	259.00	266.99
200	69.68	62.87	63.36	65.30	5.82	183.26	174.40	192.79	183.48	5.01	113.80	120.62	120.12	269.21	241.23	246.98	252.48
250	116.57	118.54	125.35	120.16	3.83	255.70	225.23	260.62	247.18	7.76	130.61	128.64	121.83	302.46	277.46	268.02	282.65

APPENDIX D

Table D-1 the adsorption data for butanol on AMBERLITE XAD 761, ratio 1:220

Initial conc. (mg/L)	C_{eq} (mg/L) no. 1	no. 2	no. 3	Avg.	%RSD	C_{blank}(mg/L) no. 1	no. 2	no. 3	Avg.	%RSD	Ads. Conc. (mg/L) no. 1	no. 2	no. 3	q (mg/g XAD 761) no. 1	no. 2	no. 3	Avg.
50	65.22	59.94	62.58	62.58	4.22	66.14	66.47	66.80	66.47	0.49	1.24	6.53	3.89	0.29	1.51	0.90	0.90
100	86.76	91.18	88.90	88.95	2.48	91.05	92.69	94.33	92.69	1.77	5.92	1.51	3.79	1.42	0.36	0.88	0.89
150	125.73	131.49	130.37	129.20	2.36	143.78	144.14	144.49	144.14	0.25	18.40	12.64	13.77	4.39	3.02	3.19	3.53
200	198.22	189.32	187.09	191.54	3.07	206.49	208.17	209.84	208.17	0.81	9.95	18.85	21.08	2.37	4.58	4.88	3.94
250	214.47	234.31	224.39	224.39	4.42	260.74	260.74	260.74	260.74	0.00	46.27	26.43	36.35	10.66	6.04	8.42	8.37

Table D-2 the adsorption data for hexanol on AMBERLITE XAD 761, ratio 1:220

Initial conc. (mg/L)	C_{eq} (mg/L) no. 1	no. 2	no. 3	Avg.	%RSD	C_{blank}(mg/L) no. 1	no. 2	no. 3	Avg.	%RSD	Ads. Conc. (mg/L) no. 1	no. 2	no. 3	q (mg/g XAD 761) no. 1	no. 2	no. 3	Avg.
50	27.93	30.29	-	29.11	5.72	49.54	51.39	53.25	51.39	3.61	23.46	21.11	-	5.42	5.04	-	5.23
100	69.69	67.32	67.99	68.33	1.79	103.71	102.52	101.34	102.52	1.16	32.83	35.20	34.54	7.91	8.36	8.25	8.17
150	-	92.81	103.39	98.10	7.63	144.11	144.24	144.38	144.24	0.09	-	51.43	40.85	-	12.30	9.76	11.03
200	128.86	133.22	-	131.04	2.36	195.87	197.64	199.42	197.64	0.90	68.78	64.42	-	16.78	15.34	-	16.06
250	182.06	162.34	168.20	170.87	5.93	250.93	247.71	244.49	247.71	1.30	65.65	85.37	79.51	15.72	20.37	18.99	18.36

Table D-3 the adsorption data for octanol on AMBERLITE XAD 761, ratio 1:220

Initial conc. (mg/L)	C_{eq} (mg/L)			Avg.	%RSD	C_{blank}(mg/L)			Avg.	%RSD	Ads. Conc. (mg/L)			q (mg/g XAD 761)			Avg.
	no. 1	no. 2	no. 3			no. 1	no. 2	no. 3			no. 1	no. 2	no. 3	no. 1	no. 2	no. 3	
50	4.52	4.50	4.10	4.37	5.34	44.10	39.22	39.59	40.97	6.63	36.45	36.47	36.87	8.14	8.70	8.81	8.55
100	13.33	14.45	15.41	14.40	7.24	-	84.12	92.06	88.09	6.38	74.76	73.64	72.67	17.04	16.40	16.90	16.78
150	28.63	32.72	-	30.68	9.43	-	157.89	138.23	148.06	9.39	119.42	115.33	-	28.50	26.32	-	27.41
200	43.84	-	38.76	41.30	8.69	205.29	191.24	185.80	194.11	5.18	150.27	-	155.35	33.91	-	36.13	35.02
250	59.86	-	58.63	59.24	1.47	245.14	229.35	253.09	242.53	4.98	182.67	-	183.90	42.21	-	44.36	43.29

APPENDIX E

Table E-1 The relationship between surface tension and concentration

Chemicals	Conc.	C/Sw	surface tension								
			no. 1	sd	no. 2	sd	no. 3	sd	Avg	Stdev	%RSD
	5000	0.056	60.169	0.029	60.401	0.026	60.030	0.027	60.200	0.187	0.311
	10000	0.111	53.561	0.028	52.977	0.029	54.262	0.028	53.600	0.643	1.200
Butanol	15000	0.167	47.928	0.028	47.898	0.026	48.364	0.029	48.063	0.261	0.543
	20000	0.222	45.033	0.027	45.231	0.030	44.839	0.025	45.034	0.196	0.435
	25000	0.278	40.562	0.027	42.641	0.030	41.543	0.029	41.582	1.040	2.501
	500	0.019	68.280	0.026	68.638	0.029	68.273	0.015	68.397	0.209	0.305
	1000	0.037	64.768	0.030	64.367	0.025	65.498	0.029	64.878	0.573	0.884
Pentanol	1500	0.056	61.531	0.027	62.257	0.029	61.838	0.025	61.875	0.364	0.589
	2000	0.074	58.101	0.011	58.201	0.028	58.486	0.011	58.263	0.200	0.343
	2500	0.093	55.568	0.025	56.272	0.027	55.955	0.028	55.932	0.353	0.630
	50	0.008	70.454	0.012	70.979	0.007	70.173	0.015	70.535	0.011	0.016
	100	0.017	70.051	0.014	70.340	0.015	70.470	0.014	70.287	0.014	0.020
Hexanol	150	0.025	68.322	0.026	68.891	0.016	69.170	0.026	68.794	0.432	0.628
	200	0.033	67.843	0.021	68.222	0.023	68.550	0.022	68.205	0.354	0.519
	250	0.042	65.208	0.030	66.152	0.019	66.755	0.021	66.038	0.780	1.181
	50	0.028	67.951	0.016	69.961	0.011	70.139	0.011	69.350	1.215	1.752
	100	0.056	64.831	0.018	66.092	0.013	66.255	0.014	65.726	0.779	1.186
Heptanol	150	0.083	61.887	0.011	62.263	0.018	62.288	0.018	62.146	0.225	0.361
	200	0.111	58.859	0.016	59.110	0.007	58.980	0.016	58.983	0.126	0.213
	250	0.139	56.907	0.026	56.625	0.026	56.599	0.010	56.710	0.171	0.301
	50	0.093	61.970	0.029	62.153	0.007	62.488	0.020	62.204	0.263	0.422
	100	0.185	53.230	0.030	53.651	0.021	53.774	0.026	53.552	0.285	0.533
Octanol	150	0.278	47.436	0.028	47.423	0.028	47.134	0.028	47.331	0.171	0.361
	200	0.370	43.488	0.011	42.996	0.029	43.352	0.029	43.279	0.254	0.587
	250	0.463	39.771	0.023	39.771	0.029	39.713	0.029	39.752	0.033	0.084

APPENDIX F

Table F-1 The contact angle (θ) onto alumina and silica

Chemicals	Alumina			Avg.	Stdev.	%RSD	Silica			Avg.	Stdev.	%RSD
	no. 1	no. 2	no. 3				no. 1	no. 2	no. 3			
Butanol	0.00	0.00	0.00	0.00	0.00	-	0.00	0.00	0.00	0.00	0.00	-
Pentanol	0.00	0.00	0.00	0.00	0.00	-	0.00	0.00	0.00	0.00	0.00	-
Hexanol	0.00	0.00	0.00	0.00	0.00	-	0.00	0.00	0.00	0.00	0.00	-
Heptanol	0.00	0.00	0.00	0.00	0.00	-	0.00	0.00	0.00	0.00	0.00	-
Octanol	0.00	0.00	0.00	0.00	0.00	-	0.00	0.00	0.00	0.00	0.00	-
Water	-	28.80	28.88	28.84	0.06	0.19	62.06	67.93	61.27	63.76	3.64	5.71

Table F-1 The contact angle (θ) onto powder activated carbon and AMBERLITE XAD 761

Chemicals	Powder Activated Carbon			Avg.	Stdev.	%RSD	AMBERLITE XAD 761			Avg.	Stdev.	%RSD
	no. 1	no. 2	no. 3				no. 1	no. 2	no. 3			
Butanol	0.00	0.00	0.00	0.00	0.00	-	N/A	N/A	N/A	-	-	-
Pentanol	0.00	0.00	0.00	0.00	0.00	-	N/A	N/A	N/A	-	-	-
Hexanol	0.00	0.00	0.00	0.00	0.00	-	N/A	N/A	N/A	-	-	-
Heptanol	0.00	0.00	0.00	0.00	0.00	-	N/A	N/A	N/A	-	-	-
Octanol	0.00	0.00	0.00	0.00	0.00	-	N/A	N/A	N/A	-	-	-
Water	18.06	15.13	16.87	16.69	1.47	8.82	N/A	N/A	N/A	-	-	-

N/A: Not Analyzed

Biography

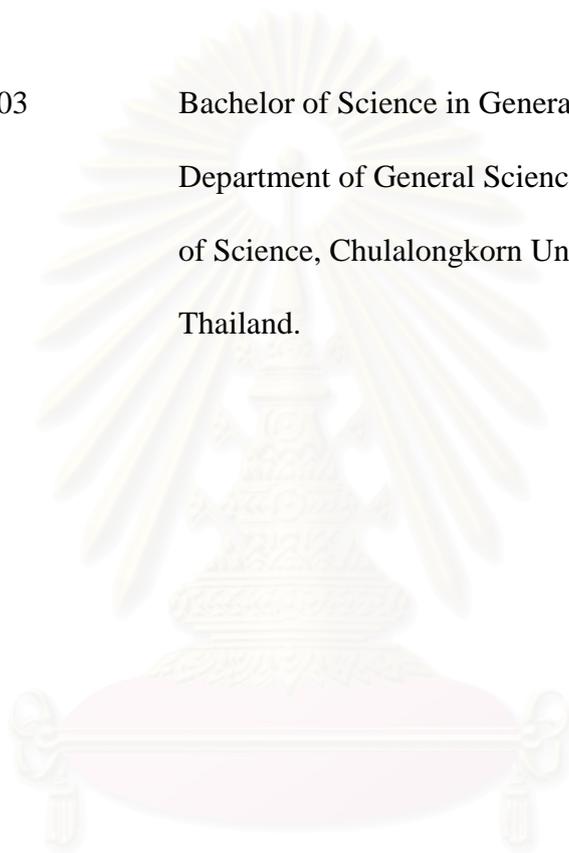**Name:**   Miss Walairat Poopa

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