ADSORPTION STUDIES OF AROMATIC COMPOUNDS IN AQUEOUS SOLUTION ONTO ACTIVATED CARBONS

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UNIVERSITI SAINS MALAYSIA

2004

ADSORPTION STUDIES OF AROMATIC COMPOUNDS IN AQUEOUS SOLUTION ONTO ACTIVATED CARBONS

by

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Thesis submitted in fulfillment of the
requirements for the degree
of Master of Science

SEPTEMBER 2004

ACKNOWLEDGEMENTS

Alhamdullillah and thankful to The Great Almighty, Allah for blessing me until finished my studies. I would like to express my genuine appreciation and gratitude to all persons upon their support, helps and assists during carried out my research. Here thousands words of thank you is uttered from me towards them upon their kindness dedication to me.

First of all, I would like to express my sincere grateful to my beloved parents and my family for their support during my study until my thesis a realism. Also, I'm not forgotten to thanks to my beloved fiancé who always encourages me during my study, always cheer me up and patient waiting for me until successfully accomplish my studies.

My deepest appreciation and gratitude to my dearest supervisor, Dr. Bassim H. Hameed and also my co-supervisor, Dr. Mohamad Zailani Abu Bakar for their patient guidance and constant help until completion this research. Without their ideas and supports, this research would not become successful.

My best regards to Universiti Sains Malaysia and Ministry of Science and Technology for giving me financial support by granting the PASCA scholarship. I would like to acknowledgment to Professor Abdul Rahman, Dean of School of Chemical Engineering and also Deputy Dean of School of Chemical Engineering for their motivation and supports. My thankful to all the technicians at School of Chemical Engineering and also to the lab technicians in main campus, Mr Simon Aw Yoong, Ms Jamilah, Mr Pachamuthu and Mr Johari for their most kindness and helps.

Last but not least, my special appreciation and thankful to all my beloved friends Norulakmal, Mahanim, Najwa, Yasmin, Siti Humairah, Sumathi, Ooi Boon Seng, Hawaiah and Azam for their endless supports and helps towards me. Thank you my friends.

Faridah Ghafar, 2004

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LIST OF SYMBOLS

		Unit
A	Area under breakthrough curve	[mg.min/L]
A_r	Arrhenius constant or frequency factor	[-]
b	Langmuir constant related to the affinity of the binding sites	[L/mg]
C	Breakthrough concentration in the effluent	[mg/L]
C_{ad}	Adsorbed concentration	[mg/L]
C_e	Equilibrium concentration of adsorbate in solution	[mg/L]
C_o	Initial concentration of adsorbate in solution	[mg/L]
C_t	Concentration at time t	[mg/L]
E_a	Activation energy	[kJ/mol]
K	Specific rate constant	[hr^{-1}]
K_1	Pseudo first order rate constant	[hr^{-1}]
K_2	Pseudo second order rate constant	[g/mg.hr]
K_{AB}	Adam-Bohart kinetic rate constant	[L/mg.min]
K_d	Equilibrium distribution constant	[L/g]
K_F	Freundlich constant related to adsorption capacity	[L/g]
K_{YN}	Yoon-Nelson kinetic rate constant	[min^{-1}]
m_{total}	Total amount of adsorbate adsorbed sent to column	[mg]
n	Freundlich constant related to adsorption intensity	[-]
N_o	Maximum adsorption capacity	[mg/L]
$(N_o)_{exp}$	Maximum adsorption capacity from experimental data	[mg/L]
$(N_o)_{pred}$	Maximum adsorption capacity from predicted data	[mg/L]
pK_a	Measure of the strength of an acid (- log K_a)	[-]
q_e	Amount of adsorbate adsorbed per unit weight of adsorbent at equilibrium	[mg/g]

$(q_e)_{exp}$	Adsorption capacity from experimental data	[mg/g]
$(q_e)_{pred}$	Adsorption capacity from predicted data	[mg/L]
q_{max}	Maximum adsorption capacity of the column	[mg/g]
q_t	Amount of adsorbate adsorbed per unit weight of adsorbent at time *t*	[mg/g]
q_{total}	Total adsorbed quantity	[mg]
R	Gas constant = 8.314	[J/mol.K]
R_L	Separation factor	[-]
t	Time	[min]
T	Absolute temperature	[K]
t_{total}	Total flow time	[min]
U_o	Superficial velocity	[m/min]
V	Volume of solution	[L]
V_{eff}	Effluent volume	[ml]
W	Weight of adsorbent	[g]
X	Amount of adsorbent in the column	[g]
Z	Adsorbent height in the column	[m]
$\% R$	Percentage removal	[-]
$\% \varepsilon$	Percentage error	[-]
τ	Time required for 50% adsorbate breakthrough	[min]
$(\tau)_{exp}$	Time required for 50% adsorbate breakthrough from experimental data	[min]
$(\tau)_{pred}$	Time required for 50% adsorbate breakthrough from predicted data	[min]
ΔG^0	Change in free energy	[kJ/mol]
ΔH^0	Change in enthalpy	[kJ/mol]
ΔS^0	Change in entropy	[kJ/mol.K]

LIST OF ABBREVIATION

2, 4-D	2, 4-dichlorophenoxy-acetic acid
Al_2O_3	Aluminium oxide
BET	Brunauer-Emmett-Teller
BTEX	Benzene, toluene, ethylbenzene and xylene
BTX	Benzene, toluene and xylene
CaO	Calcium oxide
F300	Calgon Filtrasorb 300
Fe_2O_3	Ferum oxide
HCl	Hydrochloric acid
HSDM	Homogeneous surface diffusion model
I. D.	Internal diameter
IAS	Ideal adsorption solution
MEK	Methyl ethyl ketone
N1240	Norit GAC 1240
N_2	Nitrogen
NaOH	Sodium hydroxide
PDM	Pore diffusion model
SEM	Scanning Electron Microscopy
SiO_2	Silica oxide
TCE	Trichloroethane
TiO_2	Titanium oxide
U.S. EPA	United State Environmental Pollution Agency
UV-Visible	Ultra violet visible
VOCs	Volatile organic compounds
WAO	Wet air oxidation

KAJIAN PENJERAPAN SEBATIAN AROMATIK DI DALAM LARUTAN BERAIR KE ATAS KARBON TERAKTIF

ABSTRAK

Fokus penyelidikan ini adalah untuk menyelidik penyingkiran sebatian aromatik; benzena, toluena dan o-xylena daripada larutan berair melalui penjerapan ke atas karbon teraktif komersil; Norit GAC 1240 (N1240) dan Calgon Filtrasorb 300 (F300). Eksperimen ini telah dijalankan dalam sistem berkelompok dan berterusan. Dalam sistem berkelompok, parameter-parameter operasi yang telah dikaji adalah kepekatan awal (60 – 600 mg/L untuk benzena; 60 – 480 mg/L untuk toluena dan 30 – 150 mg/L untuk o-xylena); suhu (30 - 50°C); pH larutan (3 – 10) dan masa sentuh. Dalam sistem berterusan, parameter-parameter yang telah dikaji adalah kepekatan awal (60 - 600 mg/L untuk benzena; 60 - 480 mg/L untuk toluena dan 60 - 150 mg/L untuk o-xylena); kadar aliran (40 - 100 ml/min) dan berat penjerap (3 dan 6 g). Dalam sistem berkelompok, kapasiti penjerapan oleh semua sistem bahan dijerap-penjerap telah meningkat dengan peningkatan kepekatan awal tetapi menurun dengan suhu. Masa keseimbangan dapat diterangkan dalam urutan: benzena > toluena > o-xylena. Kajian isoterma penjerapan menggunakan model-model isoterma Freundlich dan Langmuir telah menunjukkan bahawa isoterma penjerapan oleh benzena, toluena dan o-xylena ke atas kedua-dua penjerap; N1240 dan F300 boleh diterangkan oleh kedua-dua model isoterma. N1240 telah didapati mempamerkan kapasiti penjerapan yang lebih tinggi berbanding F300 untuk semua bahan dijerap disebabkan oleh luas permukaan dan keliangannya yang lebih banyak. Model kinetik pseudo tertib kedua telah didapati sesuai untuk menerangkan kinetic penjerapan semua sistem bahan dijerap-penjerap. Analisa mengenai termodinamik menunjukkan bahawa proses penjerapan tersebut adalah penjerapan fizikal, spontan, eksotermik secara semulajadi untuk kesemua

sistem bahan dijerap-penjerap. Dalam sistem berterusan, kapasiti penjerapan kedua-dua penjerap untuk semua bahan dijerap telah meningkat dengan peningkatan kepekatan awal, kadar aliran dan jumlah penjerap. Model-model kinetik Adam-Bohart dan Yoon-Nelson telah di dapati sesuai untuk mewakili data penjerapan yang diukur untuk kesemua sistem bahan dijerap-penjerap. Ia juga di dapati bahawa kapasiti penjerapan kedua-dua penjerap di dalam sistem berterusan adalah lebih tinggi daripada sistem berkelompok.

ADSORPTION STUDIES OF AROMATIC COMPOUNDS IN AQUEOUS SOLUTION ONTO ACTIVATED CARBON

ABSTRACT

The focus of this research was to investigate the removal of aromatic compounds; benzene, toluene and o-xylene from aqueous solutions by adsorption on commercial activated carbons; Norit GAC 1240 (N1240) and Calgon Filtrasorb 300 (F300). The experiments were conducted in batch and continuous systems. In a batch system, the operation parameters investigated were initial concentrations (60 – 600 mg/L for benzene; 60 – 480 mg/L for toluene and 30 – 150 mg/L for o-xylene); temperature (30 - 50°C); pH of solutions (3 – 10) and contact time. In a continuous system, the parameters studied were initial concentrations (60 - 600 mg/L for benzene; 60 - 480 mg/L for toluene and 60 - 150 mg/L for o-xylene); flow rate (40 - 100 ml/min) and weight of adsorbent (3 and 6 g). In the batch system, the adsorption capacity of all adsorbate-adsorbent systems increased with increasing initial concentrations but decreased with temperatures. The equilibrium time was described in the following order: benzene > toluene > o-xylene. Adsorption isotherm studies using the Freundlich and Langmuir isotherm models indicated that the adsorption isotherms of benzene, toluene and o-xylene on both adsorbents; N1240 and F300 can be described by both isotherm models. The N1240 was found to exhibit higher adsorption capacity than F300 for all adsorbates due to its higher surface area and porosity. The pseudo second order kinetic model was found to be suitable to describe the adsorption kinetic of all adsorbate-adsorbent systems. Analysis of thermodynamic studies shows that the adsorption process was physical adsorption, spontaneous and exothermic in nature for all adsorbate-adsorbent systems. In the continuous system, the adsorption capacity of both adsorbates for all adsorbates increased with increasing initial concentration, flow rate and amount of adsorbent. Adam-Bohart and Yoon-Nelson kinetic models were suitable to represent the measured adsorption data well for all adsorbate-adsorbent systems. It was found that the adsorption capacities of both adsorbents in continuous system were higher than those in the batch system.

CHAPTER ONE

INTRODUCTION

1.1 ENVIRONMENTAL ISSUES

The ever-increasing demands of modern day society to improve standards of living and economic development are leading to increase use of raw materials. Accordingly, the use of chemicals has played a key role in many major sectors such as agricultural, industry, housing, transport, textiles and health that have contributed significantly to the rise in the standard of living among populations around the world. Their use and activities, however, create environmental problems when the air and water sources were contaminated with toxic and hazardous pollutants released from both naturally occurring and man-made substances including gases, heavy metals, volatile organic compounds, soluble organic compounds, suspended solids, color, coal gasification, petrochemical-related processes etc. A large fraction of waste in the environment is in the form of highly dilute groundwater and surface water (Holt, 2000; Sarkar *et al*., 2003).

The presence of these contaminants destroy the natural sources especially groundwater and also gives health problems to human beings such as allergy, skin diseases, respiratory system disorders, heart disease and many others (Daifullah & Girgis, 2003). Because of that, many efforts have been made to solve the problems including increase more stringent water regulation which have lent added urgency to the need to decontaminate wastewater and polluted trade effluent due to many communities rely on groundwater as a primary source of drinking water (Okolo *et al*., 2000; Edil, 2003). This has forced many companies to find alternative methods to reduce the amount and environmental sensitivity of the liquid waste they produce.

The promising options for wastewater treatment are through biological, chemical and physical methods. The biological methods such as microbial degradation, activated sludge and biofilm process are accepted for its potentialities but applicable only to lower concentration range. The chemical and physical methods such as adsorption, chemical oxidation, solvent extraction, flocculation, precipitation, filtration, ion exchange and membrane separation are normally used to treat pollutants especially organic compounds and heavy metals. Selection and feasibility of a particular method is based on the application to the solute concentration range, capacity, cost, reusability and the reproducibility (Kentish & Stevens, 2001; Sarkar *et al*., 2003; Abburi, 2003).

1.2 RESEARCH OVERVIEW

Volatile organic compounds (VOCs) are pollutants of great concern because they are toxic and are known or suspected to be carcinogenic when present at elevated levels in the environment. These major pollutants are released in a large number from industries such as chemical, petrochemical, petroleum refining, and coal conversion. Benzene, toluene and xylene (BTX) are aromatic compounds which are categorized as volatile organic compounds and usually released in large amounts from industries. The sources of these pollutants are normally found from leakage of petrol and diesel fuel from underground storage tanks and man made sources including municipal wastes, petrochemical, industrial, plastics and agricultural effluents (Daifullah & Girgis, 2003). These compounds have been designated as priority pollutants by the United States Environmental Protection Agency.

The reduction, if not the elimination, of such pollutants can be achieved through a combination of resource management, product reformulation, process modification and some form of end-of-pipe treatment (Okolo *et al*., 2000). Application of traditional methods such as flocculation, sedimentation, filtration, wet oxidation, incineration and activated sludge treatment seems impractical for the low level contaminants of organic compounds (Daifullah & Girgis, 2003). Activated carbon adsorption is an important separation technology, which is widely used, in chemical and environmental engineering.

Activated carbon is a complex material which has a variety of surface groups, impurities and irregularities with the pore sizes ranging from micropores to macropores that are randomly connected in their pore networks (Ismadji & Bhatia, 2002). Activated carbons have been widely employed as adsorbents in decontamination processes due to their high adsorption capacity, fast adsorption kinetics, ease of regeneration, extended surface area, microporous structure and special surface reactivity (Koh & Nakajima, 2000; Ania *et al*., 2002). Many types of carbonized raw materials can be activated by means of steam activation or chemical activation (Jung *et al*., 2001). The adsorption capacity of activated carbons depend on various factors such as surface area, pore distribution and surface functional groups of activated carbon, polarity, solubility, pH and concentration of adsorbate and so on (Ania *et al*., 2002; Aksu & Yener, 2001; Koh & Nakajima, 2000).

Although several established technologies such as biodegradation, solvent extraction, chemical precipitation, membrane separation, ion exchange and many others have been employed to treat contaminants, adsorption is frequently used to remove pollutants in wastewater because the application of other techniques entails high costs. In addition, the present methods of disposing these pollutants are not reliable and do not provide a permanent solution for containment. It is essential that a safe and cost effective cleanup process be developed as an alternative to the current treatment and disposal practices. Application of the activated carbon adsorption systems has emerged and been identified as one of the most effective technologies for the removal of volatile organic compounds especially benzene, toluene and xylene.

Many studies have been reported on the adsorption of organic compounds from gas stream. However, very limited studies were reported on the adsorption from aqueous solution. The liquid phase adsorption is a more complicated process than gas or vapor phase adsorption (Castilla, 2004). Therefore, the main aims of this research were to study the adsorption of benzene, toluene and o-xylene from aqueous solution on activated carbons for better understanding of kinetics and thermodynamic of the adsorption process.

1.3 OBJECTIVES OF THE RESEARCH

In the present research, the adsorption of benzene, toluene and o-xylene from aqueous solution on commercial activated carbons; Norit GAC 1240 and Calgon Filtrasorb 300 was studied in batch and continuous systems. The objectives of this research were:

a. to study the equilibrium, isotherm, kinetics and thermodynamic of benzene, toluene and o-xylene adsorption on commercial activated carbons; Norit GAC 1240 and Calgon Filtrasorb 300 in a batch system.

b. to compare the adsorption capacities of both activated carbons for the removal of above adsorbates.

c. to determine the breakthrough characteristics of all adsorbate-adsorbent systems under various operation conditions in a continuous system.

CHAPTER TWO

LITERATURE REVIEW

2.1 VOLATILE ORGANIC COMPOUNDS (VOCs)

Volatile organic compounds (VOCs) are among the most commonly found contaminants in groundwater. These contaminants are released into the environment during their production, distribution, storage, handling and use and can enter both surface water and groundwater (Golfinopoulos *et al*., 2001).

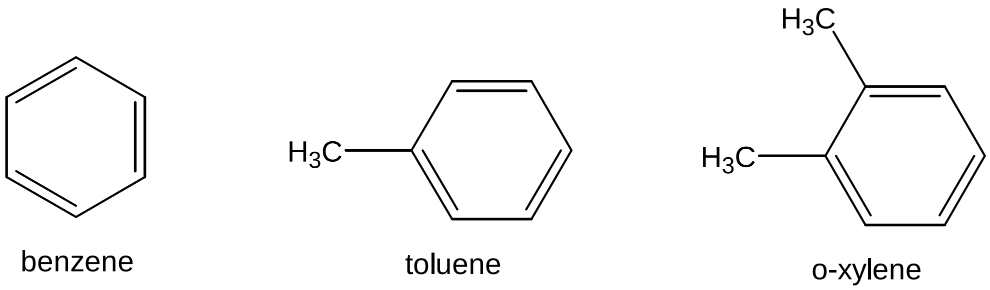
The term ‘volatile organic compound’ refers to the characteristic evaporative abilities of these compounds (Letterman, 1999). Volatile organic compounds are organic compounds which have a boiling point $\leq$ 100 ^{o}C and/or a vapor pressure > 1mm Hg at 25 ^{o}C (Golfinopoulos *et al*., 2001). More general definitions are based on physical and chemical properties of the compounds such as chemical structure, boiling point, air/water partitioning and vapor pressure (Kuran & Sojak, 1996). Generally, the volatility of a chemical, whether pure or dissolved in water, decreases with increasing ionic polarity of the chemical (Letterman, 1999).

Three broad groups of VOCs have been found in drinking water. One group includes compounds found in petroleum products especially aromatic sourced from leaking fuel oil and gasoline tanks. Another group is the halogenated VOCs, used as a solvents and degreasers. The third group includes some of the chlorinated organic disinfection by-products, particularly trihalomethanes (Letterman, 1999).

2.1.1 Benzene, toluene and xylenes

The volatile aromatic compounds such as benzene, toluene and xylene are fuel components commonly found in groundwater contamination. Benzene, toluene and xylenes (BTX) are aromatic hydrocarbons which comprised six-carbon ring structures.

The constituent carbon atoms of the benzene ring do not contain maximum possible number of hydrogen atoms; thus the molecule is unsaturated. In addition, the bonds between the carbon atoms in the benzene ring are neither single nor double but some of hybrid type (Gitipour *et al.*, 1997; 1998). Figure 2.1 shows the formula structures for benzene, toluene and o-xylene (Bruice, 2001).



benzene toluene o-xylene

Figure 2.1 Formula structures for benzene, toluene and o-xylene

The basic characteristics of BTX compounds are presented in Table 2.1 while the molecular dimensions of BTX compounds are described in Table 2.2.

Table 2.1 Physical and chemical characteristics of benzene, toluene and xylene (Gitipour *et al.*, 1997; 1998)

Compounds	**Molecular weight**	**Boiling point (^{o}C)**	**Solubility in water (mg/l)**	**Density (g/ml)**	**Vapor pressure (kPa)**
Benzene	78.11	80.1	1780	0.88	10.00
Toluene	92.10	110.8	515	0.87	2.93
Xylene	106.17	144.4	175	0.88	0.80

Table 2.2 Molecular dimensions of benzene, toluene and xylene (Gitipour *et al.*, 1997; 1998)

Compounds	**Thickness (mm)**	**Length (mm)**
Benzene	3×10^{-7}	6.6×10^{-7}
Toluene	3×10^{-7}	8.2×10^{-7}
o-Xylene	3×10^{-7}	8.2×10^{7}

Benzene, toluene and xylenes (BTX) are present in effluent from industries such as petroleum refineries and chemical plants. The contaminations of these aromatic compounds into water sources are normally from the leakage of petrol and diesel fuel from underground storage tanks. The other source of contamination is municipal sources. These chemicals are normally used as a solvent in various commercial products such as paints and pesticide (Daifullah & Girgis, 2003; Kuran & Sojak, 1996). The exposure to these aromatic compounds can cause serious health and environment problems because these contaminants are often flammable, toxic, and/or carcinogenic (Redding *et al*., 2002). High exposure to these contaminants over many years causes brain damage and moderate exposure can alter kidney and liver function or cause damage (Letterman, 1999). Besides, benzene is already known as the leukemia agent in humans (Kuran & Sojak, 1996).

Because of their strong toxicity to human being, stringent regulations have been imposed on the concentration levels of these compounds in wastewater discharge. They are designated as the priority chemicals that need to be reduced to a very low level by U.S. EPA (Lin & Huang, 2000). The removal of these compounds is not yet regulated in Malaysia.

2.2 TREATMENT TECHNOLOGIES OF VOCs REMOVAL

Over several decades, many researchers show their interests in treating VOCs from wastewater by using various methods in order to find the cost effective technology to remove these contaminants. Activated sludge treatment, incineration, wet air oxidation, sedimentation and flocculation are some of the traditional methods to remove volatile organic compounds.

Activated sludge treatment is convenient and relatively inexpensive to operate under certain circumstances. However, the microorganisms only can deal with chemical wastewater containing relatively low concentration (< 100 mg/L) even well acclimatized because of low biodegradability and/or inhibitory effects to microorganisms of BTEX. So, this technique do not solved the problems of high concentration of wastewater produced from various kinds of chemical and petrochemical wastewaters (Lin & Huang, 2000; 1999).

Incineration is an alternative method but only practical for dealing with waste solvents. It’s too costly for other applications (Lin & Huang, 2000; 1999).

Wet air oxidation (WAO) has emerged as a potential alternative and received considerable attention over the past two decades. This process is capable of oxidizing high concentration of organic compounds in aqueous phase at elevated temperatures and pressures. Although this process is rapid and efficient, it is not so easy to maintain the reaction conditions at elevated temperatures and pressures. Because of that, this process is too expensive due to high capital investment and operating cost (Lin & Huang, 2000; 1999).

Traditional methods such as flocculation, sedimentation and filtration for water treatment seem impractical for the low level contaminations of organic compounds (Daifullah & Girgis, 2003).

This urges an intensive search for the best available technology for removal and remediation of benzene, toluene and xylene (BTX). Hence, a good alternative to remove these contaminants from aqueous solutions is adsorption, which permits recovery of those compounds for possible recycling to the manufacturing process. Table 2.3 shows some investigations on the adsorption of aromatic compounds by several researchers.

2.3 ADSORPTION PROCESS

Adsorption is a process, which involves the contact of a free aqueous phase with a rigid particulate phase, which has the propensity to remove or store one or more solutes present in the solution selectively (Wong *et al*., 2004). The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. The adsorbing phase is the adsorbent and the material concentrated or adsorbed at the surface of that phase is the adsorbate (Slejko, 1985). Separation occurs due to differences in molecular weight, shape or polarity which cause some molecules to be held more strongly on the surface than others or because the pores are too small to admit the larger molecules (McCabe *et al*., 1993).

Table 2.3 Some investigations on adsorption of aromatic compounds

Adsorbate	**Adsorbent**	**System**	**Remarks**	**Researcher**
Phenol, benzene & toluene	Organo-modified minerals	Batch	-sorption capacity of phenol, benzene & toluene is in order of organo-montmorillonite > organo-zeolite > organo-sericite.	Koh & Dixon (2001)
Benzene, toluene, ethylbenzene & xylene	Macroreticular resin	Batch & column	-Freundlich isotherm represents the adsorption process. -the proposed model can be used to predict the adsorption capacity and breakthrough points.	Lin & Huang (2000)
Phenol, p-chlorophenol & p-nitrophenol	Commercial activated carbon	Batch	- Radke-Prausnitz and generalized isotherms represent the data. - the influence of different adsorbents, sorbate concentrations and pH have been discussed.	Khan *et al*. (1997)
n-Heptane, toluene & crude oil	Clay	Batch	-adsorption of petroleum on natural clay is an irreversible process. -adsorption of n-heptane and toluene on same clay are reversible process.	Cosultchi *et al*. (2004)
Naphthalene & benzothiophene	Silica gel & high-silica zeolite	Batch	-both adsorption and desorption isotherms matched each other indicating that the organic compounds were adsorbed reversibly on the adsorbate.	Furuya *et al*. (2004)

When adsorption occurs in aqueous solution, the adsorbate molecule is drawn from the bulk solution to the adsorbent phase. The net attractive forces involving the solute, solvent and adsorbent are assumed to be responsible for adsorption (Pan *et al.*, 2003). In general, adsorption involves the accumulation of molecules from a solvent onto the exterior and interior surfaces of an adsorbent. This surface phenomenon is a manifestation of complicated interactions among the three components involved, i.e. the adsorbent, the adsorbate and the solvent (Furuya *et al.*, 1997). Figure 2.2 shows a schematic adsorption model for the three components and their interactions.

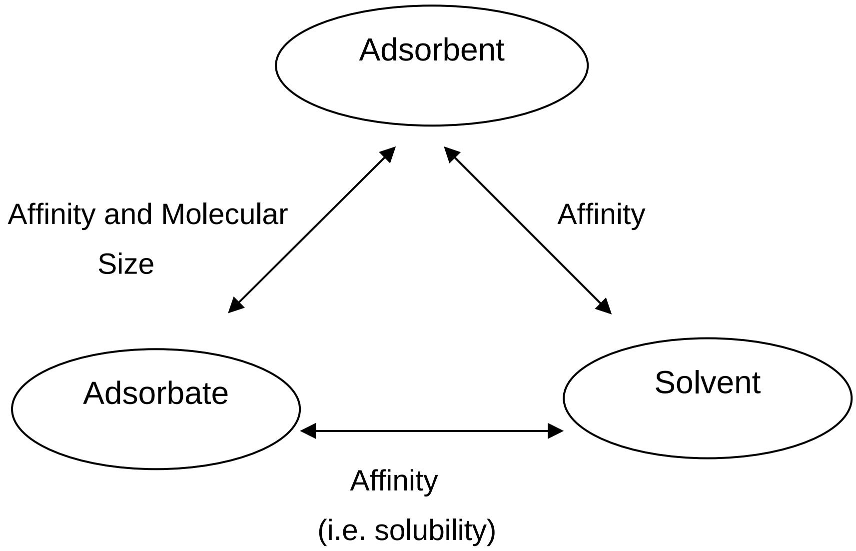


Figure 2.2 Adsorption system boundary (Furuya *et al.*, 1997)

Normally, the affinity between the adsorbent and the adsorbate is the main interaction force controlling adsorption. However, the affinity between the adsorbate and the solvent can also play a major role in adsorption (Furuya *et al.*, 1997).

The mode of adsorption can be divided into two systems; batch and continuous system. Batch adsorption is important in order to evaluate the feasibility and economics of adsorption. It is simplest mode of operation by contacting a whole volume of feed solution with a quantity of adsorbent in a vessel. The mixture is stirred until the equilibrium was attained and finally the adsorbent and the solution are separated by filtration (Slejko, 1985).

Batch adsorption is easy to use in the laboratory study, but less convenient for industrial applications (Chen & Wang, 2000). Data obtained from batch adsorption studies are useful in providing information on the effectiveness of the adsorbent. However, they do not give accurate scale up data for industrial treatment systems. Therefore, continuous system was employed in various chemical industries (Wong *et al*., 2003).

2.3.1 Physical and chemical adsorption

Physical adsorption occurs when Van der Waals and other weak forces hold the solute to the solid surface (Ruthven, 1997). The equilibrium is usually attained rapidly and easily reversible because the energy requirements are small, since the forces involved in physical adsorption is weak (Aksu & Tunc, 2004). It follows that heats of adsorption are comparable in magnitude to latent heats (10 - 70 kJ/mole). So, an increase in temperature causes a decrease in adsorption efficiency and capacity (Slejko, 1985). Because of that, physical adsorption is always exothermic reaction.

By contrast, chemical adsorption is specific and involves forces much stronger than physical adsorption (Aksu & Tunc, 2004). It results in the formation of a monomolecular layer of the adsorbate on the surface through forces of residual valence of the surface molecules (Eckenfelder, 2000). This occurs when covalent or ionic bonds are formed between the adsorbing molecules and the solid substrate. This bonding leads to a change in the chemical form of the adsorbed compounds and is therefore not reversible. Such interactions are both stronger and more specific than the forces of physical adsorption and are obviously limited to monolayer coverage (Ruthven, 1997). Thus, more heat is liberated. With chemical adsorption, higher temperature can cause improve performance (Slejko, 1985). This is indicates that the chemical adsorption is endothermic process.

Some adsorption system might be a combination of physical and chemical adsorption process. Salame and Bandosz (2003) reported that adsorption of phenol on activated carbons is a combination of two types of adsorption, which can possibly be explained from the energetic point of view. They concluded that physical adsorption occurs as a result of dispersive interactions between the aromatic part of the phenol and the carbon's basal planes while chemical adsorption takes place between the OH group of phenol and the carboxylic groups on the carbon surface. The other researchers; Juang and Shiau (1999) also obtained a transition of physical and chemical adsorption in the study of phenols adsorption onto macroreticular resins.

Generally, the physical or chemical adsorption can be determined from the magnitude of the enthalpy changes (ΔH^0). The enthalpy change due to chemical adsorption is 40 ~ 120 kJ/mol whereas the enthalpy change due to physical adsorption is less than 40 kJ/mol (Wu *et al.*, 2001). The type of adsorption can also be determined from the value of the activation energy. Low activation energy (< 4.2 kJ/mol) is a characteristic for physical adsorption while higher activation energies (8.4 – 83.7 kJ/mol) suggest chemical adsorption (Aksu & Kabaskal, 2003).

The differences in the general features of physical and chemical adsorption systems are shown in Table 2.4.

Table 2.4 Parameters of physical and chemical adsorption (Ruthven, 1997)

Parameter	Physical adsorption	Chemical adsorption
Heat of adsorption (ΔH)	Low, < 1 – 5 times latent heat of evaporation	High, > 1 – 5 times latent heat of evaporation
Specificity	Non specific	Highly specific
Nature of adsorbed phase	Monolayer or multiplayer, no dissociation of adsorbed species	Monolayer only, may involve dissociation
Temperature range	Only significant at relatively low temperatures	Possible over a wide range of temperature
Forces of adsorption	No electron transfer, although polarization of sorbate may occur	Electron transfer leading to bond formation between sorbate and surface
Reversibility	Rapid, nonactivated and reversible	May be slow, activated and irreversible

2.3.2 Adsorption mechanism

There are three major steps during the adsorption of solute molecules onto the adsorbent (Chu, 2002; Kumar *et al.*, 2003):

1. The movement of the adsorbate from the bulk phase to the exterior surface of the adsorbent.
2. The transport into the adsorbent either by pore diffusion and/or surface diffusion.
3. The adsorption on the surface of the adsorbent.

The third step is rapid for physical adsorption and one of the preceding diffusion steps will control the rate at which molecules are removed from solution. If adsorption is accompanied by a chemical reaction that changes the nature of the molecule, the chemical reaction may be slower than the diffusion step and thereby control the rate of compound removal.

2.3.3 Factors which influence adsorption

The adsorption process depends on several factors, which include the nature of the adsorbent, adsorbate and adsorption conditions. Adsorbent characteristics include the surface area, pore size distribution, particle size, ash content, hydrophobicity, and type of functional groups present on the surface. On the other hand, the nature of the adsorbate depends on its polarity, hydrophobicity, the size of the molecule and acidity or basicity. While the adsorption conditions include the temperature, the polarity of the solvent when applicable and the presence of other species competing for the adsorption sites (Salame & Bandosz, 2003; Ania *et al*., 2002; Daifullah & Girgis, 1998; Koh & Dixon, 2001).

2.3.3(a) Characteristics of the adsorbent

The characteristics of adsorbent, especially carbon, that affect the adsorption process are the pore texture, surface chemistry and mineral matter content. The adsorption capacity of carbon materials is not related in a simple form to their surface area and porosity. The adsorption capacity will depend on the accessibility of the organic molecules to the inner surface of the adsorbent, which depends on their size (Castilla, 2004). The porous structure of the carbon determines its adsorption capacity while its surface functional groups affect its interaction with polar and nonpolar adsorbates (Park & Jung, 2002).

Salame and Bandosz (2003) investigated the role of surface chemistry of phenol adsorption on activated carbons. They concluded that the phenol uptake is dependent on both the porosity and surface chemistry of the carbons. They found that phenol adsorption showed a strong dependence on the number of carboxylic groups due to two factors: (1) phenol reacts with carboxylic groups on the carbon surface forming an ester bond, and (2) carboxylic groups on the carbon surface remove the π-electron from the activated carbon aromatic ring matrix causing a decrease in the strength of interactions between the benzene ring of phenol and the carbon's basal planes which decreases the phenol uptake.

According to Li *et al*. (2002), adsorption capacity could be affected by several factors including specific surface area, adsorbent polarity and pore structures. Besides the difference in polarity, the microporous structure and the pore distribution of adsorbent also affect the adsorption capacity. In their investigation on the adsorption of phenolic compounds by polymeric adsorbent, they found that the increasing in the adsorption capacities might partially account from the polarity matching between the adsorbent and polar adsorbate. More predominant contribution in the micropore range of the adsorbent favors the solute-solute interaction for phenolic compounds. They also concluded that high hydrophobicity was found to favor the adsorption of phenolic compounds and the polymeric adsorbent.

However, Daifullah and Girgis (1998) reported that in the adsorption of phenolics on activated carbon, the uptake of the adsorbate is not simply dependent on the adsorbent texture characteristics (surface area and pore volume) but the distribution of pores seems to be a determining factor.

2.3.3(b) Characteristics of the adsorbate

Among the characteristics of the adsorptive that mainly influence the adsorption process are its molecular size, solubility, and the nature of the substituent if they are aromatics. The molecular size controls the accessibility to the pores of the adsorbent and the solubility determines the hydrophobic interactions. The substituent of the aromatic ring of the adsorptive molecules, in the case of the substituent of the graphene layers, would affect the dispersion interactions between the aromatic ring of the adsorbate and the graphene layers of the adsorbent (Castilla, 2004).

Trochimezuk *et al.* (2001) studied the sorption characterization of phenol and its derivatives on polymeric sorbents; acrylonitrile and methacrylonitrile. They found that the sorption of phenol and substituted phenols on both polymers depends on water solubility and is highest for the least soluble species. The effect of surface nitrile groups is the strongest for hydrophilic sorbates.

The other researchers, Ku and Lee (2000) reported that the presence of functional groups on the benzene ring of various phenols plays an important role on the extent of adsorption in their study of phenols removal by Amberlite XAD-4 resin. Despite of that, the adsorption equilibrium constants of various molecular phenol species by XAD-4 resin were found to correlate well with the octanol/water partition coefficients of the phenols.

An investigation on the removal of phenolic compounds onto activated carbon obtained from agricultural waste was reported by Daifullah and Girgis (1998). In their investigation, they found that the adsorption is strongest when the solubility parameter of phenolic appears to play a major role in determining the amounts adsorbed. A decrease in solubility and pK_a of the solute is always associated with an increase in adsorption capacity. They also concluded that the adsorption was found to be a direct function of the molecular dimensions of the adsorbates (molecular weight, molecular volume, area and diameter).

2.3.3(c) Characteristic of the adsorption condition

Solution’s pH, concentration and temperature are some factors that would affect the adsorption process. The pH of the solution controls the adsorption process of organic weak electrolytes and polyelectrolytes on carbon materials because it controls the electrostatic interactions between the adsorbent and the adsorbate (Castilla, 2004).

pH of the solution primarily affects the degree of ionization of the adsorbate and the surface properties of the sorbent (Aksu & Yener, 2001). Aksu and Yener (2001) investigated the effect of pH on the adsorption of mono-chlorinated phenols onto fly ash, activated sludge and granular activated carbon. For the adsorption of *o*- and *p*-chlorophenol by activated carbon, a favorable sorption at low pH is shown for both sorbates. They proposed that the larger sorption capacity at low pH is due to the reasonably strong interaction between the negatively charged adsorbent and the polar resonance contributed by the phenol structure. The adsorption decreased with further increase in pH due to repulsive force between the negative surface charge of the activated carbon and the sorbates.

The effect of pH in the adsorption of phenol onto activated carbon was also studied by Rengaraj *et al*. (2002a). In their study, they obtained that the greatest removal of phenol are in the pH range 4 – 9 and the removal efficiency decreases when the pH values was greater than 9. They concluded that the lesser uptake of phenol at lower pH may be due to the presence of H^+ ions suppressing the ionization of phenol and hence reduced its uptake on polar adsorbent. But at higher pH range, the presence of OH^- ions on the adsorbent prevents the uptake of phenols.

Daifullah and Girgis (1998) also agreed that in their study of phenolics removal onto activated carbon that the pH of the solution has a strong influence on the extent of adsorption. This is partly due to the fact that hydrogen ions themselves are strongly adsorbed and partly that pH influences the ionization.

An investigation on equilibrium adsorption studies of aromatic pollutants from dilute aqueous solution on activated carbon was conducted by Khan *et al*. (1997). In their study, they concluded that high pH depresses the equilibrium amount adsorbed but neutral salt addition increases adsorption. This is attributed to the electrostatic interaction between the adsorbent surface and the adsorbate molecule or ion.

The effect of temperature on the adsorption rate can be described on the nature of the adsorption process either exothermic or endothermic. The increase of adsorption by increasing the temperature indicates that the adsorption process is endothermic whereas a decrease in the adsorption with an increase in temperature indicates that the process is exothermic (Dogan & Alkan, 2003; Banerjee *et al*. 1997; Jain *et al*., 2002). With regard to the effect of temperature on the adsorption, an increasing uptake of organic molecules is expected when the adsorption temperature decreases because adsorption is a spontaneous process. However, some studies have reported that the amount adsorbed increased with temperature (Castilla, 2004).

Dogan and Alkan (2003) have found that the adsorption of methyl violet onto perlite increased when the temperature was increased. They reported that this might be the result of increase in the mobility of the large dye ion with temperature. An increasing number of molecules may be also acquiring sufficient energy to undergo an interaction with active sites at the surface. Furthermore, increasing temperature may produce a swelling effect within the internal structure of perlite enabling large dyes to penetrate further.

Similar results have been reported by Aksu and Kabaskal (2003) when studying the adsorption capacity of 2, 4-dichlorophenoxy-acetic acid (2, 4-D) on granular activated carbon. They reported that the adsorption of 2, 4-dichlorophenoxy-acetic acid (2, 4-D) was increased with increasing of temperature. This is maybe attributed to the enlargement of pore size or activation of the adsorbent surface or creation of some new active sites on the adsorbent surface due to bond rupture.

Jain *et al*. (2003) found that adsorption of dyes onto carbonaceous adsorbent decreased with increasing temperature indicating that the process is exothermic. Similar results were also found by Juang *et al*. (1997) in the adsorption of dyes onto activated clays from aqueous solutions.

The initial concentration provides an important driving force to overcome all mass transfer resistances of the adsorbate between the aqueous and solid phases. Hence a higher initial concentration of adsorbate enhances the sorption process (Aksu & Yener, 2001).

A study about the effect of initial concentration of *o*-xylene on fly ash by Banerjee *et al*. (1997) indicates that the amount uptake of o-xylene increase significantly with increasing initial concentration. This result was expected due to the decrease in resistance to the uptake of solute from the solution with increasing solute concentration. So, the increase in the driving force results in increasing the adsorption rate.

Similar results were also obtained in the adsorption of mono-chlorinated phenols onto activated sludge and fly ash by Aksu and Yener (2001). The adsorption capacities of all adsorbates increased with increasing initial concentrations.

2.4 TYPES OF ADSORBENTS

The success or failure of the adsorption process depends on how the adsorbent performs in both equilibrium and kinetics. An adsorbent with good capacity but slow kinetics is not a good choice as it takes adsorbate molecules too long a time to reach the particle interior. On the other hand, an adsorbent with fast kinetics but low capacity is not good either as a large amount of solid is required for a given throughput. Thus, a good adsorbent is the one that provides good adsorptive capacity as well as good kinetics by satisfying these two aspects: (Do, 1998):

(a) The adsorbent must have reasonably high surface area or micropore volume.

(b) The adsorbent must have relatively large pore network for the transport of molecules to the interior.

2.4.1 Activated carbon

Activated carbons have been widely used in many processes of gas, water and wastewater purification, for the removal of color, odor and organic pollutants (El-Sayed & Bandosz, 2004). This could be related to their extended surface area, high adsorption capacity, microporous structure and special surface reactivity (Banat *et al*., 2003). Commercial activated carbons normally have surface areas in the range of 600 – 1200 m^2/g (Ng *et al.*, 2002b). A typical activated carbon whether in a powder or granular form, has a porous structure consisting of a network of interconnected macropores, mesopores and micropores that provide a good capacity for the adsorption due to its high surface area (Aksu *et al*., 2002). The structure of activated carbon is complex and it is basically composed of an amorphous structure and a graphite-like microcrystalline structure (Watson, 1999).

Activated carbon can be made from various raw materials that have a high carbonaceous content, such as peat, coal, synthetic polymers, wood, charcoal, petroleum coke, sawdust and coconut shell (Park & Jung, 2002). The term activated carbon covers a range of materials that have been treated, or activated in order to increase the surface area available for the sorption (Redding *et al*., 2002). The processes for the preparation of activated carbons can be generally divided into two categories; physical and chemical activations. Physical activation involves carbonization of the raw materials followed by gasification of the resulting char in the presence of some oxidizing agents. On the other hand, chemical activation is performed by the thermal decomposition of the precursor materials impregnated with chemical agents such as potassium hydroxide, zinc chloride and phosphoric acid (Park & Jung, 2002).

Activated carbons are sold in powdered and granular forms. The powdered form is used for single contact (single stage) operations, usually in some water treatment operations when high mass transfer rates are needed and when extremely high removal efficiencies are not needed. Granular activated carbons most often come in size fractions between 8 and 30 mesh or between 12 and 40 mesh. Granular activated carbons can be generated and reused several times. Regeneration usually affects the properties of the carbons. Part of the carbon is effectively burned and regeneration is likely to increase the pore sizes and even the surface area of the carbon. These factors can enhance the performance of the carbon, and in many cases regenerated carbon may perform better than original carbon. However, regeneration can affect surface chemistry of the carbon, producing unfavorable changes in carbon performance (Watson, 1999).

Activated carbons are widely used as an adsorbent for the removal of a wide range of pollutants from various matrices because of their high adsorption capacity, fast adsorption kinetics and ease of regeneration (Jung *et al*., 2001). Due to the reasons stated above, the adsorption of VOCs and organic compounds using activated carbon has always been a preferred choice. Activated carbons are commonly used as adsorbents for decontamination processes such as the purification of drinking water, wastewater and sewage treatment, emissions control, etc. This led many researchers to study the performance of various activated carbons in removing various pollutants in environment. The applications of activated carbon in the adsorption of various organic pollutants are listed in Table 2.5.

Table 2.5 Application of activated carbons in the adsorption of various pollutants

Adsorbate	Adsorbent	System	Remarks	References
Benzene, toluene, ethylbenzene and xylene	Activated carbon derived from biomass residue & commercial activated carbon	Batch	- increasing surface acidity increases the polarity of the surface and reduces adsorption. - oxygen functional groups reduced adsorption capacity by localizing free electron of the carbon basal planes. - presence of surface acidic phosphate oxides contaminants reduce the BTEX uptake. - higher uptake by commercial activated carbon due to the basic nature of the carbon surface and absence of phosphorus oxides.	Daifullah & Girgis (2003)
Toluene	Commercial activated carbon (Filtrasorb 300)	Continuous	- experimental adsorption and desorption breakthrough curves were described using Homogeneous Surface Diffusion Model.	Chatzopolous & Varma (1995)

Table 2.5 continued

Adsorbate	**Adsorbent**	**System**	**Remarks**	**References**
Methyl ethyl ketone & trichloroethane	Commercial activated carbon (Norit 1240)	Continuous	- MEK adsorbs less than TCE for the same concentration. - adsorption equilibrium for TCE can be described with Redlich-Peterson isotherm Freundlich and irreversible isotherm described MEK. - the breakthrough curves for MEK and TEC can be described with Pore Diffusion Model.	Sotelo *et al*. (2003)
2, 4, 6 – trinitrophenol, 4 – nitrophenol, 4 – chlorophenol & 1, 3 – dihydroxybenzene	Activated carbon derived from fertilizer waste material	Batch & continuous	- breakthrough capacity is more than batch capacity. - after regeneration with HNO_3, the sorption capacity of the column is almost the same as that of virgin adsorbent material.	Gupta *et al*. (2000)