PHYSIOCHEMICAL AND BIOLOGICAL BEHAVIORS OF ORGANIC CONTAMINANTS IN MULTI-PHASE MEDIA UNDER ENHANCED TREATMENT CONDITIONS

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Chunjiang An

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Chunjiang An, candidate for the degree of Doctor of Philosophy in Environmental Systems Engineering**,** has presented a thesis titled, ***Physiochemical and Biological Behaviors of Organic Contaminants in Multi-Phase Media Under Enhanced Treatment Conditions,*** in an oral examination held on April 19, 2013. The following committee members have found the thesis acceptable in form and content, and that the candidate demonstrated satisfactory knowledge of the subject material.

External Examiner: Dr. Lei Liu, Dalhousie University

Supervisor: Dr. Guo H. Huang, Environmental Systems Engineering

Committee Member: Dr. Fanhua Zeng, Petroleum Systems Engineering

Committee Member: Dr. Dianliang Deng, Department of Mathematics & Statistics

Committee Member: Dr. Amornvadee Veawab, Environmental Systems Engineering

Chair of Defense: Dr. Ken Leyton-Brown, Department of History

ABSTRACT

The rapid increase of anthropogenic activities has led to the ubiquitous presence of organic contaminants. There is an urgent need for understanding the fate and behavior of organic contaminants in the environment.

In this dissertation research, the physiochemical and biological behaviors of organic contaminants in multi-phase media have been investigated. Considerable research efforts have been made in characterizing the transport of polycyclic aromatic hydrocarbons (PAHs) at solid-liquid interface, as well as exploring the remediation of pollutants through solvent extraction and composting.

The effects of short-chain organic acids (SCOAs) on the behaviors of PAHs in soil-water system have been systemically investigated. The amendment of SCOAs could influence the adsorption and desorption behaviors of pyrene in soil-water system. The mobility of phenanthrene in soil could be also enhanced by introducing organic acids.

The biosurfactant-enhanced remediation of PAH-contaminated soil in the presence of SCOAs has been studied. The results supported the combined use of biosurfactant and SCOAs could further enhance the desorption of phenanthrene from soil into aqueous phase. The quantity and species of organic acids could affect the tendency of phenanthrene distribution in the presence of biosurfactant.

The adsorption of phenanthrene on fly ash in solid-liquid system was investigated. The adsorption of phenanthrene onto fly ash showed significant stepwise pattern. The developed stepwise multisite Langmuir model can help well simulate the adsorption process. The solution chemistry played an important role in the distribution of phenanthrene in fly ash-water system.

The performance of food waste composting in the presence of fly ash and uric acid has been investigated. Different trends of degradation intensity, O_2 uptake amount, microbial population and C/N ratio were observed in the series with additional fly ash and uric acid.

The results can be used to understand the environmental patterns and mechanisms of organic contaminant behaviors in a complex system. They have important implications for environmental risk assessment and pollution control at contaminated sites.

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DEDICATION

This dissertation is dedicated to my entire family for their unconditional love, steadfast support and constant encouragement.

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LIST OF ABBREVIATIONS

2-CP	2-chlorophenol
2,4-DCP	2,4-dichlorophenol
BCD	β-Cyclodextrin
BDFA	Boundary Dam fly ash
CFU	colony forming unit
CMC	critical micelle concentration
CPC	cetyl pyridinium chloride
DAD	diode array detector
DDD	2,2-Bis(4-chlorophenyl)-1,1-dichloroethane
DDE	2,2-Bis(4-chlorophenyl)-1,1-dichloroethene
DNBP	2-*sec*-butyl-4,6-dinitrophenol
DOM	dissolved organic matter
EPA	Environmental Protection Agency
ESEM	environmental scanning electron microscopy
ESP	electrostatic-precipitator
FA	fly ash
GC	gas chromatography
HA	humic acid
HPCD	hydroxypropyl-β-cyclodextrin
HPLC	high-performance liquid chromatography
HOCs	hydrophobic organic compounds

IPD	increased percentage of desorption
LM	Langmuir model
MCD	methyl-β-cyclodextrin
MLM	multisite Langmuir model
PAHs	polycyclic aromatic hydrocarbons
PCP	pentachlorophenol
POPs	persistent organic pollutants
PTFE	polytetrafluoroethylene
SCOAs	short-chain organic acids
SEM	scanning electron microscope
SFA	Shand fly ash
SMLM	stepwise multisite Langmuir model
SOM	soil organic matter
TOC	total organic carbon
TX100	Triton X-100
UA	uric acid

CHAPTER 1

INTRODUCTIONS

1.1. BACKGROUND

The rapid increase of anthropogenic activities has led to the ubiquitous presence of organic contaminants. There has been increasing concern recently over the potential adverse effects of various organic contaminants on human health and ecology. The toxicity caused by organic contaminants has been well documented in different aquatic and terrestrial species (Black et al. 1983; Siegfried 1993; Belfroid et al. 1996; Duarte-Davidson and Jones 1996; Van Brummelen et al. 1996; Koelmans et al. 2001; Jones et al. 2002; Christensen et al. 2005). It has been also demonstrated that many organic contaminants are toxic to mammals, including organ damage, mutagenic, carcinogenic and developmental abnormalities (Loper et al. 1978; Stahl Jr 1991; Belkin et al. 1994; Henschler 1994; Johnson and Long 1998; Kropp and Fedorak 1998; Kim Oanh et al. 2002; White and Claxton 2004). Consequently, there is an urgent need for understanding the fate and behavior of organic contaminants in the environment.

Various organic contaminants are frequently detected within the soil environment as a result of air deposition, sewage irrigation, and industrial accidents (Kile et al. 1995; Maliszewska-Kordybach 1996; Wilson et al. 1997; Czaplicka 2004; Daly and Wania 2004; Semple et al. 2007; Nam et al. 2008). Soil is considered to be one of the most important pools of organic contaminants in the environment. The forms and properties of organic contaminants differ greatly from each other. In particular, due to the nature of hydrophobicity and low water solubility, hydrophobic organic compounds (HOCs) can become rapidly associated with soils when released from natural or anthropogenic sources. Knowledge on transport and fate organic contaminants in soil environment is of crucial importance in developing appropriate strategies for environmental risk assessment and remediation.

During the past decades, many physical and chemical methods including sorption, incineration, photo-oxidation, chemical oxidation, solvent extraction, filtration, and alkaline or acid hydrolysis have been developed in efforts to remove the organic contaminants (Wild et al. 1990; Watts et al. 1994; Gates and Siegrist 1995; Haigh 1996; Watts and Dilly 1996; Masten and Davies 1997; Sikdar et al. 1998; Mulligan et al. 2001; Christofi and Ivshina 2002; Kuei-Jyum Yeh et al. 2002; Chu and Kwan 2003; Pannu et al. 2004; Conte et al. 2005; Silva et al. 2005; Vreysen and Maes 2005; Rivas 2006; Viglianti et al. 2006; Yu et al. 2007; Ferrarese et al. 2008; Fabbri et al. 2009; Gan et al. 2009; Svab et al. 2009). A number of biological techniques have also been tested for the remediation of organic contaminants (Heitkamp and Cerniglia 1988; Allard and Neilson 1997; Pinelli et al. 1997; Alkorta and Garbisu 2001; Liu et al. 2001; Namkoong et al. 2002; Gerhardt et al. 2009). During these processes, transport and transformation of organic contaminants can occur in multiphase system. Both the behaviors of organic contaminants and influencing factors may play an important role and need to be well characterized for supporting treatment planning efficiently. Recently, some enhanced remediation techniques are showing increasing promise for use in soils contaminated with organic and inorganic pollutants (Sahoo and Smith 1997; Haapea and Tuhkanen

2006; Reddy et al. 2006; Yang et al. 2006; Yuan et al. 2007a; Alcántara et al. 2008; Zhou and Zhu 2008a; Chang et al. 2009; Guo et al. 2009; Wan et al. 2009). The selection of appropriate remediation strategy greatly depends on the nature of the organic contaminant and environmental conditions.

1.2. CHALLENGES IN THE TRANSPORT OF PAHS IN SOIL-WATER SYSTEM

Polycyclic aromatic hydrocarbons (PAHs) are widespread compounds in environment. They can enter the ecosphere through numerous nature processes such as volcanic eruptions and forest fires (Kim et al. 2003). Considerable amounts of PAHs are discharged into the environment through industrial production and processing, especially from petroleum-related effluents, shipping activities and spillage. Due to their toxicity and high emission loadings, PAHs have been recognized as priority environmental pollutants by U.S. Environmental Protection Agency (EPA). PAHs are slightly water-soluble at low concentrations and can migrate from soil to aquifer and groundwater systems (Liu et al. 2001). PAHs are characterized by low solubility and high hydrophobicity. These chemicals tend to persist in pedosphere. There is an urgent need for effective and safe removal of such toxic compounds from the environment. Several different biological and chemical approaches have been studied in efforts to degrade these environmental contaminants (Pinelli et al. 1997; Sabate et al. 2001; Desai et al. 2008). But the stable structure of PAHs may prevent the rapid degradation of these compounds under natural conditions of contaminated sites. Also, the relatively low aqueous solubility and high adsorptive properties of PAHs result in the limited mass transfer and poor biodegradation efficiency (Ferrarese et al. 2008). Thus the key process to facilitate the bioavailability of the PAH contaminants is to transport the pollutant from soil to aqueous phase. Recent developments have focused on the knowledge of mobility and fate of PAHs, which are of crucial importance for the remediation of polluted soil and groundwater (Zhou and Zhu 2007a; Elgh-Dalgren et al. 2009). Soil-water system is a complex matrix interacting with the contaminant molecules and other environmental factors. Although many researches on the availability of PAHs have been reported before, particularly on aspects relating to the effects of soil texture and enhanced solubilization agent (e.g. surfactant and cosolvent) (Hwang and Cutright 2002; Khodadoust et al. 2004; Cheng and Wong 2006), investigations on characteristics of complex system composition in environment are relatively limited in scope.

Organic acids, which can be produced from various biological and chemical processes, exist ubiquitously in the environment, especially in upper soil horizons, plant root exudates, and microbial secretions (Blank et al. 1994). Recently, it has been found the behavior of organic compounds in soil can be affected by organic acids. However, the behaviors and mechanisms of PAH translocations influenced by organic acids remain poorly understood under either laboratory or field conditions. Further studies are needed to determine a number of important issues about the role of organic acids in future applications.

1.3. CHALLENGES IN THE BIOSURFACTANT-ENHANCED REMEDIATION

Soil washing with extracting solutions has been proposed as a promising technique for the remediation of contaminated soils and groundwater in recent years (Deshpande et al. 1999; Chu and Chan 2003; Gan et al. 2009). These washing solutions include different types of chemical agents, such as surfactants, solvents, and cosolvents (Khodadoust et al. 2000; Silva et al. 2005; Alcantara-Garduno et al. 2008). Among these compounds, surfactant has been extensively used to increase the desorption and mobilization of pollutants in soil due to its unique characteristic. However, concerns over some synthetic surfactants have increased because they are toxic and thus present a potential risk for environment and human health (Kanga et al. 1997). In recent years, the interest in use of biosurfactants has increased. As a more prominent and less toxic alternative, biosurfactants, such as rhamnolipids, are starting to be widely used in soil remediation. They have been demonstrated to be effective to recover HOCs from soils (Noordman et al. 1998; Cheng et al. 2004; Kuyukina et al. 2005; Mulligan 2005; Anna et al. 2007). Rhamnolipids are one of the most interesting biosurfactants with high surface activity. They are anionic biosurfactants produced by *Pseudomonas sp* bacteria. With a critical micelle concentration (CMC) in the range of 5-200 mg/L, Rhamnolipids can reduce the surface tension of pure water from 72 to below 30 mN/m (Pornsunthorntawee et al. 2009). Although biosurfactants have been used in a variety of environmental applications, little is known about the detailed mechanisms of the potential application. The performance of biosurfactants can be affected by a number of environmental factors.

It is necessary to obtain a better understanding of influencing mechanisms. In addition, there is also a need for using appropriate technologies to enhance the efficiency of biosurfactants in applications.

1.4. CHALLENGES IN THE ENVIRONMENTAL FATE OF FLY ASH

Coal-based thermal power stations have been the major source of power generation in many countries. Fly ash (FA) is generated as a byproduct from coal-fired power plants (Ahmaruzzaman 2009). A large amount of FA has to be disposed at landfills or other disposal sites. FA particles, when dumped, can cause a serious problem to human and environment. FA can coexist with some HOCs such as PAHs. On the one hand, PAHs are frequently found in FA as a result of incomplete combustion (Korfmacher et al. 1980; Drakonaki et al. 1998; Mastral and Callén 2000). The disposal of FA in land storage systems can lead to contamination of PAHs when these compounds are released to the environment. On the other hand, massive quantities of such energy waste often coexist with other industrial, agricultural and municipal wastes in landfills. It will lead to the coexistence of FA and PAHs from other extraneous sources. PAHs have been found in a variety of landfills (Jiménez et al. 2002; Samsøe-Petersen et al. 2002; Richnow et al. 2003; Jiries et al. 2005; Wiszniowski et al. 2006; Xu et al. 2008; Cornelissen et al. 2009). They are introduced into the landfills from different sources. Wastes such as sewage sludge, municipal waste, industrial wastes, excavated material and ash residues may all contain PAHs (Wild and Jones 1995). These PAH may become incorporated into the landfill during disposal process (Öman and Hynning 1993; Jiménez et al. 2002; Schwarzbauer et al. 2002; Wiszniowski et al. 2006). In addition, an intensive production of biogenic PAHs in pyrolytic processes in landfills is also possible (Ahel and Tepić 2000). Therefore, the interaction between FA and extraneous PAH can become a significant issue in environment and there is an urgent need for related environmental assessment. Environmental impacts of waste FA are very complex. Further assessments and studies are needed to address the negative effects of FA in environment. Some previous studies have investigated the interaction between FA and heavy metals, dyes, phenolic and ketone compounds. However, limited studies have focused on the interactions of HOCs with FA. A number of issues about the characteristics of nonionic HOCs on FA surface are poorly understood. In solid-liquid systems, the mechanism for the distribution and transportation of solute from bulk solution to solid surface is complicated (Moreno-Castilla 2004). The exact process of PAH adsorption on FA is still uncertain and the influencing factors need to be clarified.

1.5. CHALLENGES IN THE COMPOSTING OF ORGANIC WASTE

Accelerated industrialization, urbanization and population explosion have led to the rapid growth in quantities of organic solid waste generated. Improper treat and dispose of the organic solid waste have been shown to induce adverse impacts on all components of the environment and human health. Composting is a promising and safe method for disposal of organic waste. Interest in composting has increased recently because it can compete with other disposal practices as a cost-effective alternative and the end products can be applied for improving soil fertility. There is a need to develop the composting as an environmentally sound manner for the organic waste treatment. A number of solid wastes, including sewage sludges, crop residues, animal manures and industrial biowastes have been investigated to characterize the activities in different composting processes (Sharma et al. 1997; Wong and Fang 2000; Charest and Beauchamp 2002; Gea et al. 2004; Huang et al. 2004; Alkoaik and Ghaly 2006; Bustamante et al. 2008; Bernal et al. 2009; Hu et al. 2009; Gao et al. 2010). Separation of solid waste into several categories before further treatment and recycling would favour the optimal design of composting process. However, this is quite a challenge for many areas to meet separating regulations due to high cost of maintaining and operating, which is especially poignant in the developing countries. The organic waste often coexists with other agroindustrial waste. Few studies have been conducted to investigate the composting of wastes from different sources. The behaviors and mechanisms of multi-component composting remain poorly understood under either laboratory or field conditions. Investigations on the potential influences and roles of many waste constituents are relatively limited in scope. Therefore, further study is necessary to define the role of various physical, chemical and biological factors as well as their complex interactions during the multi-component waste composting.

1.6. OBJECTIVES

In this dissertation research, we will study the physiochemical and biological behaviors of organic contaminants in multi-phase media under enhanced treatment conditions. The specific objectives of this dissertation research include the following aspects:

(1) To systemically investigate the effect of short-chain organic acids (SCOAs) on the behaviors of PAHs in soil-water system. Batch tests will be conducted to determine the adsorption and desorption of PAHs in natural soil samples. Equilibrium studies were performed with isotherm modeling. The performances of different SCOAs, as well as the effects of solution pH, soil dissolved organic matter (DOM) and ionic strength will be evaluated. The environmental implications of results for the remediation of PAHs contaminated soil and groundwater will be discussed.

(2) To investigate the rhamnolipid biosurfactant-enhanced desorption of phenanthrene as influenced by SCOAs in soil-water environment. Experiments will be conducted to determine the desorption of phenanthrene in two kinds of natural soil samples. The performances of different biosurfactant-SCOA combinations, as well as the effects of solution pH, DOM and ionic strength were evaluated. The mechanisms of interacted influence of biosurfactants and organic acids on the behaviors of PAH translocations will be discussed.

(3) To investigate the adsorption process of phenanthrene on FA. The interaction between PAHs and FA at the solid-liquid interface will be explored. The environmental issues related to PAH pollution during FA disposal will be discussed. A stepwise multisite Langmuir model will be developed to simulate the adsorption process. The effects of aqueous chemistry characteristics (i.e., temperature, pH, humic acid and ionic strength) corresponding to the in situ conditions of disposal sites are also evaluated. The

results will be used to reveal the migration patterns of PAHs in a FA-water system which can facilitate environmental risk assessment at disposal sites.

(4) To evaluate the performance of food waste composting in the presence of FA and uric acid (UA). Tests will be conducted in the in-vessel composting system. The composting process, changes occurring in the product during composting and product properties will be studied. The patterns of food waste composting are compared among various combinations to investigate the influences of FA and UA. The variations of temperature, pH, organic mass reduction rate, O_2 consumption, microbial population and C/N ratio are studied.

1.7. ORGANIZATION

The dissertation is organized into seven chapters: an introduction, a literature review chapter, four experimental result chapters, and a concluding chapter. In Chapter 2, a comprehensive literature review is provided for the previous studies on transport of PAHs in environment, sorption and desorption theory, enhanced extraction of PAHs from soils, adsorption of pollutants on FA, and solid waste composting. Chapter 3 includes the study about the effect of SCOAs on the behaviors of PAHs in soil-water system. Adsorption and desorption of pyrene in natural soils in the presence of SCOAs will be investigated. The influence of short-chain aliphatic acids on the phenanthrene desorption and mobilization from contaminated soil will also be studied. Chapter 4 focuses on the enhanced remediation with biosurfactant. Rhamnolipid is selected as a representative biosurfactant. The enhanced desorption of phenanthrene by rhamnolipid biosurfactant in soil-water environment in the presence of rhamnolipid biosurfactant will be evaluated. In Chapter 5, the interaction between PAHs and FA at the solid-liquid interface will be studied. A new isotherm model will be developed to simulate the unique adsorption process observed in experiments. The environmental issues related to PAH pollution during FA disposal will be introduced. Chapter 5 will focus on the waste composting which includes various biological processes occurring in gas-liquid-solid phase. The performance of in-vessel composting of food waste as influenced by UA and FA will be evaluated. Both the positive and negative effects of UA and FA as amendments will be analyzed. Finally, conclusions of this dissertation research are drawn towards the end in Chapter 7.

CHAPTER 2

LITERATURE REVIEW

2.1. TRANSPORT OF PAHS IN ENVIRONMENT

2.1.1. Sources of PAHs in Environment

PAHs are a group of organic molecules composed of fused benzene rings in a linear or clustered arrangement (Ferrarese et al. 2008). These compounds usually contain only carbon and hydrogen atoms, although nitrogen, sulphur and oxygen atoms may readily substitute in the benzene ring to form heterocyclic aromatic compounds (Gan et al. 2009). The chemical structures of some commonly studied PAHs are shown in Figure 2.1.

PAHs are released to the environment during various processes. Natural sources of PAHs mainly include volcanic eruptions as well as forest and prairie fires (Chauhan et al. 2008; Gan et al. 2009). Anthropogenic sources can be considered as the major route of entry of PAHs into the environment (Wakeham et al. 1980). The combustion, gasification and liquefaction of fossil fuels, coke production, asphalt production, coal tar production, fuel processing, petroleum product spillage, waste incineration, vehicle emissions and many other industrial activities can all contribute to the release of PAHs to the environment (Hites et al. 1977; McCready et al. 2000; Reddy et al. 2002).

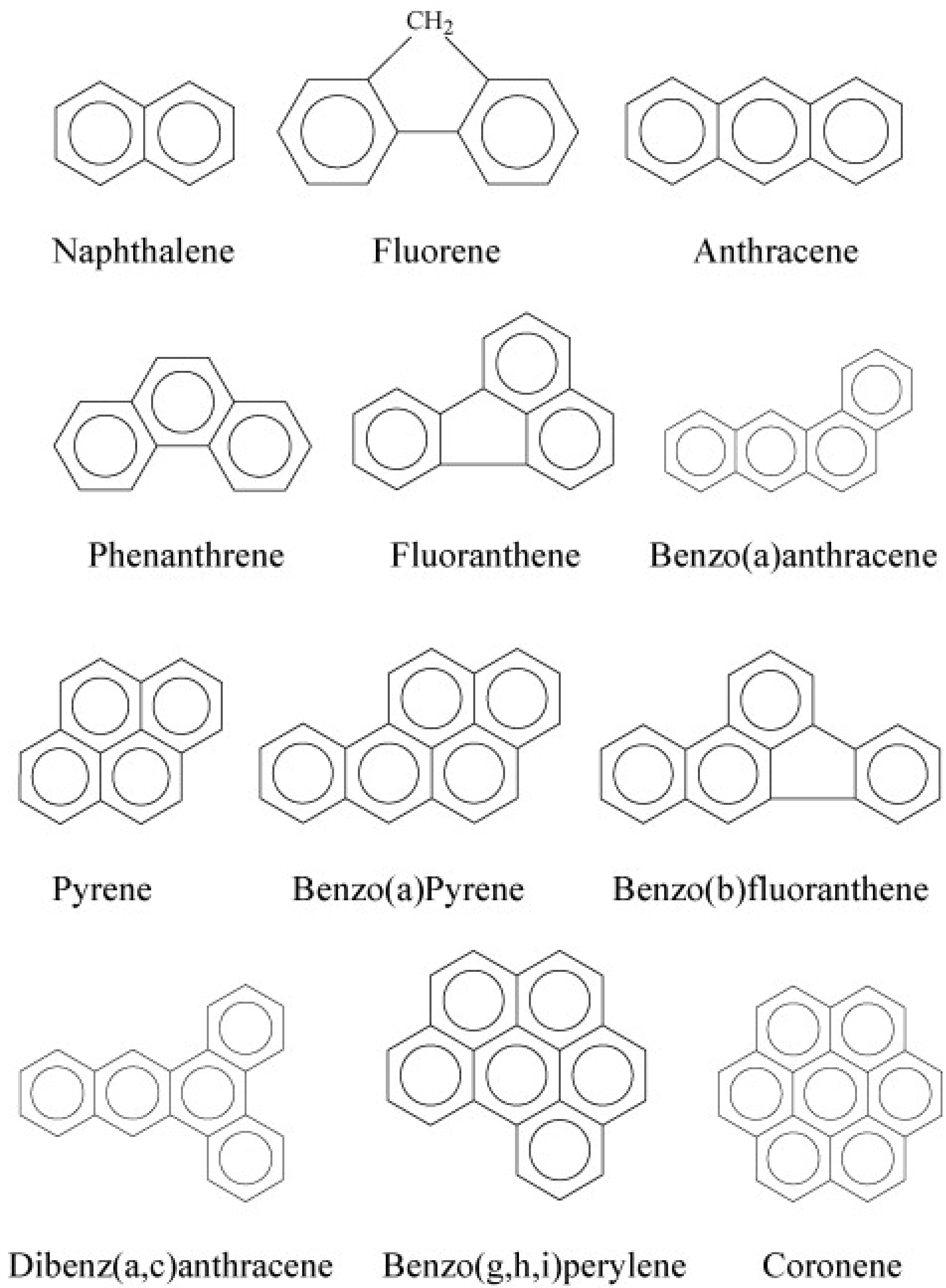


Figure 2.1 Chemical structures of some commonly studied PAHs (Haritash and Kaushik 2009)

Many PAH compounds have toxic, mutagenic and/or carcinogenic properties (Samanta et al. 2002). PAHs are highly lipid-soluble and thus readily absorbed from the gastro-intestinal tract of mammals (Cerniglia 1984). They can be rapidly distributed in a wide variety of tissues. It has been demonstrated that PAHs have detrimental effects on the flora and fauna, resulting in an accumulation of toxic chemicals in food chains (Samanta et al. 2002). PAHs can also lead to serious health problems and/or genetic defects in humans (Mastrangelo et al. 1996; Sram et al. 1999). Based on their ecotoxicity, the U.S. EPA has listed some PAHs as priority pollutants (Heitkamp and Cerniglia 1988). Some priority PAHs are listed in Table 2.1. Due to the health risk associated with the exposure to PAHs, there is an urgent need for better understanding their environmental fate.

The physical and chemical properties of each PAH compound may substantially differ from each other. But PAHs can be characterized by some common features. PAHs have low solubilities and low volatilities, except small components like naphthalene (Ferrarese et al. 2008). The lipophilicity of PAHs is high and PAHs are characterized by high octanol-water partition coefficient (K_{ow}). K_{ow} represents the ratio of the concentration of a chemical in octanol and in water at equilibrium and at a specified temperature (Dowdy and McKone 1997). High K_{ow} values indicate that a chemical tends to remain sorbed onto organic matter and low K_{ow} values indicate that a chemical tends to remain dissolved in water.

Table 2.1 Priority PAHs as listed by U.S. EPA (Agency 2008)

Number	PAH compound	Number of rings
1	Acenaphthene	3
2	Acenaphthylene	3
3	Anthracene	3
4	Benzo(a)anthracene	4
5	Benzo(a)phenanthrene (chrysene)	4
6	Benzo(a)pyrene	5
7	Benzo(b)fluoranthene	5
8	Benzo(j)fluoranthene	5
9	Benzo(k)fluoranthene	5
10	Benzo(j,k)fluorene (fluoranthene)	4
11	Benzo(g,h,i)perylene	6
12	Benzo(r,s,t)pentaphene	6
13	Dibenz(a,h)acridine	5
14	Dibenz(a,j)acridine	5
15	Dibenzo(a,h)anthracene	5
16	Dibenzo(a,e)fluoranthene	6
17	Dibenzo(a,e)pyrene	6

18	Dibenzo(a,h)pyrene	6
19	Dibenzo(a,l)pyrene	6
20	Fluorene	3
21	Indeno(1,2,3-cd)pyrene	6
22	Phenanthrene	3
23	Pyrene	4
24	1-Nitropyrene	4
25	3-Methylcholanthrene	4
26	5-Methylchrysene	4
27	7H-Dibenzo(c,g)carbazole	5
28	7,12-Dimethylbenz(a)anthracene	4

Physical and chemical properties of some representative PAHs are shown in Table 2.2. PAHs can be classified into two major types, low-molecular-weight PAHs (containing less than four benzene rings) and high-molecular-weight PAHs (containing four or more benzene rings) (Boonchan et al. 2000). Compared with the high-molecular-weight PAHs, the lower-molecular-weight PAHs are more volatile, water soluble and less lipophilic (Henner et al. 1997). Due to the nature of hydrophobicity, low volatility and high affinity, PAHs are readily adsorbed to surfaces of soil and sediment. The fate of PAHs in soils and sediments is related to their solubility, bioavailability, biodegradability, sorption and desorption processes. PAHs are regarded as persistent organic pollutants (POPs), and the corresponding persistence increases with ring number (Ferrarese et al. 2008). It was reported that the biodegradation of PAHs in soil in presence of l-phenyldecane as a primary substrate was inversely affected by the number of aromatic rings and correlated positively with water solubility of PAH compounds (Bossert and Bartha 1986). It was found that the greater the number of benzene rings in the PAH molecule, the greater the resistance to degradation.

Table 2.2 Physical and chemical properties of some PAHs (Nam et al. 2001; Haritash and Kaushik 2009)

Name	Molar mass (g/mol)	Log K_{ow}^{*}	Vapour pressure (atm at 20 °C)	Aqueous solubility (mg/L)
Pyrene	202.26	5.32	6.8×10^{-7}	0.12-0.18
Naphthalene	128.18	3.37	4.9×10^{-2}	30
Phenanthrene	178.24	4.46	6.8×10^{-4}	1-2
Anthracene	178.24	4.45	1.9×10^{-4}	0.07
Chrysene	228.30	5.61	6.3×10^{-7}	0.006
Fluorene	166.23	4.18	1.3×10^{-2}	1.9
Benzo(a)pyrene	252.32	6.04	5.0×10^{-7}	0.0038

* K_{ow} - Octanol-water coefficient.

2.1.2. Transport of PAHs in Soils

The sorption of PAHs onto soils has been widely investigated in previous studies. Zhou et al. (2004) investigated the sorption of phenanthrene on soil and sediment of different particle size. The sorption characters of soil and sediment were different. The sorption capacities increased with the decrease of particle size for both soil and sediment. That might be due to the larger total organic carbon (TOC) contents for the finer particles. But the enhancements in sorption coefficients were not strictly proportional with the equal increases in TOC contents. The effect of Ca^{2+} ions on phenanthrene sorption was stronger in short contact time than in long contact time. The sorption of phenanthrene on soil increased at low Ca^{2+} concentration, while the sorption capacity would decrease with the increase of Ca^{2+} at high Ca^{2+} concentration. However, the sorption of phenanthrene on sediment was negatively influenced over the experimental range of Ca^{2+} concentration. The different effect of Ca^{2+} ions could be attributed to differences in physicochemical properties between soil and sediment. Walter et al. (2000) investigated the adsorption and desorption behavior of PAHs on different soils by static and dynamic methods. A similar partitioning behavior in the batch and column experiments was observed for all PAHs in systems without oil. The distribution coefficients could be calculated from the octanol / water coefficient of the aromatic compounds and the organic carbon content of the soils. In the presence of oil, the sorption capacity would decrease with increasing oil content in the system. He et al. (1995) studied the sorption of fluoranthene on four soils. It is observed that the adsorption isotherms for fluoranthene on soils were linear over a range of 0-30 μg/L of fluoranthene concentration. Distribution coefficients correlated well with soil organic carbon contents. The extent of adsorption decreased with the increase of temperature.

The extent of desorption for PAHs is also a crucial factor in determining their bioavailability and toxicity in soil. Kogel-Knabner et al. (2000) investigated the effect of solution composition and aging on the desorption of ^{14}C-benzo[*a*]pyrene and ^{14}C-pyrene from soil. They suggested that decisive factor controlling desorption of PAHs was the concentration of DOM. Desorption increased linearly with increasing DOM concentration. Desorption of PAHs decreased with increasing exposure time in spiked soil and the aging process resulted that a fraction of PAH was hardly desorbed from contaminated soil. Li et al. (2013) investigated the effects of PAH concentration and chemical properties on desorption in meadow brown soil after a 1-year aging period. The results showed that the desorption of PAHs did not always decrease with increasing molecular weight. The combined consideration of PAH concentrations and properties should be taken into account for the modeling of adsorption and desorption process.

The solubility of the different PAHs and their organic fraction can affect the PAHs sorption onto soils. Various physicochemical properties of soils have been considered responsible for the retention of PAHs in soils. Other potential factors like temperature, salinity or the presence of DOM also exert some influences on the sorption stage. Different mechanisms can be included in the transport of PAHs in soil. Sorption of HOCs on soils appeared to be a two-phase process (Robinson et al. 1990). In the first step, PAHs were rapidly adsorbed on soil hydrophobic surfaces by hydrophobic interactions; in the second step, PAHs were slowly migrated to less accessible sites within the soil matrix (Murphy et al. 1990). When the incorporation capacities of soil matrices were exhausted and equilibrium was reached the second step would stop. Kan et al. (1998) proposed to partition organic chemicals in soil into two pools: (i) a labile pool that can be readily and reversibly desorbed; and (ii) an irreversible pool, resulting from covalent binding to soil organic matter.

2.1.3. Transport of PAHs in Aquatic Sediments

Sorption to sediment is a key process in determining the fate and risk of PAHs in aquatic environments. Karickhoff et al. (1979) investigated the sorption of pyrene on pond and river sediments. The sorption isotherms were linear over a broad range of aqueous phase pollutant concentrations. Different sorption behaviors within the silt and clay fractions were attributed to differences in organic carbon content. Wilcock et al. (1996) reported that low molecular weight PAHs were rapidly lost from sediments, whereas the high molecular weight ones had larger persistence. Bowman et al. (2002) studied the sorption of benzo(a)pyrene by sediment. The kinetic results showed that the sorption of benzo(a)pyrene reached equilibrium within 1 day. Due to the binding of benzo(a)pyrene by colloidal material, the sorption coefficient of benzo(a)pyrene significantly decreased with increasing sediment concentration. Colloidal particles have been quantified to calculate the corrected partition coefficient for benzo(a)pyrene. The particulate organic carbon and specific surface area of sediments showed strong influence on the partition behaviour of benzo(a)pyrene due to hydrophobic bonding and surface phenomenon. The desorption of benzo(a)pyrene from sediment was shown to be relatively rapid, indicating the potential remobilization of benzo(a)pyrene. de Maagd et al. (1998) investigated the sorption of naphthalene, phenanthrene, anthracene, benz[a]anthracene, chrysene and benzo[a]pyrene on two Dutch freshwater lake sediments. The results showed that 48 hours were sufficient to reach equilibrium. Sorption of PAHs in the lake sediments was determined by the hydrophobicity of the PAH, the organic carbon content of the sediment, and one or more unspecified sediment-specific characteristics.

Several factors affect the persistence of PAHs in aquatic sediments. Tremblay et al. (2005) studied the sorption of hydrophobic phenanthrene and fluoranthene on whole estuarine particulate matter. As the water temperature decreased or the salinity increased, the sorbed amount of phenanthrene and fluoranthene increased, which could be mainly attributed to changes in the water solubility of PAHs. The humic acid (HA) fraction was responsible for the linear and fast sorption of PAHs on river sediments and the humin contributes to the sorption non-linearity (Oren and Chefetz 2005). The higher sorption affinities for organic fractions from the downstream sediment were related to the low levels of polar domains and humin content. Means (1995) investigated the sorption/desorption of PAHs on various sediment types over a range of salinities. It was found there were no significant differences between sorption and desorption equilibrium constants. With increasing salinity, significant increases in sorption and desorption constants were obtained. The results might be due to the electrolyte effects on the aqueous activity coefficient of the solute and the salting out of the sediment organic matter.

2.1.4. Transport of PAHs in Organic Matter

Organic matter can be widely found in nature. Organic matter is often responsible for sorption of hydrophobic contaminants. The interactions between PAHs and HA have been studied previously by many researchers. Aromatic moieties in humic substances are the main sites for hydrophobic sorption of PAHs (Kopinke et al. 2001). Kang and Xing (2005) examined the sorption of phenanthrene by humic acids (HAs) and humins. All of the phenanthrene sorptions were nonlinear and sorption data were fitted to a Freundlich equation. There was a positive trend between the sorption coefficient and the aliphaticity, while there was a negative relation between the isotherm nonlinearity and the aliphaticity and between the sorption capacity and polarity of HAs. Polarity of humic substances seemed to play a more important role in phenanthrene sorption than structure of humic substances. Chefetz et al. (2000) investigated the sorption of pyrene on various types of natural organic matter (NOM), including cuticle, humin, HA, degraded lignin, peat and lignite. A positive trend of dependence was observed between the aliphaticity of the organic matter and distribution coefficients obtained from the sorption isotherms. It demonstrated the importance of the aliphatic moieties in the sorption of aromatic nonionic pollutants in complex NOM matrices. Liang et al. (2006) investigated the effect of chemical heterogeneity of HAs on the sorption of phenanthrene by HA extracts. The polarity and functionality were different for HAs extracted with the two different methods. The NaOH-extracted HA exhibited more nonlinear isotherm than the $Na_4P_2O_7$-extracted HA for the sorption of phenanthrene. There was no good correlation between sorption properties with the chemical and functional compositions of the HA.

The interaction between organic matter and PAHs depends on molecular properties of the sorbents (e.g. chemical structure or molecular weight composition) as well as on pH, ionic strength and other environmental conditions. It was reported that HAs had a distinct solubilizing effect on phenanthrene (Lassen and Carlsen 1997). The rate constant for the dissolution of phenanthrene in synthetic groundwater could be increased by 50% in the presence of 50 mg/L HAs. The interactions were influenced by macromolecular structural changes in the HAs under varying pH and ionic strength conditions of the aqueous phase. Chin et al. (1997) investigated the binding of pyrene to a number of humic substances isolated from various aquatic sources and a commercial HA. It was found there was a strong correlation between the pyrene binding coefficient and the molecular weights and aromaticity of the aquatic humic substances. The physicochemical properties of both humic materials and organic solutes were important in the binding process. Kopinke et al. (2001) described the sorption potential of pyrene to dissolved humic substances by an empirical two-parameter correlation involving the polarity (O/H atomic ratio) and the aromaticity. The sorption with poly (acrylic acid) esters indicated that aliphatic chains might be more effective than aromatic moieties in binding PAHs.

2.1.5. Transport of PAHs in Clay Minerals

The interaction between PAHs and clay mineral can play a significant role for sorbents with small amounts of organic matter. The influence of the mineral phase and solution/solute chemistry on the sorption of PAHs has been investigated in previous studies. Mader et al. (1997) studied the sorption of a series of PAHs on the pure mineral oxides α-Al_2O_3 and α-Fe_2O_3. They found sorption was reversible as sorption isotherms of the PAHs were linear to at least 50% of solute aqueous solubility. Surface area might not be the most important variable affecting the magnitude of the sorption coefficient. The type of mineral surface was important and could play a role in the sorption of nonionic HOCs. Müller et al. (2007) reported that the sorption of phenanthrene, pyrene, benzo(a)pyrene to the mineral sorbents (quartz, goethite-coated quartz, quartz-montmorillonite mixture) was fast and could be completed within 4 hours. The sorption isotherms of phenanthrene and pyrene were best described by the Freundlich isotherm model. The quartz-montmorillonite mixture was featured with the weakest affinity of phenanthrene and pyrene in spite of the combination having the greatest surface area.

The study by Ma and Zhu (2006) showed inorgano-organo-bentonite (IOB), which was bentonite mineral modified with both Fe polycations and cetyltrimethylammonium bromide (CTMAB), had strong affinity for phenanthrene in water. More than 99% phenanthrene was removed from water within 30 minutes. The removal rates were well described by the pseudo-second order model. Hundal et al. (2001) used smectites to sorb phenanthrene from aqueous solution. It was demonstrated that smectites could retain large amounts of phenanthrene from water. Hectorite exhibited the highest sorption affinity and capacity followed by Panther Creek montmorillonite. The sorption of phenanthrene by smectites was primarily a physical process in which capillary condensation into a network of nano- or micropores created by quasicrystals might be a dominant mechanism. James et al. (2005) investigated the sorption of phenanthrene on different wood chars. The uptake capacities and nonlinear sorption behaviors with the laboratory wood chars were similar to those with the field wood chars. Heterogeneous surface properties could contribute to sorptive properties of the wood chars. Moreover, the sorption of PAHs (acenaphthene, anthracene, fluorene, fluoranthene, naphthalene and pyrene) on granular activated carbon (GAC) was evaluated by Valderrama et al. (2008). The results indicated that the rate-determining step of PAH extraction was the sorbent-phase diffusion.

2.2. SORPTION AND DESORPTION THEORY

2.2.1. Main Types of Isotherms

The study of isotherm is one of the most favored approaches to the theoretical aspects of all sorption systems. Sorption isotherm is critical to evaluate the sorption capacity of adsorbents as well as to understand the sorbate-sorbent interactions. As for the sorption at solid-liquid interface, the amount of adsorbed substance in solid phase is plotted against the equilibrium concentration in the liquid phase at constant temperature. Sorption isotherm can be characterized by certain constants that reflect the surface properties and affinity of the sorbent. Giles et al. (1974) proposed a general classification of sorption isotherms. There are four main types of sorption isotherms as shown in Figure 2.2.

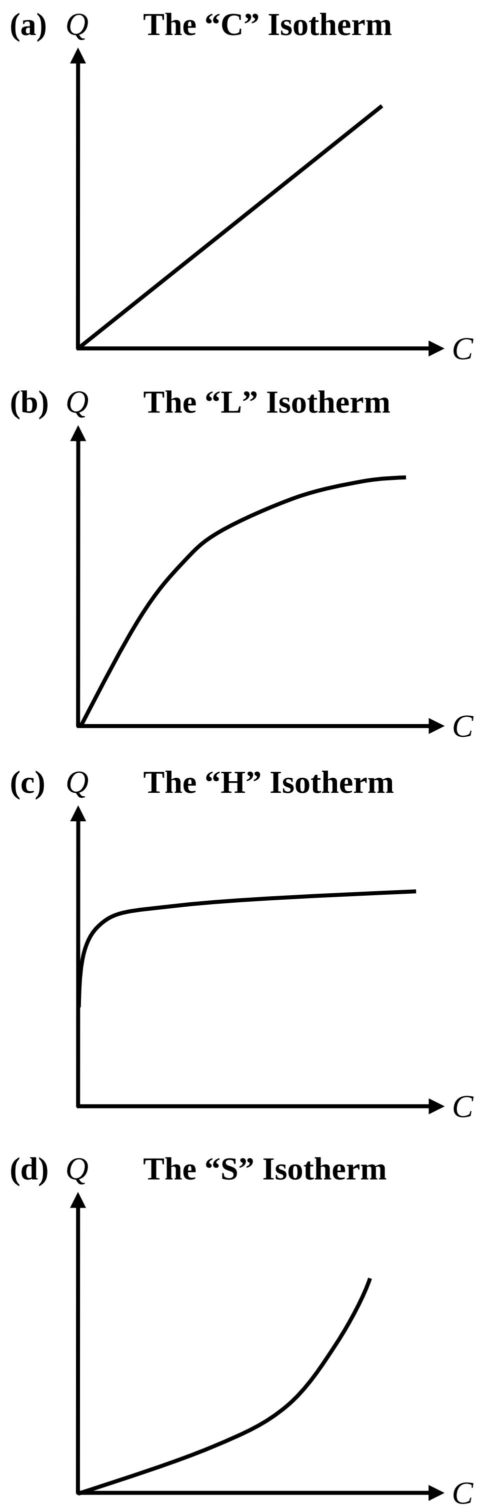


Figure 2.2 The four main types of isotherms (Giles et al. 1974)

(1) The "C" Isotherm

As shown in Figure 2.2(a), type C isotherm exhibits constant ratio between the concentration of sorbate in solution and that adsorbed on the solid at any concentration. This ratio can be usually expressed as "distribution coefficient", K_d (L/kg). Type C isotherm shows constant affinity for a wide range of concentrations. Within a narrow range of concentration or at very low concentration, many sorption processes behave this way.

(2) The "L" Isotherm

As shown in Figure 2.2(b), the ratio between the concentration of sorbate in solution and that adsorbed on the solid decreases when the concentration of sorbate in solution increases. This concave curve indicates a progressive saturation in solid-liquid system. In some cases, the curve may reach a strict asymptotic plateau, indicating there is a limited sorption capacity. In other cases, the curve does not reach any plateau, indicating there is no strictly limited sorption capacity.

(3) The "H" Isotherm

As shown in Figure 2.2(c), initial ratio between the concentration of sorbate in solution and that adsorbed on the solid is very high, while this ratio increases slowly as the concentration of sorbate in solution increases. Type H isotherm can be regarded as a particular case of type L isotherm. Under certain conditions, the sorbate exhibits such a high affinity that the initial slope cannot be distinguished from infinity.

(4) The "S" Isotherm

As shown in Figure 2.2(d), type C isotherm exhibits the sigmoidal curve. On the one hand, this type of isotherm may be caused by cooperative adsorption through sorbate-sorbate attractive forces at the surface. On the other hand, the sorption of a sorbate may be also inhibited by a competing reaction within the solution.

2.2.2. Adsorption Isotherm Models

Adsorption in solid-liquid system is a physiochemical process that involves the mass transport of an adsorbate from the liquid phase to the solid adsorbent surface. When the thermodynamic equilibrium of the adsorbate concentration is achieved between solution and adsorbent, there is no further net adsorption. Adsorption equilibrium is the most fundamental property of the adsorbate-adsorbent interaction (Ribeiro et al. 2001). Some equilibrium models as follows have been developed to describe adsorption isotherm.

(1) Freundlich Isotherm Model

Freundlich isotherm model was previously developed for representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure (Limousin et al. 2007). It has been widely used for describing the sorption at solid-liquid interface. The Freundlich empirical model is represented by:

$$Q_e = K_f C_e^n \tag{2.1}$$

where Q_e is the amount of sorbate adsorbed per unit mass of sorbent (mg/kg), C_e is the concentration of sorbate in equilibrium solution (mg/L), K_f is the Freundlich adsorption coefficient [(mg/kg)/(mg/L)^n] which provides an index of adsorption capacity, n is the Freundlich exponent that describes isotherm non-linearity. K_f depends on the temperature and the given sorbent-sorbate couple. The linearized expression of the Freundlich isotherm model is shown as follows:

$$\log Q_e = \log K_f + n \log C_e \tag{2.2}$$

The Freundlich isotherm model is an empirical equation that can describe the surface heterogeneity with non-uniform distribution of adsorption heat and affinities over the sorbent surface. This empirical model can reflect multilayer adsorption. The slope n is a measure of adsorption intensity or surface heterogeneity (Hameed et al. 2007). It becomes more heterogeneous as its value gets closer to zero. n above one is an indicative of cooperative adsorption (Fytianos et al. 2000).

(2) Langmuir Isotherm Model

The Langmuir isotherm model assumes that all the adsorption sites have equal solute affinity and that adsorption at one site does not affect the adsorption at an adjacent site (Langmuir 1918). The mathematical expression of Langmuir isotherm model is shown as follows:

$$Q_e = \frac{Q_{\max} K_L C_e}{1 + K_L C_e} \tag{2.3}$$

where $Q_{\max}$ and K_L are the maximum adsorption capacity and Langmuir affinity constant, respectively. It is used in monolayer adsorption where the adsorbed layer is one molecule thick. Once a molecule occupies a site, no further adsorption can take place at that site. Adsorption energy is constant and the adsorbent has a finite capacity for the sorbate.

(3) Redlich-Peterson Isotherm Model

The Redlich-Peterson isotherm model is an empirical isotherm incorporating three parameters (Redlich and Peterson 1959). The mathematical expression of Redlich-Peterson isotherm model is shown as follows:

$$Q_e = \frac{AC_e}{1 + BC_e^{\beta}} \tag{2.4}$$

where A is the Redlich-Peterson constant (L/g), *B* is a constant having unit of L/mg, and β is an exponent that lies between 0 and 1. This model can be applied either in homogeneous or heterogeneous systems due to its versatility. It combines elements from both the Langmuir and Freundlich isotherm models. The mechanism of adsorption is a hybrid and does not follow ideal monolayer adsorption.

(4) Tempkin Isotherm Model

Tempkin and Pyzhev (1940) developed a isotherm model which considered the effects of some indirect adsorbate/adsorbate interactions on adsorption isotherms. The mathematical expression of Tempkin isotherm model is shown as follows:

$$Q_e = \frac{RT}{b}(\ln AC_e) \tag{2.5}$$

where A and RT/b = B are the Tempkin isotherm constants. Constant B is related to the heat of adsorption. It is suggested that the heat of adsorption of all molecules in the layer would decrease linearly when ignoring the extremely low and large value of concentrations.

(5) Dubinin-Radushkevich Isotherm Model

Another model for the analysis of isotherms was proposed by Dubinin (1960). The Dubinin-Radushkevich model is represented by:

$$Q_e = Q_D \exp(-B_D \varepsilon^2) \tag{2.6}$$

$$\varepsilon = RT \ln(1 + \frac{1}{C_e}) \tag{2.7}$$

where Q_D is the Dubinin-Radushkevich model constant (mg/g); B_D is the Dubinin-Radushkevich model constant (mol^2/kJ^2); ε is the Polanyi potential; R is the gas constant (8.314 J/mol K) and T is the absolute temperature (K). The mean energy of sorption, E, is calculated by the following equation:

$$E = \frac{1}{\sqrt{2B_D}} \tag{2.8}$$

The approach was usually applied to describe the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. When adsorption data at different temperatures are plotted as a function of logarithm of the amount adsorbed versus the square of potential energy, all the data points should fall into one curve.

(6) Sips Isotherm Model

Sips isotherm model is a combination of the Langmuir and Freundlich isotherm type models and can be used for heterogeneous surfaces (Günay et al. 2007). Sips isotherm model has the following form:

$$Q_e = \frac{K_S C_e^{\beta_S}}{1 + a_S C_e^{\beta_S}} \tag{2.9}$$

where K_S is the Sips model isotherm constant (L/g); a_S is the Sips model constant (L/mg) and β_S is the Sips model exponent. At low sorbate concentrations, it effectively reduces to the Freundlich isotherm model; at high sorbate concentrations, it predicts a monolayer sorption capacity characteristic of the Langmuir isotherm model. The model parameters are mainly influenced by the operating conditions such as pH, temperature and concentration (Pérez-Marín et al. 2007).

2.3. ENHANCED EXTRACTION OF PAHS FROM SOILS

2.3.1. Extraction with Surfactants

Surfactants are of interest to environmental scientists and engineers. In an aqueous medium, surfactants are present as dispersed molecules (monomers) at low concentrations. The surfactant molecules consist of a hydrophilic moiety ("head") and a hydrophobic moiety ("tail"). When the concentration of surfactants is above a critical concentration (CMC), surfactant monomers can aggregate to form micelles. The surfactant molecules can assemble in aqueous solutions in a way that the hydrophobic tails all flock inside the micellar core, while the hydrophilic heads remain in the outer surface of the micelle (Pennell et al. 1993). The micelles and their constituent surfactant molecules are in reversible thermodynamic equilibrium. The schematic illustration of micelle formation is shown in Figure 2.3.

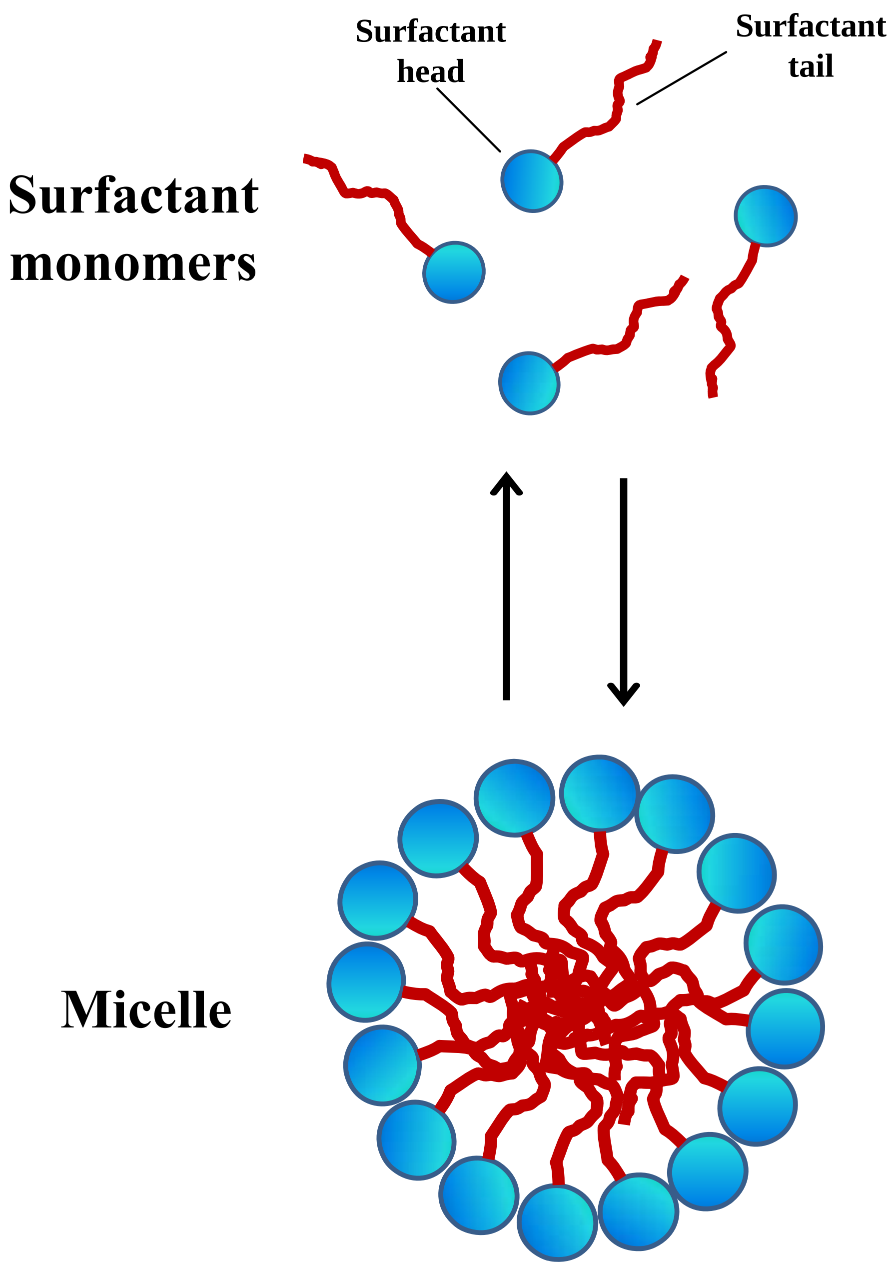


Figure 2.3 Schematic illustration of micelle formation

Surfactants can lower the surface tension of a liquid. The physical properties like surface tension, interfacial tension and adsorption can significantly change below the CMC, while there is no change in these properties above the CMC. Surfactants can also increase the solubilities of HOCs by partitioning them into the hydrophobic cores of surfactant micelles above the CMC (Makkar and Rockne 2003). The CMC of surfactant varies with surfactant structure, the temperature of the solution, the presence of electrolyte and various organic compounds (Haigh 1996). Schematic diagram of the variation of physical property with surfactant concentration is shown in Figure 2.4.

Based on the origins, the surfactants can be classified into synthetic surfactants and biosurfactants. They can also be classified as anionic, cationic, non-ionic, and zwitterionic surfactants depending on the nature of the hydrophilic group. Anionic surfactants contain anionic functional groups at their head, such as sulfate, sulfonate, phosphate, and carboxylates. Cationic surfactants contain a quaternary ammonium group that has a positive charge. Nonionic surfactants are characterized by hydrophilic head groups that do not ionize appreciably in water. Zwitterionic surfactants have both positive and negative charges on the surface-active part of the molecule.

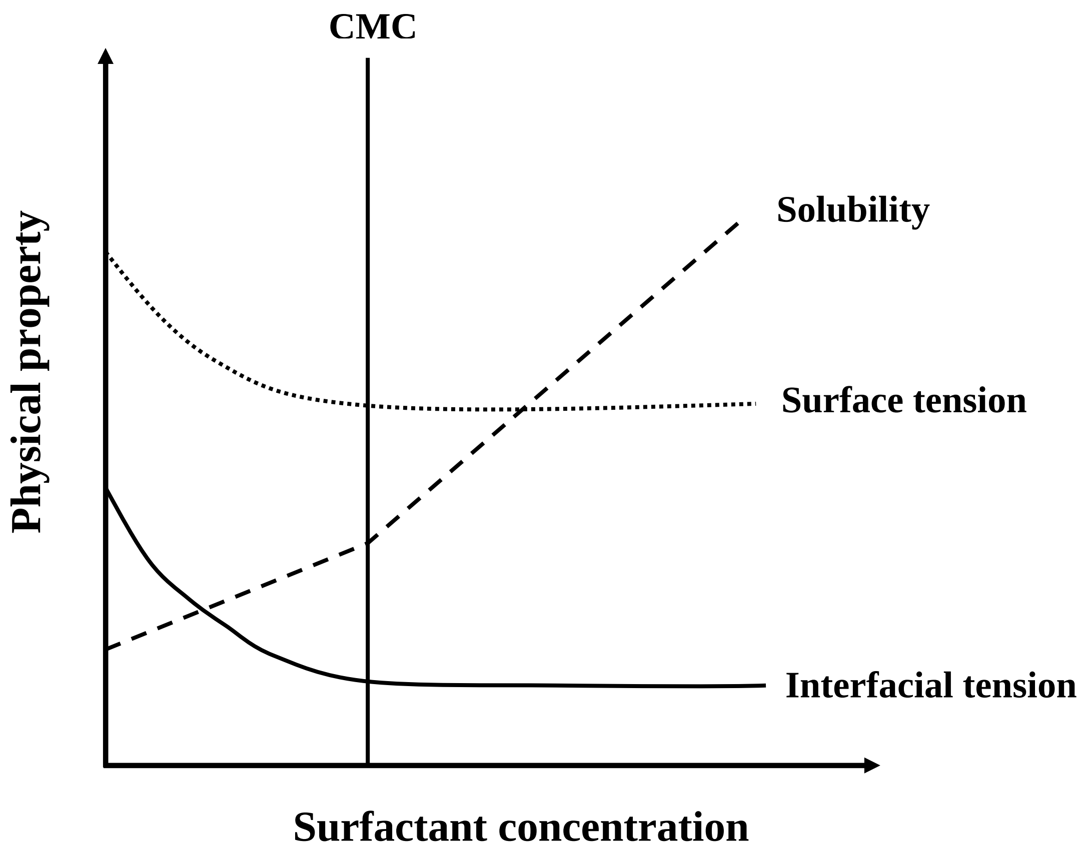


Figure 2.4 Schematic diagram of the variation of physical property with surfactant concentration (Mulligan et al. 2001)

The use of surfactants to remove PAHs in soils has been investigated in many laboratory and field studies (Khodadoust et al. 2004; Shin et al. 2006; Ahn et al. 2008). The study by Zhou and Zhu (2007a) indicated that surfactants would weaken or enhance PAH desorption depending on surfactant concentrations below or above the corresponding critical enhance desorption concentration values. Surfactants could show better performance for desorption of the relative hydrophobic PAHs from soils with lower clay and higher organic matter content. Both the relative efficiency coefficient and critical enhance desorption concentration were essential for the selection of optimum surfactant species and the corresponding operating concentration. The sorption of surfactant onto soils can have significant effects on the performance of surfactant-enhanced soil flushing for contaminated soils. In another column study by Zhou and Zhu (2008b), it was found that the removal of phenanthrene from contaminated soils was enhanced only when the sorption breakthrough of Triton X-100 (TX100) occurred and a critical enhanced flushing concentration was achieved. Cheng and Wong (2006) examined the desorption behavior of phenanthrene and pyrene in soil-water system in the presence of Tween 80 and DOM derived from manure compost. The combined effects of surfactants and DOM on the desorption of PAHs had a much stronger effect on the release of PAHs than either one of them.

Besides the synthetic surfactants, there has been an increasing interest in the application of biosurfactants. As the natural compounds, biosurfactants in general exhibit greater environmental compatibility, better surface activity, lower toxicity, and higher biodegradability (Lai et al. 2009). Among the best known biosurfactants, rhamnolipids are widely used and produced by several *Pseudomonas* species (Mata-Sandoval et al.

1999). The effect of rhamnolipid biosurfactant on the transport of a mixture of three PAHs (naphthalene, fluorene, and phenanthrene) in silica, octadecyl-coated silica, and HA-coated silica columns were investigated by Noordman et al. (2000). In the presence of rhamnolipid, the facilitated transport of the PAHs could be predicted by accounting for sorption, solubilization and admicellar sorption. Shin et al. (2006) reported the relatively high removal efficiencies in the presence of rhamnolipid were found at pH 5 and 6. The results indicated that the pH-dependent rhamnolipid structure displayed varied solubilizing capacity in this flushing process. Song et al. (2008) evaluates the performance of saponin, a plant-derived biosurfactant, for simultaneously removing phenanthrene and cadmium from the contaminated soils. The results showed that the efficiencies of saponin for the removal of phenanthrene were greater than that of TX100.

Some surfactant mixtures exhibit synergistic properties. Such combinations show considerable decrease in surface tension and a lower CMC value can be obtained when compared with each of the individual surfactant (Yang et al. 2006). Some researchers have attempted to use mixed surfactants with an aim to improve the performance of surfactant-enhanced soil remediation. Zhang and Zhu (2010) studied the distribution of PAHs in the presence of single Tween 80 or sodium dodecyl benzene sulfonate (SDBS) and their mixture. It was observed that the greatest desorption efficiency was observed within a proportion of SDBS/Tween 80 = 1:9. Sorption of surfactants on soil could reduce the desorption efficiency and mixed surfactant SDBS-Tween80 reduced their sorption on soil mutually. The mixing of TX100 with sodium dodecyl sulfate (SDS) was also used to remove phenanthrene from soil (Zhou and Zhu 2008a). It was found there was less sorption of TX100 onto the soil in the presence of SDS. The solubilization of

TX100 for phenanthrene increased with the addition of SDS. The formation of mixed surfactant micelles could lead to the decrease in the CMC of TX100 in mixed surfactant solutions.

Recently, a few studies have also indicated the potential for using surfactant extraction associated with other remediation techniques. Alcántara et al. (2008) used the extraction of PAHs from the soil with surfactant followed by electrochemical degradation of the liquid collected. The surfactant with best performance for removal of anthracene, benzo[*a*]pyrene and phenanthrene removal was Tyloxapol, Brij 35 and Tween 80, respectively. In the following electrochemical process, the complete degradation of PAHs was obtained when electrodes of graphite or Ti and Ti/Pt were used. Saxe et al. (2000) evaluated the feasibility of using a combination of soil washing and Fenton oxidation to remove PAHs from soil. The results showed that nonionic ethoxylatetype surfactants could increase the efficiency of soil washing. The utilization of Fenton's reagent to treat wastewater from soil washing was a feasible technique. The removal of PAH in soil washing wastewater for a given dose of Fenton's reagent was inversely proportional to the water solubility of the PAH species (anthracene greater than fluoranthene greater than phenanthrene).

2.3.2. Extraction with Organic Solvents

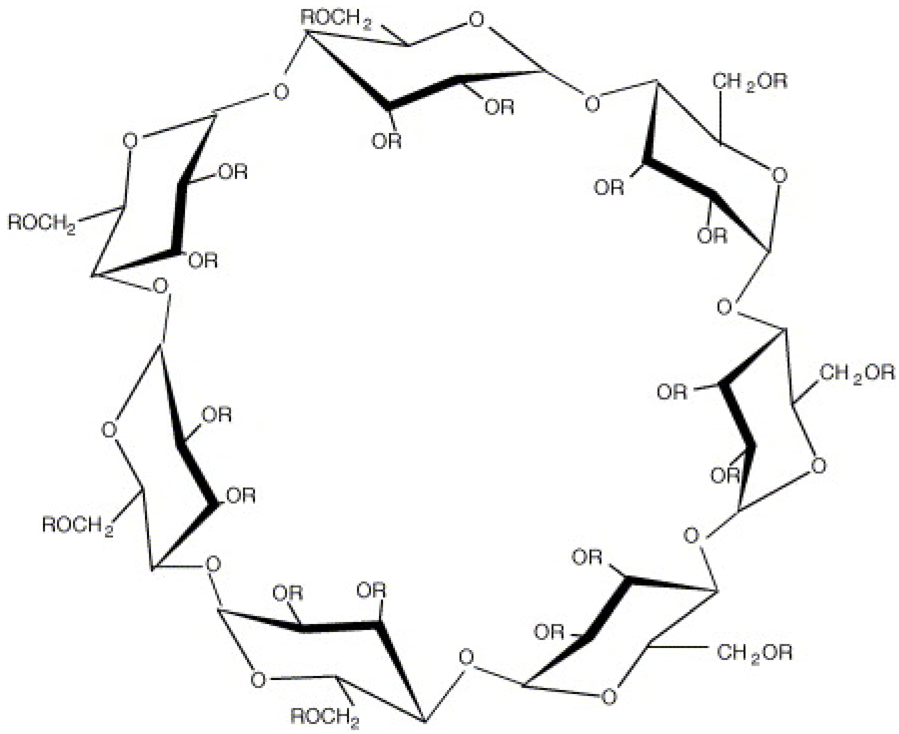
Various organic solvents as well as mixtures of solvents have been tested for the exaction of PAHs from contaminated soil. Ethanol, 2-propanol, acetone, and 1-pentanol were used as water miscible co-solvents in the removal of PAHs from highly contaminated soil (Khodadoust et al. 2000). The results showed that a ternary mixture of

5% 1-pentanol, 10% water, and 85% ethanol was effective in solvent washing process. More than 95% of the PAH was removed from highly contaminated field soils through a three-stage cross-current solvent washing train. Li et al. (2000) evaluated the feasibility of using a cosolvent-assisted electrokinetic technique for remediating soils contaminated by PAHs. The results showed the desorption of phenanthrene from soil increased with the addition of cosolvents to the conducting fluid. Electroosmosis played an important role in helping a cosolvent to be effective in the remediation process. Rababah and Matsuzawa (2002) reported that the optimum operational conditions for fluoranthene extraction (about 93%) from soil were observed when the mixture of cyclohexane and ethanol (3:1) was used at 40 °C for 20 minutes.

2.3.3. Extraction with Cyclodextrins

Cyclodextrins have been proposed as an alternative agent for extraction of PAHs from soil. Cyclodextrins are cyclic oligosaccharides generated from the enzymatic degradation of starch by bacteria (Wang et al. 2004c). Cyclodextrins are often constituted by 6-8 glucopyranoside units, and can be topologically represented as toroids with the larger and the smaller openings of the toroid exposing to the solvent secondary and primary hydroxyl groups respectively. They have a hydrophilic shell and an apolar (hydrophobic) cavity with toroidal shape (Figure 2.5). Cyclodextrins have feature to form water-soluble inclusion complexes with hydrophobic organic molecules (Dean and Scott 2004). Due to this arrangement, the interior of the toroids is able to host other hydrophobic molecules. In contrast, the exterior is sufficiently hydrophilic to impart cyclodextrins (or their complexes) water solubility.

Therefore, the extractable organic molecules in soil can be encapsulated by the cyclodextrin macromolecule to form an inclusion complex. Ko and Yoo 2003 (2003) investigated the effects of hydroxypropyl-β-cyclodextrin (HPCD) on the phenanthrene sorption and desorption from sands. It was observed that distribution coefficient of phenanthrene was continuously decreased as HPCD concentration increased. Flushing of contaminated sands by HPCD solution was effective and the efficiency was dependent on the HPCD concentration. Interaction among phenanthrene, water, HPCD, and solid phase could be also affected by soil types and organic matter contents. In another study, Viglianti et al. (2006) evaluated the effectiveness of β-Cyclodextrin (BCD), hydroxypropyl-β-cyclodextrin (HPCD) and methyl-β-cyclodextrin (MCD) solutions to remove PAH occurring in industrially aged-contaminated soil. The results showed the use of cyclodextrins was effective for the removal of PAH compounds. Kinetic studies showed that PAHs solubilization by cyclodextrins was a fast process. The improvement of PAHs extraction was directly proportional to cyclodextrin concentration. There was no significant difference in extraction efficiency when the temperature ranged between 5 and 35 °C.



where R=$CH_2CHOHCH_3$ or H

Figure 2.5 Structure of cyclodextrin (Dean and Scott 2004)

2.3.4. Extraction with Vegetable Oil

It has been demonstrated that vegetable oil can be used as an effective solvent in the field of soil remediation for HOCs. Vegetable oil can be used as a solvent to physically extract PAHs and it can also be used as soil amendment to enhance biological and non-biological treatments (Yap et al. 2010). Pannu et al. (2004) reported a method for remediation of PAH-contaminated soil using peanut oil as the extractant. With the peanut oil concentrations of 2.5-20%, extraction efficiency for the removal of anthracene was higher than 90%. Optimal pH for these extractions was 6 and 7. A sequential extraction using 5% peanut oil followed by another 5% oil was better than a single 10% oil extraction. Gong et al. (2006) conducted column experiments to remove PAHs from contaminated soils using sunflower oil. Results showed that the sunflower oil was effective in removing PAHs from manufactured gas plant-contaminated soils. After the treatment, approximately 4-5% of the sunflower oil remained in the soils. This remaining fraction of sunflower oil was degraded eventually by allowing air exchange and supplying with nutrients. Organic carbon content of the soil was restored to original level after 180 days of incubation.

2.4. ADSORPTION OF POLLUTANTS ON FLY ASH

2.4.1. Fly Ash Properties

(1) Physical Properties

FA is one of the waste products produced from combustion processes (Singh 2009). FA consists of fine, powdery particles which are predominantly spherical in shape. These particles are either solid or hollow, and filled with smaller amorphous particles and crystals (plerospheres). Figure 2.6 shows the typical SEM images of FA. The characteristics of FA are related to the source and uniformity of the coal, conditions of combustion, type of emission control devices and storage and handling methods. FA particles have an average diameter less than 10 μm (Jala and Goyal 2006). The fine particles are aggregated into micron and sub-micron spherical particles with size of 0.01-100 mm and the sub-micron particles can be further entrapped into large spheres (Davison et al. 1974; Fisher et al. 1976). The particle size distribution of most bituminous coal FA is generally similar to that of silt (Ahmaruzzaman 2010). Campbell et al. (1978) studied the particle size distribution of FA obtained from an electrostatic-precipitator (ESP). The results showed that most of the FA was in the range of 1-50 μm. The particle size distribution of FA obtained from the a power station was found to be between 3.6 and 181 μm (Dizge et al. 2008). The specific gravity of FA usually ranges from 2.1 to 3.0 g/cm^3. The specific surface area of FA may vary from 170 to 1000 m^2/kg (Mattigod et al. 1990). FA, from different power plants or with different coal sources, may have different colors. The color of FA varies from tan to gray to black, depending on the amount of unburned carbon in the ash. Lignite and subbituminous FA are usually with color of light tan to buff, showing relatively low amounts of carbon and the presence of some lime or calcium. The color of bituminous FA is usually some shade of gray.

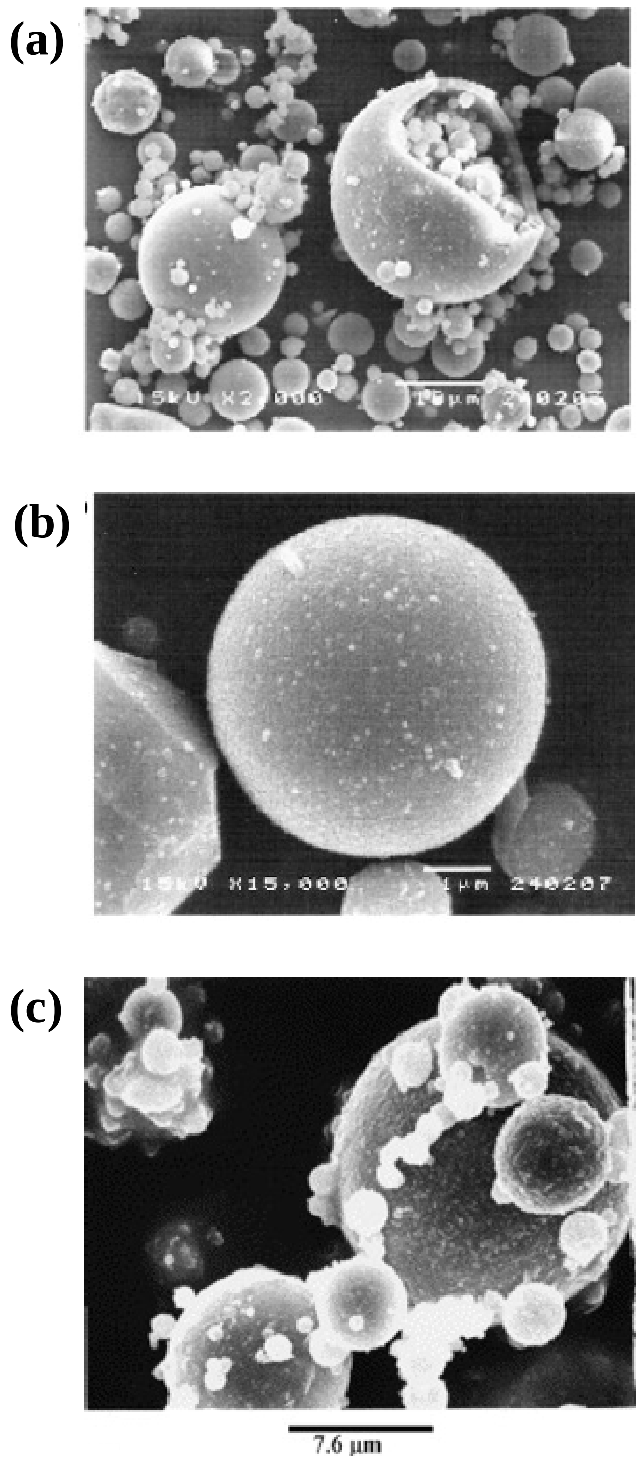


Figure 2.6 SEM images of FA (a) (b) (Pengthamkeerati et al. 2008a), (c) (Wang and Wu 2006)

(2) Chemical Properties

The primary components of power station FA are silica (SiO_2), alumina (Al_2O_3) and iron oxides (Fe_2O_3). FA also includes varying amounts of carbon, calcium, magnesium, sodium, potassium, and sulphur. There are mainly two types of ash: Class F (low lime) and Class C (high lime). Most Class F FA are produced from anthracite, bituminous, or sub-bituminous coals and containing less than 7 wt.% CaO; most Class C FA are produced from lignite coals and containing more lime (5-30 wt.%). Class F FA contains more than 70 wt% SiO_2+Al_2O_3+Fe_2O_3 and Class C FA contains a SiO_2+Al_2O_3+Fe_2O_3 content of 50-70 wt%. The main difference between Class F and Class C FA is in the amount of calcium, silica, alumina, and iron in the ash. The main forms of calcium in FA include calcium hydroxide, calcium sulphate, and glassy components, in combination with silica and alumina. Class F and Class C FA also differs in the amount of alkalis and sulphates.

The pH of FA varies from 4.5 to 12.0. Electrical charge on the interface is also determined by zero point charge (pHzpc) of FA. The oxides of metals in FA can form aquo complexes with water and develop a charged surface through amphoteric dissociation at varying pH values (Ahmaruzzaman 2009). At low pH level, a positive charge is developed at the oxides surface of FA; at high pH level, the surface of FA tends to be negatively charged.

2.4.2. Adsorption of Contaminants in Gas Phase

(1) Adsorption of Sulphur Compounds

FA can be used as a cheap absorbent for the adsorption of sulphur compounds. Al-Shawabkeh et al. (1995) have used two types of FA from fluidized bed and pulverised coal combustors to adsorb SO_2 under the treatment of calcium hydroxide. It was found 92-100% conversion of CaO to $CaSO_4$ could be achieved within 1 hour. The desulphurization activity of sorbents obtained by mixing certain FA with calcium hydroxide has also been studied (Davini 1995). The results showed that flue gas desulphurization by FA could be a promising application for large already installed industrial boilers. Kastner et al. (2002) investigated the potential of using coal FA for removal of H_2S and other reduced sulfur compounds. The results showed that coal FA from a selective catalytic reduction process could promote the catalytic oxidation of H_2S and ethanethiol at room temperature (23-25 °C). The removal efficiency for H_2S or ethanethiol could achieve at 99% and 50%, respectively.

(2) Adsorption of Nitrogenous Compounds

In previous studies, FA was also applied as an adsorbent for the removal of NO_x from flue gases. Lu and Do (1991) proposed to use power plant FA as an adsorbent for NO_x removal from flue gases. It was found that the unburned carbon remaining in the FA particles played an important role in the removal of NO_x. The unburned carbon was related to the main surface area of FA and it could be activated to further improve the adsorption ability. Kulaots et al. (2001) reported that pure gaseous ammonia may be reversibly adsorbed on the surfaces of FA under ordinary ambient conditions. There was some extent of irreversible chemisorptions which might be associated with the oxides on the carbon surface.

(3) Adsorption of Mercury

Mercury emissions from coal-fired utility boilers have become a great environmental concern. FA has been studied for potential application in mercury emission control. Hassett and Eylands (1999) conducted laboratory experiments about mercury sorption on coal FA. The results showed that a direct correlation existed between carbon content and mercury partitioning among ash samples. The mercury-sorbing capacity of ash was highly temperature dependent. Hower et al. (1999) separated carbon from the FA and demonstrated the varying role of carbon types in the capture. The results indicated that variability in the carbon forms could influence the amount of mercury adsorbed on FA. Another study showed FA could promote Hg emission control when fabric filters were used (Karatza et al. 1998). Malerius and Werther (2003) investigated mercury removal in flue gas of electrostatic precipitator. The adsorption isotherms for the FA were of the Langmuir type.

(4) Adsorption of Gaseous Organics

FA has also been used for the adsorption of organic gas. Peloso et al. (1983) studied the adsorption of toluene vapours on FA. The roles of some geometric, physical and chemical parameters of FA particles on toluene recovery were assessed. The results showed that FA samples, obtained after particle aggregation and thermal activation at a suitable temperature, presented satisfactory adsorption performance for toluene vapors. In another study, the adsorption of m-xylene on FA was evaluated (Rothenberg et al. 1991). It was observed there was no increase in adsorption rates with increased temperature and adsorption rate constants decreased with increase in vapor pressure. Kinetics of m-xylene adsorption on FA were similar to kinetics reported for penetration of absorbates into porous adsorbents.

2.4.3. Adsorption of Contaminants in Aqueous Phase

(1) Adsorption of Inorganic Components in Aqueous Phase

(i) Adsorption of Heavy Metals

As a low-cost adsorbent, FA has been used to remove metals in aqueous phase. During the removal, both adsorption and precipitation may be involved. Erol et al. (2005) studied the removal of Cu^{2+} and Pb^{2+} ions by using six types of FA with different compositions. It was observed that both the Cu^{2+} and Pb^{2+} removal capacities depended strongly on CaO content of FA. In another study, the effect of FA characteristics on the removal of Cu^{2+} from aqueous solution was investigated (Lin and Chang 2001). The results indicated that the carbon fraction of the FA was a significant parameter for Cu^{2+} adsorption. The adsorption of Cd^{2+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, and Pb^{2+} by Class F coal FA has been studied by Wang et al. (2004a). Results indicated that the presence of anionic metal ions had no influence on the adsorption of cationic metal ions by the FA.

The utilization of coal FA as a low cost adsorbent material was also applied for the adsorption of heavy metal ions (Zn, Pb, Cd, Mn and Cu) in the municipal solid waste leachate (Mohan and Gandhimathi 2009). FA possesses the higher adsorption capacity for lead and cadmium compared to other heavy metals. The Freundlich isotherm was fitting well for the adsorption process. The chemical sorption or chemisorptions could be the rate-limiting step for the adsorption of Pb^{2+}, Cd^{2+}, and Cu^{2+} on FA, while intraparticle diffusion could be rate-limiting step for the adsorption of Zn^{2+} and Mn^{2+}on FA. The generation of mine drainage which contains toxic heavy metals is an important environmental concern facing the mining industry. Ríos et al. (2008) evaluated the use of coal FA, natural clinker and synthetic zeolites to clean-up acid mine drainage. It was found that pH played a very important role in the sorption/removal of the contaminants. The use of these materials could provide improved methods for the treatment of mine drainage.

The adsorption performance is closely related to the characteristics of FA. Various approached have been developed to treat FA before the application for the adsorption of heavy metals. Nascimento et al. (2009) studied the adsorption of heavy metal cations using coal FA modified by hydrothermal method. The treated FA was effective adsorbent for removal of Pb^{2+}, Zn^{2+}, Mn^{2+} and Cu^{2+} ions from aqueous solutions. An increase of time and temperature could increase the capacity of adsorption and ion-exchange adsorption might be the related mechanism. Wu et al. (2008) found zeolites synthesized from FA were efficient for Cr^{3+} immobilization from aqueous solution. The mechanism of Cr^{3+} removal involved ion exchange and precipitation as chromium hydroxide. The pH level strongly influenced the Cr^{3+} removal by the zeolites. The application of the FA has been investigated for removal of Mn^{2+} from aqueous solutions. Sharma et al. (2007) found FA could be successfully used for Mn^{2+} removal and the adsorption process was spontaneous and exothermic. Banerjee et al. (2005) reported that impregnated FA could be used efficiently as an adsorbent for the removal of Cr^{6+} and

Hg^{2+}. The adsorption can be explained by surface complex formation and ligand exchange reactions. Alinnor (2007) investigated the removal characteristics of lead and copper ions from aqueous solution by FA under various conditions. The kinetic study showed that lead and copper ions could be adsorbed onto the FA within 20 minutes, while equilibrium was attained within 2 hours. The hydration of FA could increases the system pH, leading to a higher degree of precipitation of metal ions and removal efficiency.

(ii) Adsorption of Phosphate

The FA can be used as the adsorbent for phosphate removal (Yildiz 2004; Oguz 2005). The effectiveness of FA in removing phosphate from aqueous solution was studied by Lu et al. (2009). It was found the removal of phosphate by FA included a fast and large removal representing precipitation, followed by a slower and longer removal due to adsorption. The formation of phosphate precipitation as a brushite and the adsorption on hydroxylated oxides could contribute to the removal of phosphate by FA.

Chen et al. (2006) studied the removal of phosphate from aqueous solution by zeolite synthesized from FA. Results showed that there was a remarkable increase in phosphate immobilization capacity (from 1.2 to 7.6 times) following the synthesis process. Pengthamkeerati et al. (2008a) investigated the chemical modification of coal FA for the removal of phosphate from aqueous solution. Results showed that CaO content in the FA and pH at equilibrium solution played an important role in phosphate removal by precipitating calcium phosphate and adsorption.

(iii) Adsorption of Other Inorganic Components

The adsorption of other inorganic components on FA was also investigated previously. Diamadopoulos et al. (1993) have evaluated the use of FA for removing arsenic from water. The results indicated that arsenic could be removed from water by FA and the adsorption process was almost irreversible. The removal efficiency depended markedly on the pH level. In a previous study, boron removal from aqueous solutions by adsorption was investigated (Öztürk and Kavak 2005). The results showed that FA was an effective adsorbent for the removal of boron. The adsorption process was exothermic in nature and equilibrium adsorption data followed Langmuir isotherm. Polat et al. (2004) presented a methodology for boron removal by using coal and FA as adsorbents. They examined the effect of different factors (pH, liquid/solid ratio, time of reaction, and pre-treatment) on the boron removal capacity.

(2) Adsorption of Organic Components in Aqueous Phase

(i) Adsorption of Phenolic Compounds

Phenolic compounds are among the most important organic pollutants in existence. FA has a good adsorption potential for phenolic compounds. The adsorption of phenolic compounds has been studied in many previous studies (Kumar et al. 1987; Srivastava et al. 2006; Kamble et al. 2008; Potgieter et al. 2009; Sharan et al. 2009). The use of FA for removing mono-chlorinated phenols (*o*-chlorophenol and *p*-chlorophenol) was evaluated by Aksu and Yener (2001). The adsorbing capacity correlated with substituted group, initial pH and initial mono-chlorinated phenol concentration. The adsorption of mono-chlorinated phenols was dependent on the position of chlorine substituted on the phenol molecule. The power plant FA was observed to be effective for the removal of 2-*sec*-butyl-4,6-dinitrophenol (DNBP) from wastewater (Wang and Jiang 2007). The high adsorption capacity and sufficient removal efficiencies of DNBP from solutions could be achieved at pH 4.0 with an adsorbent dosage of 5 g/L of FA particles with a size of 160-200 mesh at 20 °C and a contacting time of 120 minutes. FA could also be a good natural and cheap sorbent for 2,4-dichlorophenol (2,4-DCP) and pentachlorophenol (PCP) adsorption from waters (Estevinho et al. 2007). FA exhibited more affinity towards the sorption of PCP, in comparison to 2,4-DCP. Kao et al. (2000) reported that the adsorption of 2-chlorophenol (2-CP) and 2,4-dichlorophenol (2,4-DCP) on FA was affected by the pH of the solution, and both the carbon content and specific surface area of the FA. There was a nonpolar interaction between chlorophenols and FA. Sarkar and Acharya (2006) investigated the ability of FA in the removal of phenol, *o*-hydroxyphenol, *m*-hydroxyphenol and 4-nitrophenol. It was observed that the adsorption of these phenolic compounds was favored at a lower solute concentration, smaller particle size of FA, increased agitation time and speed, increased dose of FA and higher temperature. The leaching test showed that there was no release of phenolic compounds from the FA bed.

(ii) Adsorption of Dyes

Synthetic dyes have been increasingly used in textile industries, dye manufacturing industries, paper and pulp mills, tanneries, electroplating factories, food companies, and many other industries (Sun et al. 2010). The adsorption by FA provides an attractive alternative for the treatment of water contaminated with dyes (Khare et al.

1987; Viraraghavan and Ramakrishna 1999; T. ALBANIS 2000; Acemioglu 2004; Eren and Acar 2007; Karagozoglu et al. 2007; Matheswaran and Karunanithi 2007; Pengthamkeerati et al. 2008b; Demirbas and Nas 2009; Chatterjee et al. 2010). Without any pre-treatment, the coal FA could be used for the sorption of both basic as well as acid dyes from aqueous solutions (Janoš et al. 2003). Dizge et al. (2008) conducted adsorption kinetic and equilibrium studies of three reactive dyes, Remazol Brillant Blue, Remazol Red 133 and Rifacion Yellow HED on FA. It was found that the reaction was spontaneous and endothermic in nature, while external mass transfer and intraparticle diffusion were involved. Rastogi et al. (2008) investigated the performance of hydrocyclone for removal of methylene blue by using FA as an absorbent in a continuous mode. A maximum removal of 58.24% was observed at adsorbent dosage of 900 mg/L at pH 6.75 for an initial methylene blue concentration of 65 mg/L. The study by Kumar et al. (2005) indicated that the adsorption of methylene blue on FA involved a monolayer and particle-diffusion-controlled adsorption process. Sun et al. (2010) investigated the adsorption of two reactive dyes (Reactive Red 23 and Reactive Blue 171) and two acid dyes (Acid Black 1 and Acid Blue193) from aqueous solution on FA. Adsorption of four anionic dyes was found to be dependent on the initial pH of solution and adsorption processes followed the pseudo-second-order kinetics rate expression.

Different approaches have been developed for the treatment of FA before the application for dye adsorption. The FA treated by H_2SO_4 was used as adsorbent for the removal of methylene blue from aqueous solution (Lin et al. 2008). After the acid treatment, an increase in dye-adsorption capacity was observed. Freundlich isotherm and pseudo-second-order model could be used to describe the adsorption behavior. Li et al.

(2006) reported that coal FA was treated by a solid-state fusion method using NaOH and amorphous aluminosilicate geopolymers would be formed. These treated FA exhibited higher adsorption capacity than original FA and natural zeolite. FA exhibited higher capacity than red mud for the adsorption of methylene blue from aqueous solution (Wang et al. 2005b). Heat treatment adversely influenced the adsorption while acid treatment by nitric acid positively enhanced the adsorption capacity of FA. Wang et al. (2005a) also used sonochemical and microwave method for the pretreatment of FA and applied treated ash in dye adsorption.

The other components in water can have influence on the adsorption of dyes on FA. Visa et al. (2010) studied the simultaneous adsorption of methylene blue dye and cadmium, copper and nickel from multi-component solutions using FA. Some surfactants have influence on the adsorption of dyes by FA. Talman and Atun (2006) studied the adsorption of toluidine blue at a FA/water interface in presence of cationic surfactant cetyl pyridinium chloride (CPC) or SDS. It was concluded that the adsorption of toluidine blue depended on both the charge and the bulk concentration of the surfactants. It was also found by Janoš et al. (2003) that the dye sorption on FA was affected considerably by the presence of oppositely charged surfactants.

(iii) Adsorption of Other Organic Compounds

The adsorbent developed from bagasse FA was found to be effective for the removal of DDD [2,2-Bis(4-chlorophenyl)-1,1-dichloroethane] and DDE [2,2-Bis(4-chlorophenyl)-1,1-dichloroethene] pesticides from wastewater (Gupta and Ali 2001). The adsorption process showed exothermic in nature and followed both Langmuir and

Freundlich models. It was also found that coal FA had high retention capacity for metribuzin, metolachlor and atrazine (Singh 2009). Freundlich adsorption isotherm could be used to explain the adsorption of these herbicides on the FA. Atrazine showed a maximum assorption followed by metolachlor and metribuzin. FA was also shown to be an effective adsorbent for HA (Wang et al. 2008). The heavy metal ions could compete with HA for the adsorption on the active sites of FA. Wang and Zhu (2007) used several FA samples with varying contents of unburned carbon for HA adsorption. The unburned carbon in FA samples correlated with the BET surface area and HA adsorption behavior. Andersson et al. (2011) investigated the use of FA for removing lignin-related material. The results showed that FA exhibited good sorption performance, although its sorption capacity was lower than that of activated charcoal.

2.5. SOLID WASTE COMPOSTING

2.5.1. Composting Process

Composting is an aerobic process during which organic matter can be decomposed into humus-like substances and minerals by the action of microorganisms combined with chemical and physical reactions (Peigné and Girardin 2004). During the process, bacteria, fungi and other microorganisms can break down organic materials into stable and usable organic substances. The main products of composting are carbon dioxide, water, mineral ions and stabilised organic matter (Sharma et al. 1997). Organic matter can be also used to synthesise the microbiological biomass (Hartlieb et al. 2003). The composting process can help reduce the volume of wastes and induce the destruction of pathogenic microorganisms. The main types of composting systems include nonreactor, enclosed reactor and in-vessel systems (Peigné and Girardin 2004). Composting can be used as an environmentally sound, economically feasible and socially acceptable manner for recycling and disposal of organic solid waste (Imbeah 1998). Among the available technologies for the disposal of organic wastes, composting is presented as one of the most promising options (Gea et al. 2004). Composting can be used to treat a wide variety of solid wastes. The wastes include municipal solid waste (Finstein and Morris 1975; Hassen et al. 2001; Hartlieb et al. 2003; Lhadi et al. 2006; Belyaeva and Haynes 2009), animal manure (Lau et al. 1992; Tiquia et al. 1996; Imbeah 1998; Charest and Beauchamp 2002; Kelleher et al. 2002; Tiquia and Tam 2002; Huang et al. 2004; Wang et al. 2004b; Lhadi et al. 2006; Zhang and He 2006; Larney and Hao 2007; Vinnerås 2007; Zhu 2007; Bao et al. 2008), crop residues (Singh and Sharma 2002; Gaind and Gaur 2003; Tumuhairwe et al. 2009), fisheries waste (Schaub and Leonard 1996; Liao et al. 1997; Laos et al. 2002; Kwon and Lee 2004; Hu et al. 2009), paper and pulp residues (Atkinson et al. 1997; Jokela et al. 1997; Hackett et al. 1999; Charest and Beauchamp 2002; Marche et al. 2003), and sewage sludge (Nakasaki et al. 1985; Witter and Lopez-Real 1988; Racke and Frink 1989; Díaz-Burgos et al. 1993; Fang and Wong 2000; Wong and Fang 2000; Amir et al. 2005; Ling and Isa 2006; Doublet et al. 2011).

The successful composting process will generate the compost which is rich in nutrients. As a soil conditioner, a fertilizer, addition of vital humus or humic acids, this product can be used in gardens, landscaping, horticulture, and agriculture. It should be noted that the production of compost with a high nutrient content requires the control and reduction of nutrient losses during the process.

The composting process generally includes several stages (Figure 2.7). The first stage is the mesophilic phase which microorganisms such as mesophilic bacteria, actinomycetes, fungi and protozoa are involved. These organisms can grow between 10 and 45 °C (Cooperband 2000). During the mesophilic stage, easily degradable components such as sugars and amino acids can be broken down, producing CO_2, NH_3, H_2O, organic acids and heat (Hellmann et al. 1997). The accumulation of this heat leads to an increasing temperature in the pile. The second stage is the thermophilic phase. When the temperature is above 45-50 °C, thermophilic microorganisms replace mesophilic ones. Thermophilic phase is an active phase during which most of the organic matter is degraded. After the thermophilic stage, there is a cooling and maturation stage. The compost temperature decreases and falls to ambient temperature gradually. This is also an important stage because humus-like substances are produced to form mature compost (Cooperband 2000).

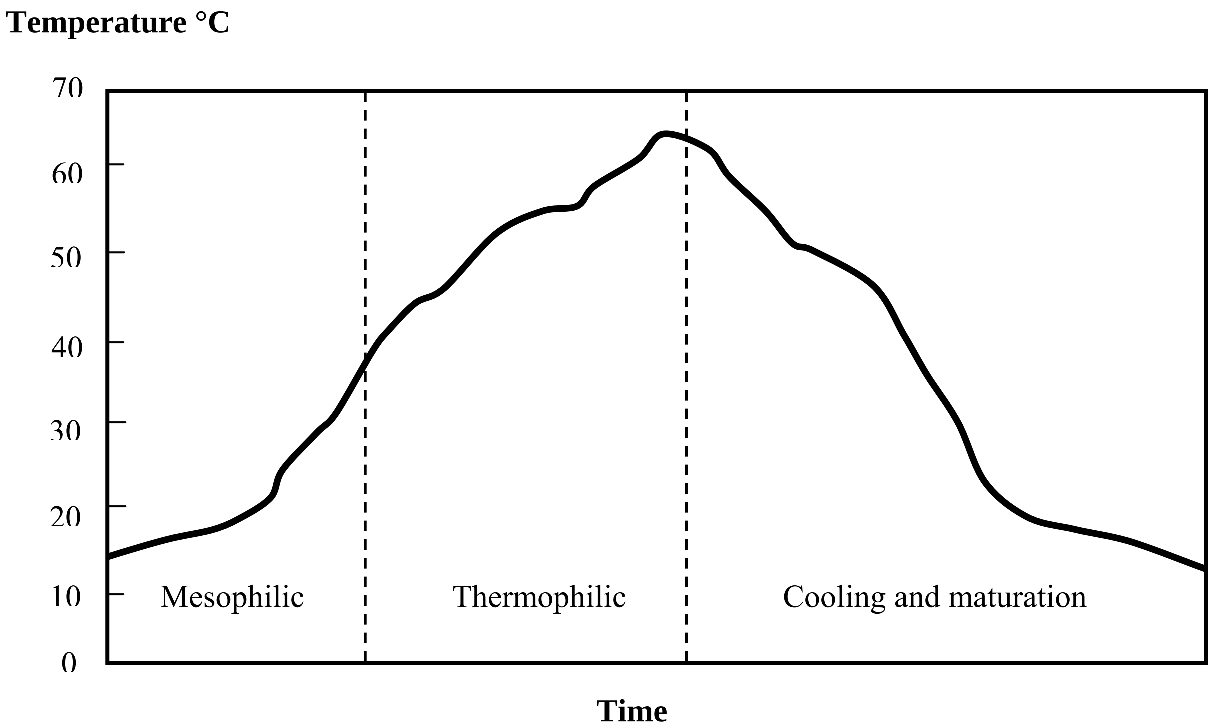


Figure 2.7 Temperature variation during natural composting process

2.5.2. Composting System

Composting system can be classified into the windrow, aerated static pile, and the in-vessel composting systems.

(1) Windrow Composting System

The windrow system is a traditional nonreactor, agitated solid bed system. The windrows can be from 2 to 6 m in width at the base and 1 to 3 m in height and of any length (Kuhlman 1990). The actual size will vary due to weather, turning equipment utilized, and initial waste characteristics. Since windrows are aerated mainly by natural or passive air movements, the rate of air exchange depends on the porosity of the windrow. If a windrow is without any mechanical agitation or turning, the composting might proceed very slowly. However, if periodic turning is adopted, the composting process can be greatly speeded up. Turning process facilitates remixing and gas exchange. In addition, some external amendments or bulking agents can be added. These can include recycled finished compost, sawdust, rice hulls, and other agricultural wastes (Hay and Kuchenrither 1990). The volumes of amendments required in the composting mixture are related to amendment properties. Windrows composting system generally requires large areas of land and can cause odor problems especially during the turning operations.

(2) Aerated Static Pile System

Aerated static pile composting refers to systems without physical manipulation during primary composting. The blended mixture can be placed on perforated piping, providing air circulation for aeration. The aerated static pile composting system is controlled by blowing air into the mass (positive pressure) or taking air through the mass

(negative pressure) using pressurized air systems (Sesay et al. 1998). The initial mixing of raw materials is important because the piles are not turned during composting. It is necessary to keep good air distribution and even composting. Some bulking agent such as straw or wood chips can be used to increase the porosity. The initial height of the piles depends on the porosity of the material, weather conditions, and operating equipment.
In some applications, additional 6 inches of finished compost and clay/garden soil on top of the pile can be used to retain heat and protect the pile surface from drying. This system is commonly used by larger, professionally managed composting facilities.

(3) In-Vessel Composting System

In-vessel composting system is used to confine the composting materials within a container or vessel. Since the composting process occurs within an enclosed space, it is possible for the process conditions to be strictly controlled. Air flow and temperature can be controlled within in-vessel composting system. In-vessel composting systems are designed to achieve better process efficiency, process control, and optimization. Forced aeration and mechanical turning devices are adopted to optimize aeration in the in-vessel systems. Compared with the other composting systems, the in-vessel composting system generally needs less land space and composting time. The early in-vessel composting systems include the rotary drum composting system and composting bins. Recently, a number of in-vessel composting systems based on reactor engineering have been developed.

2.5.3. Factors Controlling the Composting Process

(1) Microorganisms

Composting is carried out by many different groups of microbial populations. Bacteria play a dominant role during the composting process. They can grow rapidly on soluble proteins and other readily available substrates (Gajalakshmi and Abbasi 2008). Bacteria may degrade more complex materials. Fungi can efficiently use carbon source to build up biomass. Actinomycetes also utilize complex organic material. Temperature is one of the most important factors affecting microbial growth. Mesophilic bacteria are partially killed or inhibited during the thermophilic stage. The majority of the fungi prefer mesophilic conditions, which can range from 5 to 37 °C. Most fungi are eliminated at high temperature, but they can recover when temperatures are moderate (Tiquia et al. 2001). Actinomycetes predominate during stabilization process, and are able to degrade resistant polymers.

(2) pH

The optimum pH range suitable for bacterial development is 6.0-7.5, while fungi prefers a pH range of pH 5.5-8.0 (Chen and Xin-Wu 2010). Considerable change of pH would be observed during the composting process (Sharma et al. 1997). It was reported that the optimum pH range for composting is 7-8 (Nakasaki et al. 1993). Generally, the formation of carbon dioxide and organic acids would lead to a drop of pH level in the beginning. The growth of active microorganisms can be inhibited by the presence of fatty acids and low pH (Smårs et al. 2002). Some amendments can be applied for avoiding excessively low pH values during composting. With the evolution of CO_2, utilization of volatile fatty acids, and formation of ammonia from the decomposition of protein and amino, pH level will increase subsequently (Jakobsen 1994). As composting progresses, the pH value can increase and reach even up to 8-8.5. The high pH level may also lead to the loss of nitrogen as ammonia.

(3) Temperature

The temperature pattern reflects the microbial activity and the performance of composting process. In an aerobic composting system, the temperature can rise to 50-60 °C within a few days. The high temperature can help to destroy weed seeds, pathogenic microorganisms, maggots, and worms. The composting process is slow when the temperature of composting material is below 20 °C. But composting will also be negatively influenced if the themperature level exceeds the tolerance range of the thermophilic decomposers. High temperature combined with high air flow rate will increase the loss of ammonia (Vinneras et al. 2003). The optimum temperature range for composting is 40-65 °C (de Bertoldi et al. 1983). The regulation of the temperature is necessary to get the better performance of composting. For example, excess heat can be removed through the control of composting mass size, turning operations, and ventilation.

(4) Aeration

Since composting is an aerobic biodegradation process, oxygen is crucial for the process performance. Aeration may occur spontaneously by diffusion of ambient air into composting pile. But it happens very slow and makes the composting time-consuming. To achieve better aeration, mechanical turning can be employed and oxygen can also be supplied through pipes. In such aeration process, air can be pushed into the composting pile under precise and programmed control. It can help maximize the microbial activity and optimize the utilization of process heat. Proper aeration strategies can not only provides sufficient O_2 for biological processes, but also removes excess moisture and CO_2 from composting system.

(5) Moisture

Moisture is another important variable that affects composting process. Moisture in composting system can provide a medium for the transport of dissolved nutrients and support the activities of microorganisms. The optimum moisture of composting materials varies with different wastes to be treated. It is reported that the general moisture of composting mixture should be at 50-60% (Bernal et al. 2009). When the moisture content is very low, the growth and proliferation of microorganisms is inhibited, leading to less decomposition of the organic material. When the moisture content is very high, the rate of decomposition can also decrease. When the moisture is higher than 60%, O_2 movement is inhibited (Das and Keener 1997). The space between substrates is filled with water and anaerobic conditions might be observed. During composting, water can be evaporated and appropriate water content can be added when necessary. It is noted moisture variation also correlates with aeration and temperature.

(6) Carbon/Nitrogen Ratio

The carbon/nitrogen ratio is an important controlling factor in the composting process. The high N concentration and low C/N ratio favors NH_3 volatilization during composting (Steiner et al. 2010). Carbon serves as the major energy source for the microorganisms. Nitrogen is the constituent of protein and it is critical for microbial population growth. The total nitrogen concentration increases during composting due to the concentration effect (Bernal et al. 1996). Bari et al. (2000) and Zenjari et al. (2006) reported that the optimal C/N ratio have a value of 30. A low C/N ratio can lead to excessive losses of nitrogen and a high C/N ratio can lead to the inhibited microbiological activity through lack of available nitrogen (El Hajjouji et al. 2008). The C/N ratio also represents very good index of maturity level for the organic substance (Gajalakshmi and Abbasi 2008).

2.6. LITERATURE REVIEW SUMMARY

In the past decades, many research efforts have been made in the area of characterizing the transport of PAHs at solid-liquid interface, as well as exploring the remediation of organic contaminants through solvent extraction and composting. All the above noted efforts help to clarify the environmental fate of organic contaminants. However, improvements in the following areas are still required:

(1) The literature review indicated the relatively low aqueous solubility and high adsorptive properties of PAHs result in the limited mass transfer and poor biodegradation efficiency. Thus the key process to facilitate the bioavailability of the PAH contaminants is to transport the pollutant from soil to aqueous phase. Although many researches on the availability of PAHs have been reported before, particularly on aspects relating to the effects of soil texture and enhanced solubilization agent, investigations on characteristics of complex composition in environment are relatively limited in scope. The behaviors

and mechanisms of PAH translocations influenced by organic acids, especially SCOAs, remain poorly understood. Further study is necessary to better understand the mobility and fate of PAHs.

(2) Previous efforts using extracting solutions for soil remediation have been well documented. These washing solutions include different types of chemical agents, such as surfactants, solvents and cosolvents. Among these compounds, surfactant has been extensively used to increase the desorption and mobilization of pollutants in soil due to its unique characteristic. As a more prominent and less toxic alternative, biosurfactants, such as rhamnolipids, are starting to be widely used in soil remediation. The application of rhamnolipid in the removal of PAHs from soil has been demonstrated in many previous studies. However, a good understanding of the various factors involved in biosurfactant-enhanced remediation is still a challenge in many respects. Further study is still necessary to enhance the efficiency of biosurfactant remediation.

(3) The adsorption of toxic metals, phosphate, fluoride, and boron, has been demonstrated in many previous studies. Adsorption of some organic compounds including dyes and phenolic compunds from aqueous solutions on FA has also been reported. However, limited studies have focused on the interactions of HOCs with FA. In solid-liquid systems, the mechanism for the distribution and transportation of solute from bulk solution to solid surface is complicated. A number of issues about the adsorption characteristics of HOCs on FA surface are poorly understood.

(4) Many studies on composting have been reported before. The composting process can help reduce the volume of wastes and cause profound morphological and chemical transformations of composted materials. Although composting is as a suitable

option for food waste with economic and environmental profits, investigations on food waste treatment by in-vessel composting are relatively limited in scope. The produced food waste often coexists with other agroindustrial waste. However, the behaviors and mechanisms of food waste composting influenced by other waste constituents remain poorly understood. Further study is necessary to define the role of various physical, chemical and biological factors as well as their complex interactions during the food waste composting.

CHAPTER 3

EFFECT OF SHORT-CHAIN ORGANIC ACIDS ON THE BEHAVIORS OF POLYCYCLIC AROMATIC HYDROCARBONS IN SOIL-WATER SYSTEM

3.1. BACKGROUND

PAHs are an important group of environmental contaminants with the wide distribution in the ecosphere (Berset et al. 1999). PAHs include chemical compounds which are generally composed of carbon and hydrogen atoms and arranged in the form of fused benzene rings (Ferrarese et al. 2008). Anthropogenic activities are of considerable importance as the major route of entry of PAHs into the environment. Large amounts of PAHs have been generated in incomplete combustion and pyrolysis of petroleum products and various other industrial materials (Ling and Gao 2004). The toxicity caused by such chemicals has been well documented in a variety of flora and fauna species (Alcántara et al. 2008), and, in some instances, can be amplified by the accumulation in different components of natural food chains. PAHs have been shown to induce cancer and genetic defects in humans (Dodor et al. 2004) and they are classified as priority environmental pollutants by U.S. EPA.

The ubiquitous release of these toxic pollutants into the lithosphere results in a worldwide environmental problem. Due to their properties of high hydrophobicity, low water solubility, low vapour pressures and high adsorption capacity, PAHs can readily become associated with sediment particles and show obvious accumulation and enrichment in soils (Bordas et al. 2005). Their persistence in soil matrices is of great public concern and there is an urgent need for effective and safe remediation strategies for such toxic compounds. In previous studies, physical and biological soil remediation technologies have been proven feasible in many laboratory and field applications (Lagadec et al. 2000; Zhang et al. 2004). The major difficulty in these approaches lies in the low aqueous solubility and high adsorptive properties of PAHs, causing limited bioavailability and mass transfer of the pollutants in system. Investigation of the adsorption and desorption of PAHs has significant environmental effects during the remediation of contaminated soil and groundwater. Several studies have been carried to investigate the effects of soil texture, solution property, and other organic chemicals (e.g. surfactants and solvents) on the contaminant behaviors in soil-water system (ter Laak et al. 2006; Zhou and Zhu 2007b). However, further study is necessary to define the role of various factors in the complex interactions among medium, sorbent and target contaminant, and better assess their associations with fate and behavior of PAHs in environment.

SCOAs, which can be produced from various biological and chemical processes, exist ubiquitously in the environment, especially in upper soil horizons, plant root exudates, and microbial secretions (Blank et al. 1994). SCOAs may influence phosphate nutrition adsorption and availability for variable-charge soil minerals through complexation reactions with Al and Fe (Bhatti et al. 1998). Increasing evidences also have suggested that SCOAs can form soluble complexes with metal cations and hence play an important role in the fate of metals. Such properties have been used to facilitate the metal release from soil and speciation in soil solution. SCOAs are highly reactive with some soil fractions (Luo et al. 2006), and the fate of organic contaminants might be influenced by a variety of SCOAs in soils. Although there were several reports on the effect of SCOAs on the nutrient availability and translocation of metals (van Hees et al. 2003), however, there was very little information about the effect of SCOAs on the behavior of HOCs. White et al. (2003) studied the effect of organic acids on the abiotic desorption of weathered *p,p'*-DDE and the extraction of polyvalent inorganic ions from soil. Zhang et al. (2008) reported that the adsorption of norfloxacin onto three kinds of variable-charge soils could be significantly influenced in the presence of citric acid, malic acid and salicylic acid. Despite these studies, the influence of SCOAs on PAHs remediation in soil-water system is poorly understood. There are a number of important issues about the role of SCOAs that need to be better understood to improve the future applications.

The present study therefore investigated systemically the effect of SCOAs on the behaviors of PAHs in soil-water system. Batch tests were conducted to determine the adsorption and desorption of PAHs in natural soil samples. The performances of different SCOAs, as well as the effects of solution pH, soil DOM and ionic strength were evaluated. The results of this study will have important implications for the remediation of PAHs contaminated soil and groundwater.

3.2. MATERIALS AND METHODS

3.2.1. Chemicals

Pyrene and phenanthrene were selected as representative PAHs, and was obtained from Aldrich Chemical Co. (WI, USA) with purity greater than 99%. Dichloromethane was obtained from Fisher Scientific (PA, USA). SCOAs, including acetic acid, lactic acid, oxalic acid, tartaric acid, citric acid and malic acid, obtained commercially as pure chemical reagents (Sigma Aldrich, MO, USA), were used in the study as representative organic acids. Structures of selected SCOAs are shown in Figure 3.1. All other chemicals used were of reagent grade quality or higher.

3.2.2. Soils

The soil was derived from Coleville site in Saskatchewan, Canada (51º39'N, 109º13'W). Two soils, under-plant soil and ditch soil which represent the predominant soil type of the site, were chosen for evaluation in this study. Soil samples were collected at a depth of 3-5 feet below the ground surface. They were dried and sieved through a 2-mm sieve. The sieved soils were homogenized as much as possible and stored in plastic containers. The physical and textural characteristics of these soils are given in Table 3.1.

Contaminated soil was then prepared by dissolving an appropriate quantity of phenanthrene in dichloromethane and a known weight of soil was added with continuous mixing. The resultant mixture was placed in a ventilation hood to allow the complete evaporation of the solvent. The contaminated soil had a final concentration of 90 mg/kg for phenanthrene and was used directly in the batch experiments.

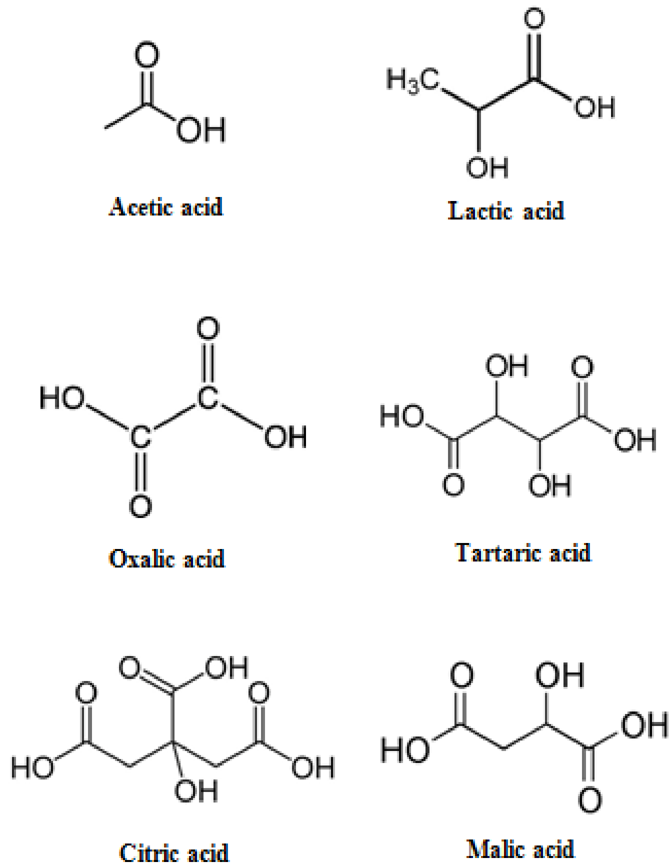


Figure 3.1 Structures of selected SCOAs

Table 3.1 Characteristics of the selected soils

Sorbents	Organic matter (%)	pH(H_2O)	Sand (%)	Silt (%)	Clay (%)*	Texture
Under-plant soil	8.84	7.2	14.3	11.9	28.7	Sandy loam
Ditch soil	4.57	7.2	2.9	24.8	36.2	Clay loam

*Soil grain size classification is according to international criterion: clay < 0.002 mm, silt < 0.02 mm, 0.02 mm < sand < 0.2 mm.

3.2.3. Adsorption and Desorption Experiments

All the experiments were carried out in 25 mL glass centrifuge tubes with Teflon-lined screw caps. For the adsorption of pyrene, an appropriate volume of pyrene dichloromethane stock solution was added to each vial. Dichloromethane was allowed to evaporate, and then 0.5 g soil and 10 mL background solution were added to each vial. The background solution was comprised of 0.2 mol/L NaCl in deionized water as well as 0.01 mol/L NaN_3 as a biocide. Considering the conditions in contaminated environment (Potin et al. 2004), initial concentrations ranging from 0 to 100 mg/kg (the amount of pyrene per unit mass of soil in the system) were used in present study. The centrifuge tubes were vortexed for 20 seconds, and then placed on a reciprocal shaker at 20 ± 1 °C and 125 rpm for 24 hours to reach the adsorption equilibrium. Preliminary experiments showed that 24 hours were enough for the adsorption of pyrene to reach equilibrium, and the adsorption or degradation of the pyrene by the tubes was negligible. The tubes were then centrifuged at 5000 rpm for 25 minutes. Pyrene in the aqueous phase was extracted with dichloromethane, and their concentrations were analyzed by gas chromatography (GC). The amount of pyrene adsorbed to the soil was the difference between the initial amount added and the amount of the pyrene remaining in the solution. For the desorption of pyrene, experiments were performed immediately after the adsorption experiments. All the supernatant was removed and replaced by the same amount of fresh background solution. The vials were mixed for the same equilibration time of 24 hours as used in the adsorption experiments. Subsequent separation of soil and aqueous phase and analyses were conducted as described above. All the tests were conducted in triplicate.

For the desorption of phenanthrene, 0.5 g contaminated soil and 10 mL background solution were added to each vial. The centrifuge tubes were vortexed for 20 seconds, and then placed on a reciprocal shaker at 20 ± 1°C and 125 rpm for 24 hours to reach the desorption equilibrium. Preliminary experiments showed that 24 hours were enough for the desorption of phenanthrene to reach equilibrium, and the phenanthrene degradation or adsorption by the tubes was negligible. The tubes were then centrifuged at 5000 rpm for 25 minutes. Phenanthrene in the aqueous phase was extracted with 2 mL dichloromethane, and their concentrations were analyzed by GC. The amount of phenanthrene adsorbed to the soil was the difference between the initial amount in the system and the amount of the phenanthrene remaining in the solution.

3.2.4. Effect of SCOAs

The effect of SCOAs on the behaviors of pyrene was examined using five organic acids including acetic acid, lactic acid, oxalic acid, tartaric acid and citric acid. Adsorption experiments were carried in the presence of each SCOA. Desorption experiments in the presence of SCOAs were performed following the adsorption experiment without the additional SCOAs. The solution removed at the end of adsorption experiment was replaced with background solutions containing different SCOAs. The organic acid concentration was 100 mmol/L for the above tests and adsorption and desorption coefficients for pyrene were then determined. Additionally, the adsorption experiments were carried with the initial organic acid concentrations ranging from 1 to 500 mmol/L. The medium composition was similar to that in original background solution, except pH was adjusted to 7 in these assays to eliminate the pH-induced variation. The standard batch equilibration method was adopted as above. Batch tests were performed in triplicate for each experimental condition to ensure the reproducibility of the results.

The effect of SCOAs on the desorption of phenanthrene was also evaluated. Five species of SCOAs, including acetic acid, oxalic acid, malic acid, tartaric acid and citric acid, were adopted. The desorption experiments were carried with the initial SCOAs concentrations ranging from 1 to 500 mmol/ L. The standard batch equilibration method was adopted as above. All the tests were conducted in triplicate.

3.2.5. Effect of pH

The nature of SCOAs can vary at different pH due to their different pK_a values, so combined effect of pH and SCOAs should be studied. Prior to the test, pH of background solution was adjusted to 3, 4, 5, 6, 7, 8 and 9 with appropriate HCl and NaOH, respectively. The ion concentration in the system was kept constant by adding NaCl. Then tests were performed in triplicate in the same way as the batch adsorption experiments described above. The initial concentration for each SCOA was 100 mmol/L.

3.2.6. Effect of DOM in the Soil

To investigate the influence of soil DOM on pyrene adsorption in the presence of SCOA, the DOM in the soils was removed, following the method as described by Cookson et al. (2005). The treated soils were air dried and mildly grounded to pass through the sieve and homogenized. Then adsorption tests were done in the presence of different SCOAs following the procedures detailed above and all the tests were conducted in triplicate. The initial concentration for each SCOA was 100 mmol/L.

3.2.7. Effect of Ionic Strength

To investigate the influence of ionic strength on phenanthrene desorption in the presence of SCOAs, the desorption tests were done in the presence of different SCOAs following the procedures detailed above and all the tests were conducted in triplicate. NaCl was added at different concentrations (0.2 and 0.4 mol/L). Ionic strength is equal to the ion concentration for uni-univalent system considered. The initial concentration for each SCOA was 100 mmol/L and initial pH value was 7. When the pH level of the solution was adjusted with NaOH or HCl, the increment of ionic strength due to the pH-adjusting solution was corrected.

3.2.8. Analytical Methods

The concentrations of pyrene and phenanthrene were determined with analysis by GC. The GC instrument, a Varian GC 3800-FID system coupled with a Varian 8200 autosampler (CA, USA), was equipped with a 25 m × 0.32 mm ID (DB-5) column with 0.25 µm film thicknesses (J&W Scientific Inc., CA). Helium was used as the carrier gas (1.5 mL/min). The temperature program was as follows: the oven temperature was held at 40 ^{o}C for 1.5 minutes then ramped to 175 ^{o}C at a rate of 50 ^{o}C/min. The temperature was held at 175 ^{o}C for 1 minute, then ramped to 220 ^{o}C at 7 ^{o}C/min, and held at this final temperature for 1 minute. The injector temperature was 250 ºC, and the detector temperature was 230 ºC. Injection was made in the split mode with a split ratio of 1:50 (since 1.75 minutes).

3.3. RESULTS AND DISCUSSION

3.3.1. Effect of SCOAs on the Behaviors of Pyrene in Soil-Water System

3.3.1.1. Adsorption and Desorption of Pyrene in Natural Soils

Adsorption is the primary process controlling the transport and fate of many HOCs in aquifer systems. Isotherm data for pyrene on the two different natural soil samples were fitted to Freundlich's model. It was shown that the empirical Freundlich equation described well the adsorption behaviors and the calculated constants are given in Table 3.2. In this study, the values of K_f for pyrene adsorption by under-plant and ditch soils were 6528 and 4982 (mg/kg)/(mg/L)^n, respectively. Different values of K_f were presented, suggesting different sorption capacity for pyrene in these two soils. The organic carbon-normalized adsorption coefficient (K_{foc}) can be obtained from $K_{foc} = K_f / f_{oc}$, where f_{oc} is the fractional organic carbon content of soil (%).The calculated K_{foc} value for under-plant soil was 73846 (mg/kg OC)/(mg/L)^n, about 32% lower than the K_{foc} values for ditch soil (Table 3.2). In all cases the adsorption isotherms were nonlinear, with slopes (*n*) different from unity. The data showed that the *n* values with under-plant soil and ditch soil were 1.352 and 1.237, respectively.

The higher K_f was observed in under-plant soil, which contained the greater amount of organic matter, suggesting that pyrene were adsorbed more strongly to under-plant soil than ditch soil. It becomes evident that sand fractions often showed less adsorption ability than clay and fine silt fractions which have the larger surface areas

(Wilcke 2000). In our study, however, more adsorption was observed on under-plant soil with higher sand along with organic matter contents. The results indicated the organic matter in the soil might play an important role in the adsorption process. Previous studies have shown the adsorption of PAHs had a positive relation with the amount of soil organic matter (Chiou et al. 1998). If the organic matter in these two soils played the sole role for the adsorption and had a common affinity for pyrene, the K_{foc} values might be expected to be nearly equal. However, the values of the K_{foc} for the two soils were different from each other, indicating different properties of the soil organic matter or other soil characteristics might be related to the adsorption mechanisms. Besides partitioning into the organic matter of the soils, pyrene can also be trapped by microaggregates in the soil. The different organic matters have influence on the structure and porosity of microaggregates in the soil, which are related to the diffusion of pyrene into the microaggregates. The factor n is related to the energy distribution of adsorption sites (Weber et al. 1992). The non-linearity parameter n deviated significantly from 1 for under-plant soil than ditch soil. Thus under-plant soil, with the higher n value, might have a more heterogeneous structure or composition than ditch soil with relatively lower n value.

Table 3.2 Sorption and desorption parameters obtained from the Freundlich isotherms for the two soil samples

Soils	Sorption				Desorption		
	K_f [a]	n	R^2	K_{foc} [b]	K_f	n	R^2
Under-plant	6528±224[c]	1.352±0.017	0.993	73846	25776±1526	1.516±0.038	0.986
Ditch	4982±219	1.237±0.021	0.991	109015	14385±922	1.348±0.041	0.982

[a] The unit of K_f is (mg/kg)/(mg/L)^n; [b] the unit of K_{foc} is (mg/kg OC)/(mg/L)^n ; [c] standard deviation.

Desorption is another important process affecting the release of PAHs from soils. The parameters for pyrene Freundlich desorption isotherms in different soils are presented in Table 3.2. The K_f for the tests with under-plant and ditch soils were 25776 and 14385 (mg/kg)/(mg/L)^n, respectively. Larger K_f value in under-plant soil showed larger amount of non-desorbable pyrene on this soil than on ditch soil. The n values ranged from 1.348 to 1.516, demonstrating the desorption isotherms were also nonlinear. The values of K_f and n parameters were different for adsorption and desorption behaviors. Indeed, the K_f values for desorption of pyrene were higher than the respective values for adsorption. Compared with the adsorption at the same equilibrium concentration, a larger proportion of the pyrene was retained on the soil during desorption. The pyrene desorption showed hysteretic and irreversible behaviors for the two soil samples. This is similar to results found with other HOCs and natural sorbents (Mitra et al. 2000; Cao et al. 2008). It could be the result of irreversible bonding between the HOCs molecule and the adsorption sites in soil (Chung and Alexander 2002).

3.3.1.2. Effect of SCOAs on Adsorption and Desorption of Pyrene

In present study, we compared the adsorption-desorption behaviors of pyrene in the presence of SCOAs. The data of pyrene adsorption in the presence of acetic acid, lactic acid, oxalic acid, tartaric acid and citric acid at the concentration of 100 mmol/L was described using Freundlich model, and the results are shown in Table 3.3.

Table 3.3 Sorption and desorption parameters obtained from the Freundlich isotherms for the two soil samples in the presence of SCOAs

Soils	SCOAs	Sorption			Desorption		
		K_f	n	R^2	K_f	n	R^2
Under-plant	Acetic acid	6158±171	1.427±0.026	0.976	23630±1294	1.394±0.023	0.990
	Lactic acid	5774±212	1.173±0.034	0.983	22369±1505	1.238±0.041	0.984
	Oxalic	5372±243	1.076±0.042	0.992	20596±1490	1.076±0.061	0.991
	Tartaric acid	5581±324	0.908±0.015	0.986	21107±734	1.545±0.045	0.974
	Citric acid	4697±189	0.871±0.020	0.977	18554±979	1.183±0.034	0.987
Ditch	Acetic acid	4781±142	1.284±0.028	0.989	13576±661	1.249±0.018	0.986
	Lactic acid	4388±201	1.023±0.019	0.977	12609±495	1.381±0.037	0.992
	Oxalic acid	4183±115	0.948±0.017	0.993	11168±896	0.957±0.028	0.974
	Tartaric acid	4339±167	1.131±0.039	0.991	12745±709	1.094±0.043	0.985
	Citric acid	3674±178	1.065±0.031	0.982	10498±477	0.895±0.012	0.989

As compared with Table 3.2, it was noted that SCOAs had the inhibitory effect on pyrene adsorption, and the influencing performances were different from each other. For the tests with under-plant soils, the K_f and n for pyrene adsorption was ranging from 4697 to 6158 (mg/kg)/(mg/L)^n and from 0.871 to 1.427, respectively. The results showed the inhibitory extents on adsorption ability decreased in the following order: citric acid > oxalic acid > tartaric acid > lactic acid > acetic acid. A similar trend was also found in other treatments with ditch soils.

When the HOCs enter into soils, different soil properties exert different effects on the adsorption and desorption behaviors of HOCs through varying mechanisms. Soil organic matter (SOM) has a soft and flexible structure and HOCs have the tendency to partition into its inner matrix (Sun and Li 2005). Metal ions in soil may serve as cross-linking agents by binding SOM to inorganic matter in soil and forming complexes that are difficult to be desorbed (Qin et al. 2004). It has been reported that PAHs adsorption was significantly higher in heavy metal-contaminated soils, due to the enhancement of adsorbed organic matter on soils (Saison et al. 2004). Thus the presence of SOM and metals might play an important role in the retention of pyrene. The results of present study showed the adsorption ability of pyrene decreased with the addition of SCOAs. As the non-specific agents, organic acids can complex metals and form organically complexed metals with less affinity to the soil surface. They may contribute to the disruption of SOM-metal-mineral linkages. It has also been found that the treatments with organic acids could promote the release of SOM (Elgh-Dalgren et al. 2009).

Contaminants may be released into the aqueous phase along with the desorbed organic matter. Therefore, SCOAs could alter the association of pyrene and other soil constituents, and affect the mobility of pyrene in the soil-water system. Besides the organic matter, mineral surfaces also influence the pyrene adsorption onto soils, especially for the soil with low organic matter content. The adsorption of SCOAs has been observed in previous research (Jones and Brassington 1998). In this study, a large proportion of adsorption sites on the soil surface of soils might be occupied by organic acids and thus the adsorption process of pyrene was hindered. Several effects discussed above could all inhibit the adsorption process of pyrene. The relative importance of the different mechanisms depends on the physical and chemical properties of the interactive sorbate-sorbent system.

The extent of pyrene desorption from soil in the presence of SCOAs is also shown in Table 3.3. As expected, pyrene desorption could be increased with the addition of SCOAs. The different effects on pyrene desorption in the presence of SCOAs might be related to the different chemical structures of organic acids. Among the SCOAs used, oxalic acid and citric acid had more significant influences on the desorption behaviors than the other acids, while the effect of acetic acid was not as pronounced as that of other acids. As a ternary organic acid (pK_{a1} = 3.13, pK_{a2}=4.76, pK_{a3}=6.4), citric acid could provide more anions for complexing than the other acids. Ions of acetic acid can only form monodentate complexes with metals, while ions of other binary and ternary organic acids can form chelates with 5- or 6- membered ring structure which are more stable (Qin et al. 2004). Such influence could lead to the greater efficacy of citric acid in desorbing metals and SOM from soils, carrying more adsorbed pyrene molecules with them. Citric acid showed a stronger effect than oxalic acid at the acid concentration of 100 mmol/L. The results presented in this study were in contrast to previous work in which oxalic acid was observed to enhance more desorption of *p, p'*-DDE from soils than citric acid (White et al. 2003). Such difference is perhaps ascribed to the differences of contaminants and soil properties and further researches are necessary to elucidate the mechanism.

3.3.1.3. Effect of pH on Adsorption of Pyrene in the presence of SCOAs

The solution pH might be affected by the addition of organic acids. In order to investigate the contribution of pH-dependent mechanisms to the pyrene adsorption in the presence of SCOAs, the experiments with pH modification were conducted and the results described using Freundlich model are summarized in Figure 3.2. In the absence of SCOA additions, the results showed that solution pH affected the pyrene behaviors in soil-water system (Figure 3.2). For the series with under-plant soil, the extent of pyrene adsorption on soils was rather high at low pH range between 3 and 4. Then it decreased with the increasing pH values of the system. Furthermore, the adsorption reactions in ditch soil were shown to be less influenced by pH, whereas for under-plant soil, adsorption of pyrene decreased strongly with increasing pH. In the same range of pH, under-plant soil followed by ditch soil, showed the greater adsorption capacities. Varied pH changed the affinity of soils for pyrene.

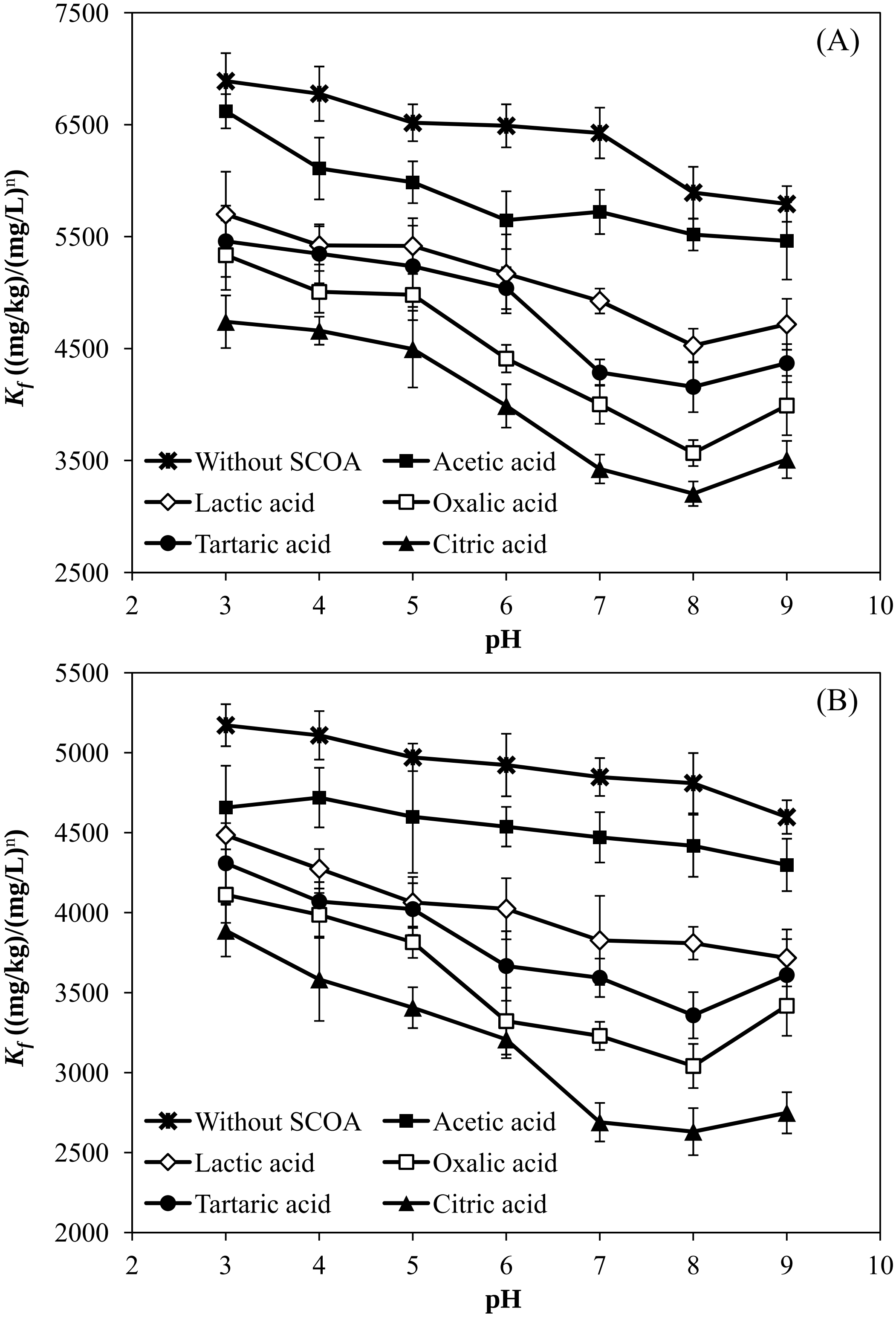


Figure 3.2 Sorption of pyrene on (A) under-plant soil and (B) ditch soil in the presence of different SCOAs under pH controlled conditions

In earlier studies, it has been observed that elevated pH had the favorable influence for the removal of HOCs (Ping et al. 2006). This may be due to the increased polarity of the organic material at higher pH, which will lead to lower affinity for hydrophobic compounds. With the increasing pH, SOM tend to be ionized and dissociated (You et al. 1999), and is also released into solution carrying pyrene. High pH could also increase soil particle dispersion, which resulted in more disassociated soil minerals and organic matter, as well as the pyrene molecules in the solution.

It has been recognized that pH was an important factor affecting pyrene adsorption. Then the effect of SCOAs at different pH values was further investigated in this study. In the presence of SCOAs, pyrene adsorption capacities decreased with a similar trend with that observed in the absence of SCOAs. The results showed that the pyrene adsorption capacities in all treatments were greatest when soil solution pH was 3 (Figure 3.2). Then the adsorption ability of pyrene decreased with increasing pH. However, for the oxalic acid, tartaric acid and citric acid, the minimum adsorption of pyrene occurred normally when pH was near 8, followed by slight increase of adsorption with the further increasing pH. At the optimum pH value, the minimum K_f for pyrene adsorption on under-plant soil ranged from 3204 to 5462 $(mg/kg)/(mg/L)^n$ for different SCOAs. Adsorption amounts of pyrene on ditch soil were lower than those on under-plant soil at the same pH value. All series with pH control and SCOAs adsorbed less pyrene than those without SCOAs at corresponding pH values, which indicated that the presence of SCOAs played a dominant role in pyrene adsorption. The addition of SCOAs may promote the mobilization SOM, and may explain the differences observed between the treatments with pH adjustment only and the treatments with both pH adjustment and SCOAs. Adsorption behaviors of PAHs can be significantly influenced by soil properties and characteristics of SCOAs.

Solution pH determines the SCOA species available for a surface reaction. It has been reported that increasing pH might result in enhanced complexing tendency when SCOAs were introduced to the system (Qin et al. 2004). Adsorbed pyrene with additional oxalic, tartaric and citric acids varied more significantly than that with acetic acid in response to pH change. Therefore, the quantity and species of organic acids capable of complexing could affect the tendency of pyrene distribution. The different performances of these five organic acids also revealed that complexing process played an important role in the pyrene adsorption affected by SCOAs. Thus the decrease of the pyrene adsorption ability could be ascribed to the combination of SCOA ionic effect and varied pH induced by the addition of acid. Moreover, compared with the pH-modified results in the absence of SCOAs, there was no obvious continuing decrease in pyrene adsorption in presence of oxalic acid, tartaric acid and citric acid above pH 8. The result indicated organic matter alone could not control the pyrene distribution. It was postulated that, as pH increases, the affinity between dissolved metals and organic matter could increase to some extent, due to decreased competition with protons, decreased surface potential, and increased hydrolysis of metal ions (Wilkin 2008).

3.3.1.4. Effect of SCOA Concentrations on Adsorption of Pyrene

In the present study, the effect of SCOA concentrations in soil-water system was also investigated by comparing the pyrene adsorption behaviors with different SCOAs.

The adsorption performances of two soils were inhibited substantially at nearly all organic acid concentrations tested. The extent of K_f decreased in soil-water systems was calculated in order to assess the effect of SCOA concentrations on the adsorption of pyrene. Figure 3.3 shows the decreased percentage of K_f, compared with the results without the supplemented SCOAs, as a function of SCOA concentrations with under-plant and ditch soils. In general, the decreased extents of pyrene adsorption performance increased with increasing SCOAs concentration up to 500 mmol/L. At concentrations of 100 mmol/L or higher, lactic acid, oxalic acid, tartaric acid and citric acid showed more significant inhibitory effect on pyrene adsorption than acetic acid. For the series with under-plant soil, acetic acid, lactic acid, oxalic acid, tartaric acid and citric acid at the 500 mmol/L concentration levels had the impact on K_f with decreases of 8.83, 14.87, 29.59, 22.88 and 37.65%, respectively. At 10 mmol/L or lower, the effects were all less insignificant.

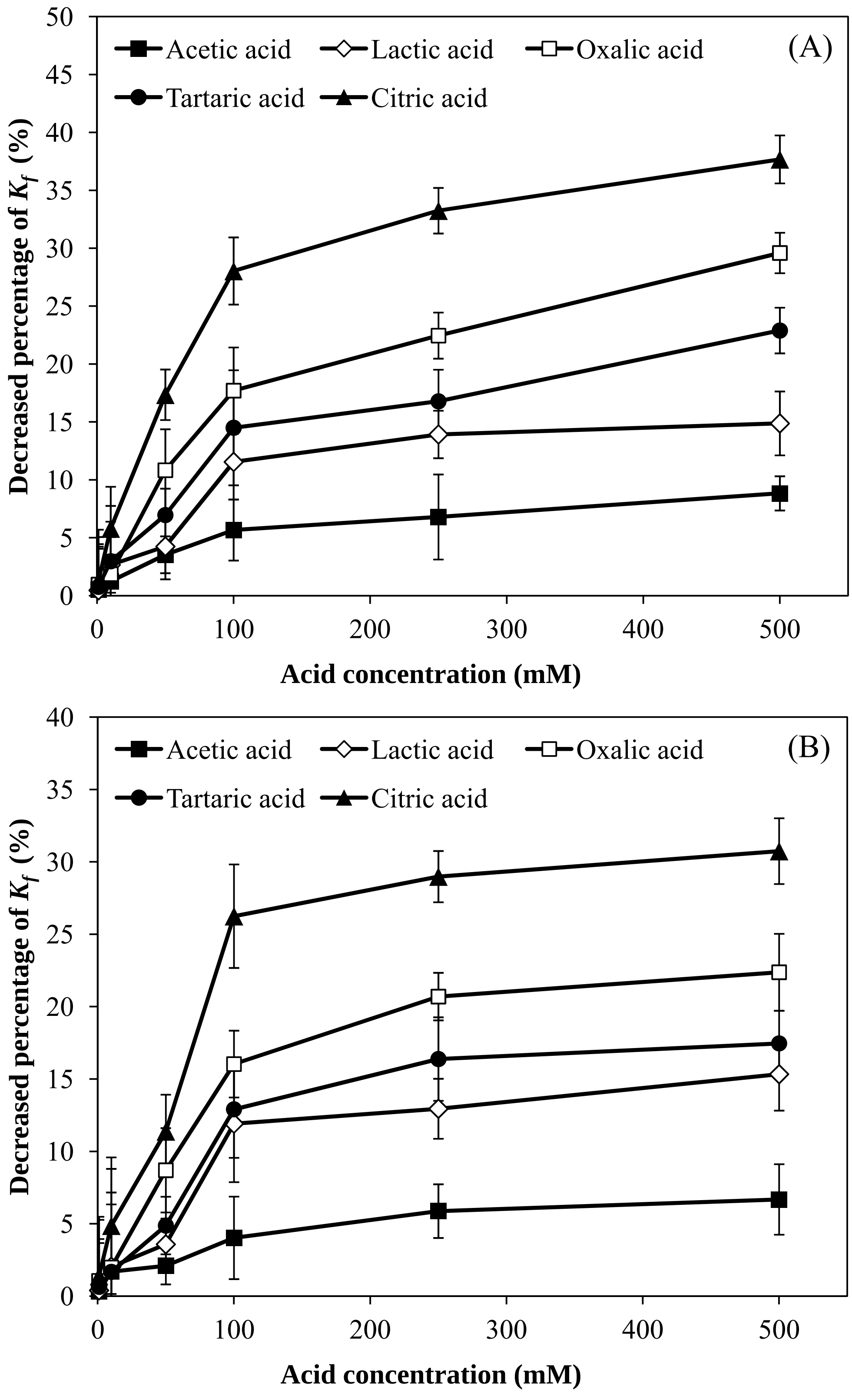


Figure 3.3 Decreased sorption of pyrene on (A) under-plant soil and (B) ditch soil under different SCOA concentrations

The addition of SCOAs resulted in less adsorption of pyrene on soils. Although the decreasing extents for different soils were not same in the presence of each organic acid, the general trend was similar (Figure 3.3). An insignificant decrease was observed at very low SCOA concentration. When low amount of organic acids were present in the solution, they could be rapidly adsorbed onto the soil's exchange complex (Jones and Brassington 1998). With increasing SCOAs concentrations, the inhibition on adsorption became more pronounced. It has been previously noted that desorbed norfloxacin increased with increasing concentrations of the three SCOAs (citric acid, malic acid and salicylic acid) (Zhang and Dong 2008). The low decreasing rate of K_f noted at concentrations above 100 mmol/L was possibly due to excess quantities of organic acids approaching the maximum effectiveness to mobilize metal, organic matter and pyrene from the soil. It also provided another evidence that there might be a limit to the extent of dissociated organic matter and adsorbed contaminant.

3.3.1.5. Effect of Soil DOM on Adsorption of Pyrene in the presence of SCOAs

Soil DOM might be an important factor influencing the mobility behaviors of HOCs (Xing et al. 2008). It is necessary to study pyrene adsorption with DOM-removed soils to obtain the theoretical foundation for the PAH mobility with additional SCOAs. The adsorption of pyrene treated by SCOAs with DOM retained and DOM removed soils could be also well described by the Freundlich model (Table 3.4). When compared with the Table 3.2, the results showed that the capacity for pyrene retention differentiated significantly between the treated and untreated soils. In the absence of additional SCOAs, the K_f of DOM-removed under-palnt and ditch soils were 8865 and 6093

$(mg/kg)/(mg/L)^n$ respectively, which were higher than the values of corresponding untreated soils. Binding affinity of pyrene to the sediment increased considerably after the removal of soil DOM. Furthermore, the lower K_f values were observed in the series with the additional SCOAs for DOM-removed soils, suggesting that the presence of organic acids was favorable for the decrease of pyrene adsorption. The clear difference of pyrene adsorption on DOM-removed soil between treatments with organic acid and without organic acid must be attributed to the presence of SCOAs. Similar trend was observed for different SCOAs with treated soils, except the pyrene adsorption on DOM-removed ditch soil was slightly lower in the series with tartaric acid as compared with the tests with oxalic acid. After the treatment, the K_f values in the presence of SCOAs were from 2.64% to 23.17% lower and from 1.97% to 22.1% lower than those with treated under-plant and ditch soils in absence of SCOAs, respectively.

Table 3.4 Sorption parameters obtained from the Freundlich isotherms for the two DOM-removed soil samples in the presence of SCOAs

	SDOM-removed under-plant soil			SDOM-removed ditch soil		
	K_f	n	R^2	K_f	n	R^2
Without SCOA	8865±420	1.473±0.037	0.986	6093±322	1.143±0.020	0.991
Acetic acid	8631±341	1.271±0.021	0.984	5972±293	1.192±0.031	0.987
Lactic acid	7998±469	1.321±0.042	0.993	5771±198	1.087±0.035	0.984
Oxalic	7702±524	0.923±0.018	0.988	5509±235	1.068±0.026	0.975
Tartaric acid	7781±293	0.987±0.024	0.992	5144±307	0.942±0.017	0.985
Citric acid	6811±336	1.115±0.023	0.979	4746±229	0.858±0.018	0.990

The organic matter in soil plays a predominant role in the transport and fate of HOCs (Salloum et al. 2002). The present study indicated that the adsorption of pyrene increased when soil DOM was removed. This result is in contrast to previous studies where adsorption of contaminants on soil decreased after removal of total organic matter (Cox et al. 1998; Cao et al. 2008). It has been demonstrated that dissolved organic carbon exhibited a higher affinity for HOCs than other soil solids (Kilduff and Wigton 1999). When the DOM was retained in soils, it would be dissolved in the solution. A portion of pyrene tended to be adsorbed by DOM in soil-water system, resulting the decreasing adsorption of pyrene. When the DOM was removed, the amount of high affinity ligand in the system decreased and more pyrene could be retained in soils. If all the organic matter is removed, pyrene would deposit mainly on mineral surface which exhibits a limited adsorbing capacity. In addition, it has been found that the behavior of many HOCs in soil-water systems was correlated with clay mineral (He et al. 2006). Therefore, the increased adsorption with DOM-free soil could also be attributed to increasing mineral surface area and forming of new adsorption sites.

The results of this study showed that pyrene adsorption decreased in the presence of SCOAs for DOM-free soils. Although the great mass of soil DOM has been removed, SCOAs could disrupt the remaining organo-mineral linkages in soil matrix, and promote the mobilization of soil organic matter. Thus, the presence of SCOAs will further increase the DOM concentration in the equilibrium solution and the extractability of pyrene from soil. These observations suggested that DOM was a critical factor affecting the adsorption processes with the addition of organic acids. Meanwhile, in the presence of SCOAs, it was noteworthy that even though most of the DOM was removed, the adsorbed amounts of pyrene in under-plant soil were still higher than those in ditch soil after the removal of DOM. This might be attributed to residue organic matter and clay minerals. In soil, clay and organic components are usually intimately associated such that their individual effects on adsorption are difficult to separate (Mitra et al. 2000). In the presence of SCOAs, although the K_f values for treated soil were greater than those for untreated soil, the inhibitive influence on the adsorption became less significant than that observed with untreated soil. Thus the effect of SCOAs on the adsorption of pyrene could also be influenced by the soil organic matters. The overall adsorption behavior of pyrene by a soil can be assumed to be a sum of a large number of individual adsorption events with different mechanisms.

3.3.2. Influence of SCOAs on the Phenanthrene Desorption and Mobilization from Contaminated Soil

3.3.2.1. Influence of SCOAs on the Phenanthrene Desorption

The extent of HOC desorption from soil has a major influence on its transport and fate in the environment. In this study, desorption of phenanthrene was investigated in the presence of five SCOAs, and the results are shown in Figure 3.4.

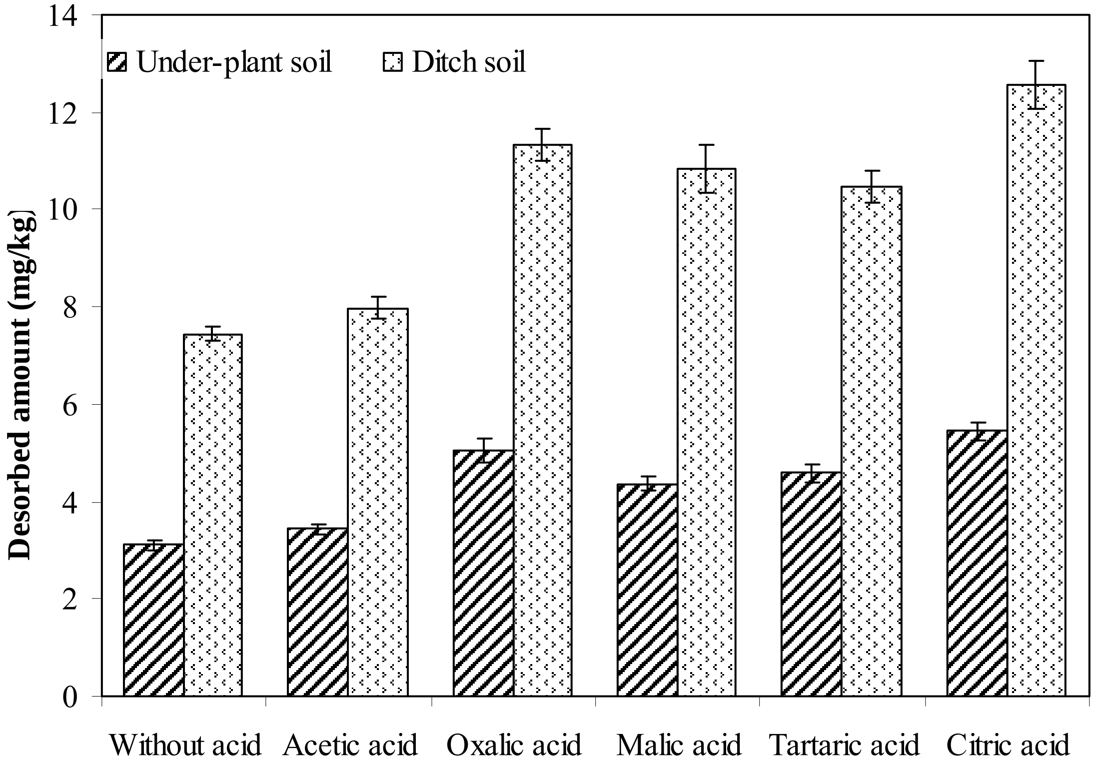


Figure 3.4 Desorption of phenanthrene in the presence of different SCOAs

It is noteworthy that the phenanthrene desorption from the two assayed natural soil constituents was increased at all organic acids tested. In the tests without SCOA amendment, 3.12 and 7.44 mg/kg of phenanthrene was desorbed after the treatment with under-plant and ditch soils, respectively. When 100 mmol/L different SCOAs were added respectively, the phenanthrene desorption amount with under-plant soil was from 3.44 to 5.45 mg/kg. Of the five organic acids examined, citric acid was related to the most extracted amount of phenanthrene. Additionally, acetic acid enhanced phenanthrene desorption to a less significant extent than other organic acids. It was observed that the presence of several SCOAs caused an increase of phenanthrene desorption in under-plant soil with the following order: citric acid > oxalic acid > tartaric acid > malic acid > acetic acid. As for the ditch soil, the release of phenanthrene was increased from 7.98 mg/kg to 12.56 mg/kg in the presence of different organic acids. The similar trend was also found except that the desorbed amount with amendment of malic acid was slightly higher than that with additional tartaric acid.

It has been reported that SCOAs such as citric and oxalic acids could promote the solubilization of several metals (Krishnamurti et al. 1997; Shan et al. 2002; Wang et al. 2009). Indeed, in situ soil washing with organic acids has been proposed as an effective remediation technique to reduce heavy metal contamination in soil. The main mechanism of action is through the formation of complex between metal ions and organic acids, showing lower sorption affinities and faster diffusivities. The SOM often bonded with metal ions, may constitute the most important pool of HOCs in soil systems. SOM has relatively open and flexible three-dimensional structure that allows nonpolar contaminants to be sorbed by partition into organic matter (Heyse et al. 2002). The phenanthrene molecules may get trapped within the organic matter due to their hydrophobic nature. Based on our results, the phenanthrene desorption efficiency was found to increase with the addition of SCOAs. The mobility of SOM in soil could be enhanced by introducing organic acids that complex with metals and therefore reduce the binding of organic matters onto soil particles. The complexation could partially disrupt or change the structure of the soil matrix that effectively hold organic matter and sorbed hydrocarbons within the soil matrix, resulting in a release of previously bounded metals and hydrocarbons. Furthermore, by competing with the adsorption sites for phenanthrene, the presence of organic acid may decrease phenanthrene adsorption. The enhanced phenanthrene release is either due to the organic acid complexation with other inorganic elements or direct displacement of phenanthrene by organic acids from the soil surface. Previous studies have shown that citric acid amendments could promote the release and bioavailability of PCBs for plant uptake (White and Kottler 2002; White et al. 2006). Therefore, the presence of SCOAs can influence the fate of phenanthrene and potentially impact on the remediation of petroleum polluted soil.

Although phenanthrene desorption all increased in soils with these organic acids, the increments of phenanthrene desorption were different in the tests with various SCOAs. The present study indicated citric acid offered a higher desorption effect on phenanthrene compared with other organic acids. Ions of citric acid can form both tridentate and bidentate complexes, which are more stable than monodentate complexes (Qin et al. 2004). Citric acid could be more effective in complexation process than the other weak organic acids such as oxalic acid and acetic acid, and thus may show a greater effect on phenanthrene desorption. This is also supported by the results in present study that acetic acid had little effect on phenanthrene desorption. Moreover, it has been reported that binary and ternary organic acids could be sorbed to soils more strongly than monobasic acids (Jones and Brassington 1998). Compared with acetic acid, therefore, citric and oxalic acids showed higher affinity for exchange sites, which resulted in more desorbed phenanthrene in present study. However, acetic acid has earlier been shown to remediate metal contamination more efficiently than oxalic acid (Maturi and Reddy 2008), suggesting metal complexation may be not the only process contributing to phenanthrene desorption with organic acids.

In the absence of SCOAs, desorption amounts of phenanthrene from under-plant soil were lower than those from ditch soil. It suggests that under-plant soil is capable of holding more phenanthrene compared to ditch soil which has lower content of organic matter. Previous study has shown that the adsorption of PAHs had a positive relation with the amount of soil organic matter (Chiou et al. 1998). The data in Figure 3.4 also indicate that sorption behaviors of phenanthrene in each soil in the presence of the five SCOAs are different. The results presented in this study with under-plant soil are in contrast to previous study by White et al. (2003) who reported that the addition of malic acid presented more significant effect on organochlorine pesticide desorption than tartaric acid. Such differences could be due to contaminants and soil properties in the system. The mobility of phenanthrene can be significantly influenced not only by the characteristics of SCOAs, but also by the properties of soils.

3.3.2.2. Effect of pH on the Phenanthrene Desorption in the absence of SCOAs

The use of organic acid can change the acidity and pH values of the system. To study the effect of pH in the presence of SCOAs, the relevant desorption behaviors of phenanthrene in soils were determined initially without the addition of SCOAs at various pH between 3 and 9. As shown in Figure 3.5, increasing the pH of system appeared to influence phenanthrene removal from soil regardless of the soil used. The desorption changed little in the low pH range, but it increased sharply in relatively high pH range. When pH value increased, desorption amount of phenanthrene in both soils increased. The phenanthrene desorption percentage increased to 3.86% and 8.97% at pH 9 for the series with under-plant and ditch soil, respectively. Solution pH in natural waters significantly affects the environmental fate of HOCs in the soil (Sheng et al. 2005). The direct effect of pH on the desorption of the phenanthrene was studied by conducting batch studies and the results showed the mobility of phenanthrene in the soil-water system may vary due to change of pH. The mechanism by which pH affected the desorption of phenanthrene was complex. Many of ionic compounds undergo pH-dependent speciation, thus increasing the possibility of ionic adsorption between the contaminant molecules and soil surface (Abu-Zreig et al. 1999; Cao et al. 2008).

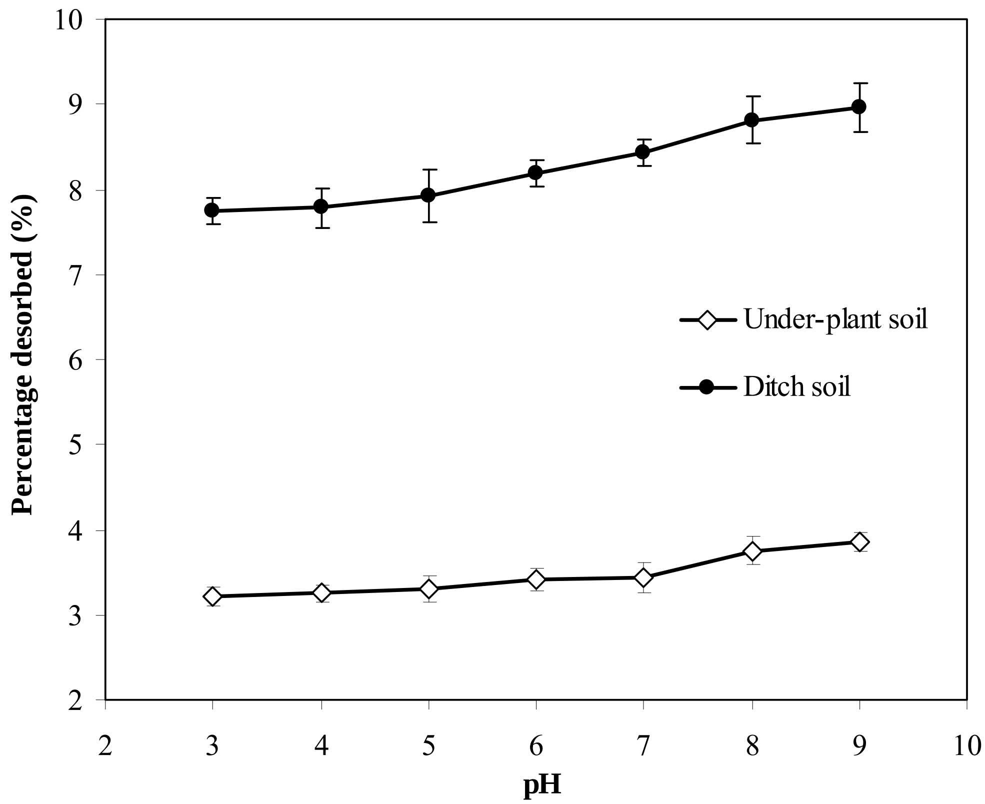


Figure 3.5 Effect of pH on the phenanthrene desorption in the absence of SCOAs

In contrast, phenanthrene, as the non-ionic compound, is not much influenced by the pH variation in its cation existence. The repulsion between the organic matter and soil surface could increase because of the high negative charges on both organic and inorganic matter surfaces under high pH range (You et al. 1999). The increased polarity of the humic material at higher pH would also result in the lower affinity for hydrophobic compounds (Ping et al. 2006). Thus, increase in pH might result in the disassociated organic matter as well as the bounded phenanthrene. This suggests that phenanthrene desorption can be increased when combined with suitable pH adjustment.

3.3.2.3. Effect of pH on the Phenanthrene Desorption in the presence of SCOAs

The effect of pH on phenanthrene desorption in the presence of five SCOAs is shown in Figure 3.6. The phenanthrene desorption was enhanced as the pH increased. Compared with the series with only pH control (Figure 3.5), the addition of SCOAs made more favorable desorption at the same pH value. This difference indicates that some factors other than pH can be responsible for the changes of phenanthrene desorption. In the presence of SCOAs at pH below 4, the desorption of phenanthrene by two soils was not noticeably affected. The maximum desorption for phenanthrene was observed at the pH around 8. The phenanthrene desorption efficiency with different SCOAs at pH 8 was from 4.29% to 6.95% and 9.56% to 15.78% for under-plant and ditch soil, respectively.

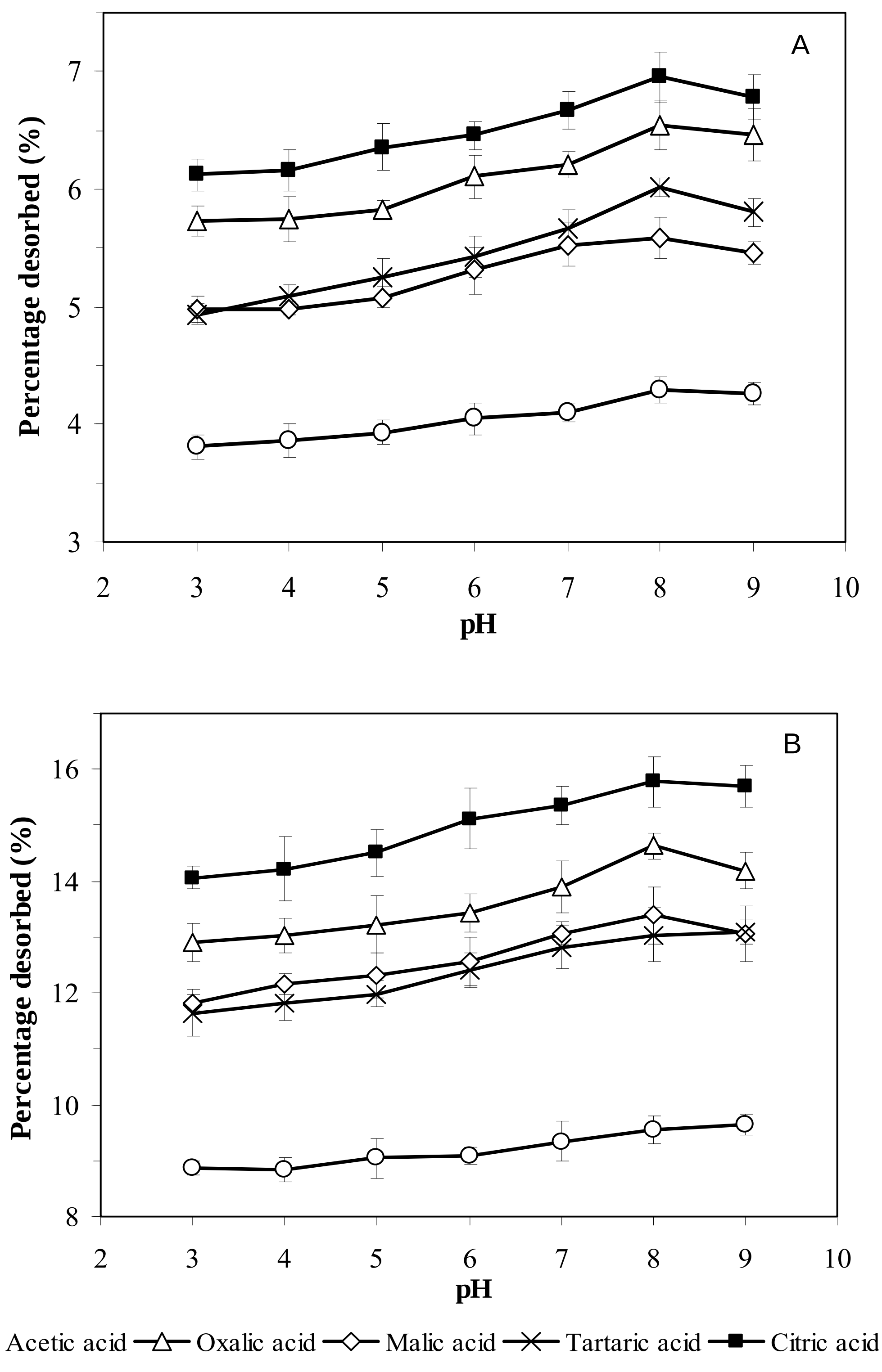


Figure 3.6 Effect of pH on the phenanthrene desorption from (A) under-plant soil and (B) ditch soil in the presence of SCOAs

Beyond pH 8, the increase of pH would result in a slight decrease of the desorption efficiency of phenanthrene in most tests. The variation of phenanthrene desorption with ditch soil were not as significant as noticed in the series with under-plant soil. Also, the variation of desorption efficiency with pH is closely related with the speciation of the organic acids. The amount of phenanthrene desorbed at pH 7 in the presence of 100 mmol/L malic acid was 13.07% , 85.14% of applied citric acid for the ditch soil. The desorption of phenanthrene seemed less susceptible to pH variation in the presence of acetic acid than other organic acids tested. The results indicated that the pH has effect on the phenanthrene desorption, and the presence of SCOAs can influence the transfer of phenanthrene from soil phase to aqueous phase.

Because pH is one of the most critical parameters affecting the nature of SCOAs (Jones and Brassington 1998), it is important to investigate its influence on the phenanthrene desorption in the presence of SCOAs. Desorption of phenanthrene in the pH-controlled treatment with SCOA amendment was stronger than the series with only pH control. It indicates that the presence of SCOAs other than pH variation is responsible for the different behaviors of phenanthrene desorption. Phenanthrene adsorbed by soil can be desorbed at low pH when there are SCOAs present. At low pH range, the competition could be responsible for the increased phenanthrene desorption. When the pH increases, the chelate become stable, and then complexation is more important. At the near-neutral pH range, organic acids are almost entirely dissociated from their protons and exist as organic acid anions. The maximum desorption was achieved when the solution pH was near 8. But when pH value was above 8, increased hydrolysis of metal ions could cause precipitation of hydroxide, with adverse effect on the phenanthrene desorption from soil surface. Although the high pH may also lead to precipitation of hydroxide, the phenanthrene desorption at pH 8 still maintained at high level conditions due to more effective complexation considerations than precipitation.

The existing forms of SCOAs are different at different pH values. The variations of phenanthrene desorption with increasing pH depended on the organic acid anions, and might relate to the different dissociation constants of organic acids involved. With the increase of pH, the complexing ability of organic acid will increase, especially for the polyprotic weak acid. As for citric acid, $HCit^{2-}$ and Cit^{3-}, as the major forms of this acid at high pH, have greater chelating ability than H_2Cit^- and H_3Cit, which mainly exist at low pH range (Gao et al. 2003). The desorption of phenanthrene with the addition of acetic acid, however, showed less dependence on pH variation. The lower increases in phenanthrene desorption with acetic acid amendment are possibly due to weak complexing ability restricting the diffusion of resident contaminants in soils. The above results indicates that the variation of system pH is likely to influence the overall phenanthrene desorption efficiency with the addition of SCOAs. Because of changes in organic acid content, adjusting the pH can control the effect of SCOAs, allowing higher remediation efficiency at specific pH values.

3.3.2.4. Effect of SCOA Concentrations on the Phenanthrene Desorption

The extraction of phenanthrene from soil was quantified at different acid concentrations. The extent of phenanthrene desorption increased in soil-water systems was calculated as follows in order to assess the effect of SCOAs.

Increased percentage of desorption (IPD) = $(S - S_0)/S_0 \times 100$

S_0 is the amount of phenanthrene desorbed per unit mass of sorbent without the addition of SCOAs (mg/kg); S is the amount of phenanthrene desorbed per unit mass of sorbent in the presence of SCOAs (mg/kg). Figure 3.7 shows the IPD of phenanthrene as a function of SCOA concentrations with under-plant and ditch soils. As seen, the concentration of organic acids has significant effect on phenanthrene desorption. The IPD of phenanthrene increased with increasing SCOA concentration up to 500 mmol/L. It is notable that the enhancement in release of phenanthrene was not significant for all the organic acids at low concentration range. The IPD with under-plant soil reached 18.83%, 79.77%, 60.08%, 64.09% and 93.28% in the presence of 100 mmol/L acetic acid, oxalic acid, malic, tartaric acid and citric acid, respectively. However, when SCOA concentrations were above 100 mmol/L, the changes of IPD became less remarkable. In addition, the phenanthrene desorption performance in the presence of different SCOAs showed different increments with increasing organic acid concentrations. For example, the IPD for the series with under-plant soil increased from 5.71% to 106.06% in the presence of citric acid, and 4.54% to 90.28% in the presence of oxalic acid, at organic acid concentrations ranging from 1 to 250 mmol/L. At the same concentration range, the IPD with acetic acid only varied from 0.52% to 25.93%, which is less than the series with other organic acids. The variation of IPD for ditch soil was less significant than that for under-plant soil with SCOA amendments.

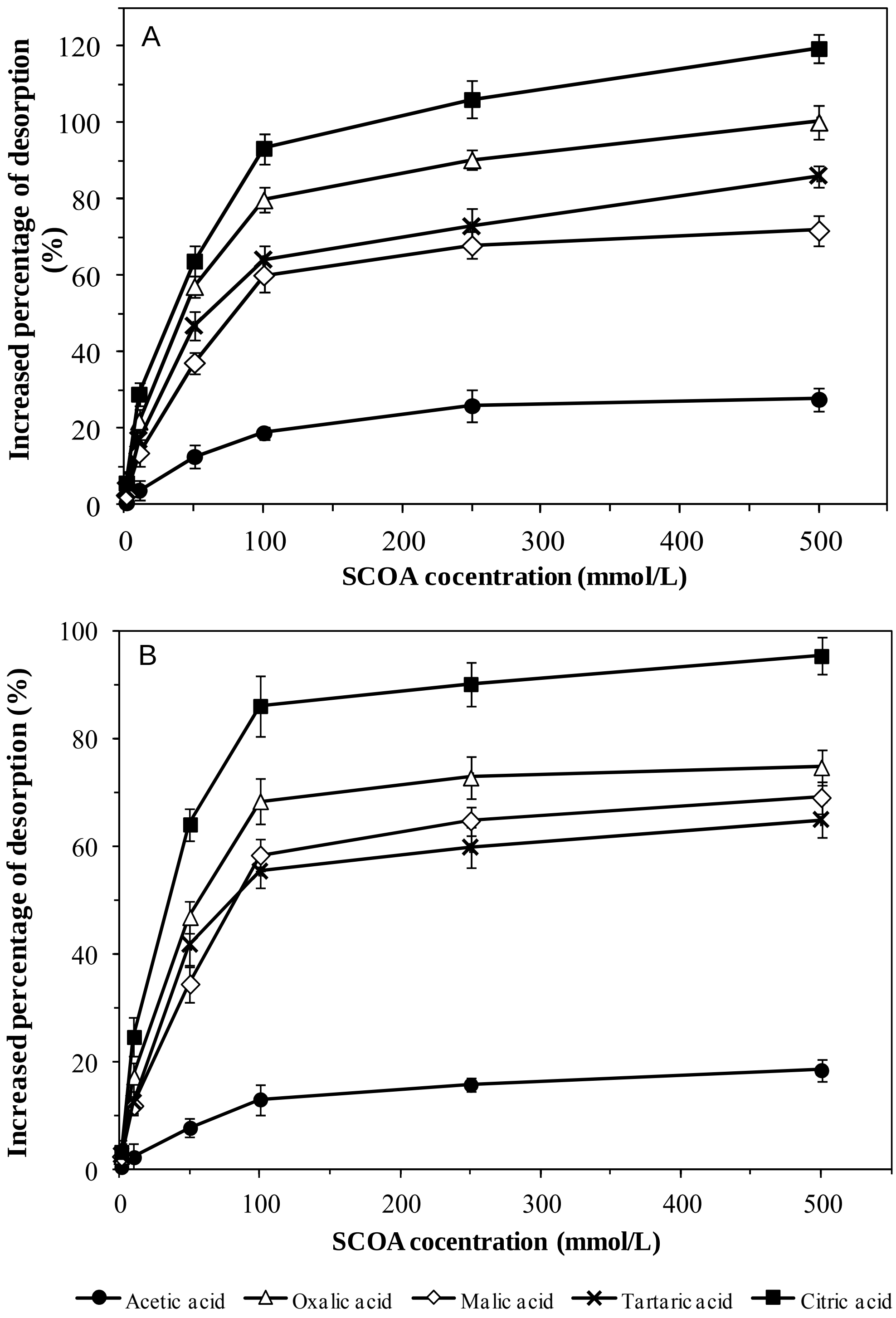


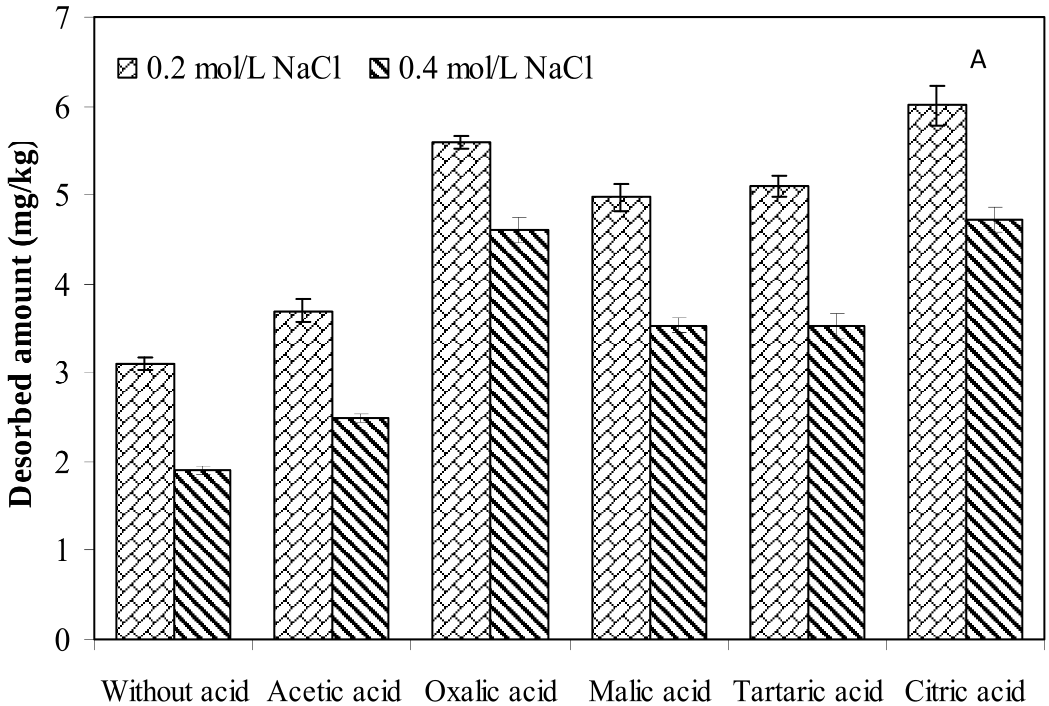
Figure 3.7 Effect of SCOA concentrations on the phenanthrene desorption from (A) under-plant soil and (B) ditch soil

These data show that an increase in the concentration of organic acids results in an increase in phenanthrene desorption for all soils. When SCOAs were added into the system, the connection between organic matter and soil particles could be influenced by the complexing process. Part of the phenanthrene will thus be released into solution along with the mobilized organic matter. In a previous study about organochlorine compound dispersion as a function of organic acid concentration, it was observed an increase in desorbed *p,p'*-DDE with from 0 to 50 mmol/L organic acids, but that was followed by an decrease above 50 mmol/L (White et al. 2003). In contrast, citric acid at high concentration resulted in greater increases in phenanthrene desorption than did at low concentration in present study. At any rate, the addition of SCOAs would further enhance phenanthrene removal from the polluted soil. Although a low concentration of SCOAs may affect the phenanthrene desorption performance, the influence is not as significant as that observed at high organic acid concentration. This observation can be explained by that with a small amount of SCOAs, organic acid was mainly adsorbed by the soil particles. However, when the amount of organic acid was higher than certain value, more mechanisms could also be responsible for the desorption process and enhance the transfer of phenanthrene from soil phase to aqueous phase. Although the phenanthrene desorption varied at different SCOA concentrations, the general trend was consistent. With increasing organic acid concentrations, the increase in desorption became less pronounced. The differences of the SCOA properties may be the reason for the different trend of phenanthrene desorption in response to organic acid concentration change.

3.3.2.5. Effect of Ionic Strength on the Phenanthrene Desorption in the presence of SCOAs

Ionic strength is usually a critical factor for the sorption and desorption of HOCs by soil (Guo et al. 2010). The experiments were based on a series of batch tests with a same initial concentration of SCOAs but different dosages of sodium ions. It can be seen that the phenanthrene desorption decreased slightly with the increase of sodium concentration from 0.2 to 0.4 mol/L (Figure 3.8). Without the amendment of SCOAs, the desorption amounts of phenanthrene under 0.4 mol/L NaCl were 1.90 and 4.92 mg/kg for the under-plant and ditch soils respectively, 38.57% and 35.22% lower than that under 0.2 mol/L NaCl. The effect of ionic strength on phenanthrene desorption in present study is also under the influence of SCOA contents. When the organic acids were introduced into the system, the desorption amounts of phenanthrene under 0.4 mol/L NaCl were found to be from 2.48 to 4.72 mg/kg for the under-plant soil, 17.52% to 32.94% lower than that under 0.2 mol/L NaCl. Similar variation trend was also found for the tests by ditch soil with the increase of ionic strength.

As the system pH and SCOA concentration were fixed, the variation was most likely due to the present metal ions available to immobilize phenanthrene contaminant. This is similar to the findings of other studies that the high ionic strength values are usually correlate with the low mobility of HOCs (El-Nahhal and Safi 2004). As a matter of fact, the aqueous solubility of HOCs has been reported to be increased by the salt-out effect process at high ionic strength (Brunk et al. 1996). Literature also showed that phenanthrene could be less partitioned to dissolved organic substances, limiting its concentration in solution (Saison et al. 2004). The varied interaction between organic matter and HOCs was primarily caused by the type of cations instead of the anions (Lee et al. 2003). Consequently, the presence of more salt ions can make phenanthrene more persistent on the solid phase and adversely affect its desorption from contaminated soil. In contrast, Murphy et al. (1994) observed that soil humic substance tend to exist as a "coiled" configuration at high ionic strength, resulting in the decrease of HOC sorption potential. The competition of high concentrations of cations can promote the desorption of inner metals from soils, which may be beneficial to the dissociation of organic matter along with combined HOC. Although these factors may all play a part in determining transmission of HOC in soil-water system, the mechanism of adverse effects may mainly contribute to desorption behavior of phenanthrene at high ion concentration in this study. Additionally, the less significant variations in inhibitory effect of phenanthrene desorption were observed when ion concentration increased in the presence of SCOAs. This indicated that the availability of desorbed phenanthrene molecules can be influenced by organic acids as the ionic strength value increased. The information will be important for deciding the role of SCOAs in HOC behaviors under field condition with metal ion enrichment and variable soil texture.



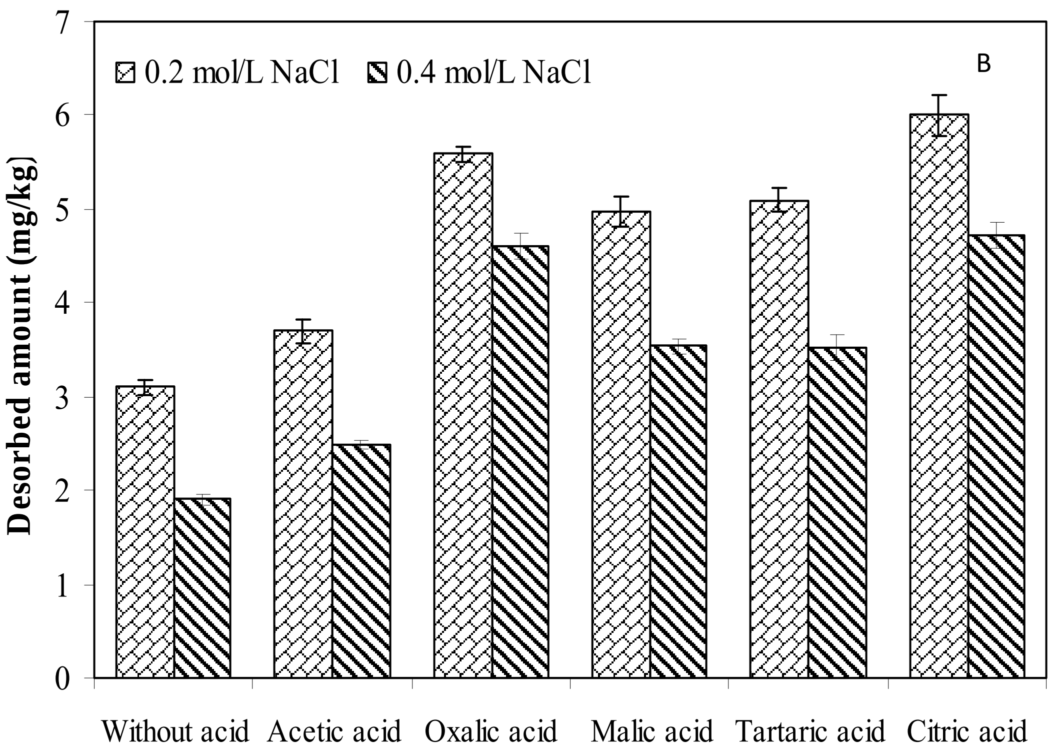


Figure 3.8 Effect of ionic strength on the phenanthrene desorption from (A) under-plant soil and (B) ditch soil in the presence of SCAAs

3.4. SUMMARY

The results showed that under-plant soil was capable of holding more pyrene compared to ditch soil. The amendment of SCOAs could influence the behaviors of pyrene in soil-water system. In the presence of SCOAs, adsorption of the pyrene was significantly inhibited while desorption was promoted. SCOAs could alter the association of pyrene and other soil constituents, and affect the mobility of pyrene in the soil-water system. Among different organic acids tested, oxalic acid, tartaric acid and citric acid showed stronger effects than acetic acid and lactic acid. Furthermore, since solution pH could determine the SCOA species available for a surface reaction, the effects of SCOAs on adsorption of pyrene were pH dependent. With the increasing of SCOA concentration, the inhibition on pyrene adsorption became more pronounced with different trends. Pyrene adsorption performances also decreased in the presence of SCOAs for DOM-free soils, suggesting the quantity and species of organic acids, as well as the properties of media and sorbents could all affect the fate of pyrene.

In the present study, the amendment of different SCOAs was found to be capable of influencing the desorption performance of phenanthrene from soil. The mobility of phenanthrene in soil could be enhanced by introducing organic acids that partially disrupt and change the structure of the soil matrix. The complexation could result in a release of metals and organic matter, along with the bounded hydrocarbon contaminants. The results of phenanthrene desorption were different in the tests with various SCOAs, indicating SCOA properties could also play a major role in the desorption process. Furthermore, there were several factors affecting the desorption of phenanthrene in the presence of SCOAs. These factors included the pH, SCOA concentration and the ionic strength. Phenanthrene desorption could be increased when combined with suitable pH adjustment. The results evidenced that the desorption amount of phenanthrene varied both as a function of pH and of the organic acid present in system. It was also shown that more phenanthrene could be released into solution with increasing organic acid concentration, although the increase in desorption became less pronounced at high SCOA concentration. The existence of NaCl became a rate limiting factor at high ionic strength condition.

In general, this work revealed the potential influence of SCOAs on the fate of PAH contaminant in natural system. The overall behaviors of PAHs in soil-water system could be assumed to be a sum of a large number of individual adsorption and desorption events with different mechanisms. It is necessary to consider all these factors to study a real contaminated system and effectively predict the fate of PAHs in the environment. The results of present study can potentially be used in the application and optimization of remediation system for facilitating contaminant mobility in contaminated soils. As the cost-effective, nontoxic, and readily degradable alternative, amendment of SCOAs may be of even more significance for future study.

CHAPTER 4

EFFECT OF SHORT-CHAIN ORGANIC ACIDS ON THE ENHANCED DESORPTION OF PHENANTHRENE BY RHAMNOLIPID BIOSURFACTANT IN SOIL-WATER ENVIRONMENT

4.1. BACKGROUND

PAHs are frequently found in the environment as a result of various natural processes and anthropogenic activities (Nadal et al. 2004). During the past decades, large amounts of PAHs have been generated in incomplete combustion of organic materials and the refining of crude oil (Ferrarese et al. 2008). Contamination from the release of petroleum hydrocarbons into the environment by deliberate discharges, accidental spills and leakages is a particularly significant problem. These contaminants have been demonstrated to be a threat to human health and ecological safety (Djomo et al. 2004). Pollution caused by these compounds is becoming a widespread problem for the ecosystem across the world. The U.S. EPA has already classified PAHs as priority pollutants (Kanaly and Harayama 2000). Due to the low solubility and high hydrophobicity, a significant proportion of these organic contaminants can bind to soil sediments (Gomez et al. 2010). Mass transfer limitation from the solid phase to the liquid phase seriously impedes the bioavailability and reduces the bioremediation efficiency of these compounds. PAHs often persist in soil and groundwater system, posing a long-term threat to the environment.

Soil washing with extracting solutions has been proposed as a promising technique for the remediation of contaminated soils and groundwater in recent years (Deshpande et al. 1999; Chu and Chan 2003; Gan et al. 2009). These washing solutions include different types of chemical agents, such as surfactants, solvents, and cosolvents (Khodadoust et al. 2000; Silva et al. 2005; Alcantara-Garduno et al. 2008). Among these compounds, surfactant has been extensively used to increase the desorption and mobilization of pollutants in soil due to its unique characteristic. Surfactant is composed of both a hydrophilic and hydrophobic moiety, which can form micelle aggregates in aqueous phase when surfactant concentration exceeds CMC (Deshpande et al. 2000). These micelles significantly facilitate the solubilization of HOCs and their transport from contaminated soil to aqueous phase. However, concerns over some synthetic surfactants have increased because they are toxic and thus present a potential risk for environment and human health (Kanga et al. 1997). As a more prominent and less toxic alternative, biosurfactants, such as rhamnolipids, are starting to be widely used in soil remediation. Rhamnolipids are anionic biosurfactants produced by *Pseudomonas sp* bacteria and they can show greater environmental compatibility and surface activity (Clifford et al. 2007). The application of rhamnolipid in field remediation of PAH-contaminated soil has been successfully demonstrated in many previous studies (Noordman et al. 1998; Bordas et al. 2005; Mulligan 2005). However, a good understanding of the various factors involved in biosurfactant-enhanced remediation is still a challenge in many respects. Further study is necessary to define the role of complex system composition and heterogeneity in contaminant behaviors.

The technology of soil washing with SCOAs has also been employed to remediate polluted soils. In natural environment, these organic acids can be produced from incomplete carbohydrate oxidation and chemical acidification within root exudates, microbial secretions, and decomposition processes (Blank et al. 1994; Wang et al. 2009). These simple carboxylic acids can act as chelating agents and facilitate the translocation of metals in soils (Jones 1998; van Hees et al. 2003). Such properties have been used to increase the treatment efficiency for heavy metal contaminated soil in many applications (Yuan et al. 2007b; Zhang et al. 2008). Recently, it was found the presence of SCOAs could have an influence on the behavior of HOCs. White et al. (White et al. 2003) reported that the availability of weathered *p,p'*-DDE increased in the presence of seven organic acids. It was also observed in our previous studies that the addition of SCOAs showed adverse effect on adsorption process of pyrene (An et al. 2010). Although these findings are encouraging, a number of important issues about the role of SCOAs remain poorly understood under either laboratory or field conditions. Moreover, with the prevalence and concern of biosurfactant, few studies have focused on the interacted influence of biosurfactants and organic acids on the behaviors and mechanisms of PAH translocations.

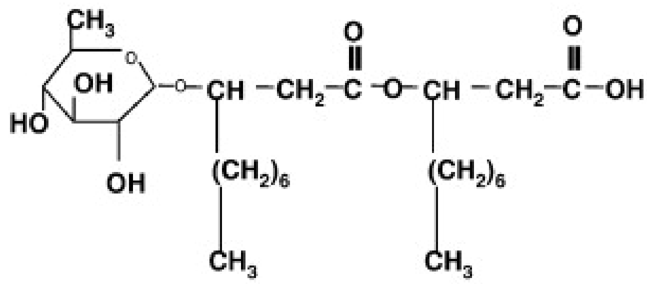
The present study therefore investigated the effect of SCOAs on the mobilization of phenanthrene by rhamnolipid biosurfactant in soil-water environment. Batch tests were conducted to determine the desorption of phenanthrene in two kinds of natural soil samples. The performances of different biosurfactant-SCOA combinations, as well as the effects of solution pH, DOM and ionic strength were evaluated. The results from this study may have important implications for soil washing technologies used to treat PAH-contaminated soil and groundwater.

4.2. MATERIAL AND METHODS

4.2.1. Biosurfactant

The biosurfactant used in this study was a rhamnolipid obtained from the Jeneil Biosurfactant Company (WI, USA). Jeneil product RECO-10, with a mono- to di-rhamnolipid ratio of 1:1, was used and the biosurfactant was supplied as a 10% aqueous solution. It is an extra-cellular natural substance produced during precisely controlled fermentation processes utilizing certain bacterial strains (Wei et al. 2005). The two major rhamnolipid components in this solution are a monorhamnolipid (α-L-rhamnopyranosyl-β-hydroxydecanoyl-β-hydroxydecanoate), and a dirhamnolipid (2-O-α-L-rhamnopyranosyl-α-L-rhamnopyranosyl-β-hydroxydecanoyl-β-hydroxydecanoate). Chemical structure of rhamnolipids is shown in Figure 4.1. The molecular weight of monorhamnolipid ($C_{26}H_{48}O_9$) and dirhamnolipid ($C_{32}H_{58}O_{13}$) are 504 g/mol and 650 g/mol, respectively. The critical micellar concentration of this biosurfactant is 24 mg/L.

R1



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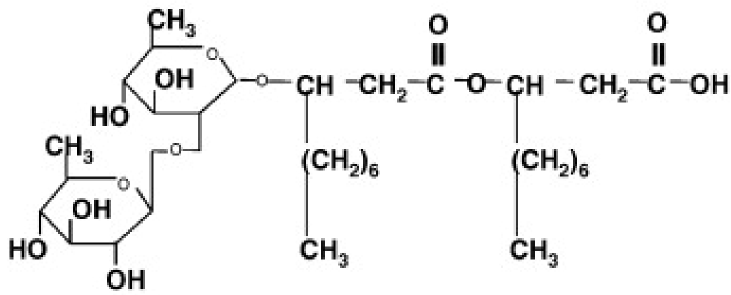


Figure 4.1 Chemical structure of rhamnolipids (Mulligan 2009)

4.2.2. Chemicals

Phenanthrene was selected as representative PAH, and was obtained from Aldrich Chemical Co. (WI, USA) with purity greater than 99%. Four species of SCOAs, including acetic acid, oxalic acid, tartaric acid and citric acid, obtained commercially as pure chemical reagents (Sigma Aldrich, MO, USA), were used in the study. Dichloromethane was obtained from Fisher Scientific (PA, USA). All other chemicals used were of reagent grade quality or higher.

4.2.3. Soil Preparation

The clean natural soil was derived from Coleville site in Saskatchewan, Canada. Two soils, under-plant soil and ditch soil which represent the predominant soil types of the site, were chosen for evaluation in this study. The physical and textural characteristics of these soils are given in Table 3.1. Soil samples were dried and sieved through a 2-mm sieve to remove coarse fragments. Contaminated soil was then prepared by dissolving an appropriate quantity of phenanthrene in dichloromethane and a known weight of soil was added with continuous mixing. The resultant mixture was placed in a ventilation hood to allow the complete evaporation of the solvent. The contaminated soil was stored in a vessel at room temperature for 7 days. Such soil had a final concentration of 100 mg/kg for phenanthrene and was used directly in the batch experiments.

4.2.4. Desorption Experiments

All the experiments were carried out in 25 mL glass centrifuge tubes with Teflon-lined screw caps. The effects of biosurfactant and SCOAs on the behaviors of phenanthrene were examined using the combinations of rhamnolipid and four organic acids including acetic acid, oxalic acid, tartaric acid and citric acid. For the desorption experiment, 0.5 g contaminated soil and 10 mL background solution were used. The background solution was comprised of appropriate rhamnolipid and organic acids, as well as 0.01 mol/L NaN_3 as a biocide. System pH was adjusted to 6 at a constant ion concentration. The centrifuge tubes were vortexed for 20 seconds, and then placed on a reciprocal shaker at 20 ± 1°C and 125 rpm for 24 hours to reach the desorption equilibrium. Preliminary experiments showed that 24 hours were enough for the desorption of phenanthrene to reach equilibrium, and the phenanthrene degradation or adsorption by the tubes was negligible. The tubes were then centrifuged at 5000 rpm for 25 minutes. Phenanthrene in the aqueous phase were extracted with dichloromethane, and their concentrations were analyzed by GC. The amount of phenanthrene adsorbed to the soil was the difference between the initial amount in the system and the amount of the phenanthrene remaining in the solution. All the tests were conducted in triplicate.

4.2.5. Effect of pH

The nature of biosurfactant and SCOAs can vary at different pH, so combined effects of rhamnolipid and SCOAs under different pH conditions should be studied. Prior to the test, pH of background solution was adjusted to 3, 6 and 9 with appropriate HCl and NaOH, respectively. The ion concentration in the system was kept constant by adding NaCl. Then tests were performed in the same way as the batch desorption experiments described above. The initial concentration for each SCOA was 100 mmol/L, and the rhamnolipid concentrations were 50 mg/L.

4.2.6. Effect of DOM in the Soil

To investigate the influence of soil DOM on phenanthrene desorption in the presence of biosurfactant and SCOAs, the DOM in the soils was removed, following the method as described by Cookson et al (2005). The treated soils were contaminated and mildly grounded to pass through the sieve and homogenized. Then desorption tests were done in the presence of rhamnolipid and different SCOAs following the procedures above. The initial concentration for each SCOA was 100 mmol/L, and the rhamnolipid concentrations were 50 mg/L.

4.2.7. Effect of Ionic Strength

To investigate the influence of ionic strength, the desorption tests were done in the presence of rhamnolipid and different SCOAs following the procedures detailed above. NaCl was added at different concentrations (0.2, 0.3 and 0.4 mol/L). The initial concentration for each SCOA was 100 mmol/L and initial pH value was 6. When the pH level of the solution was adjusted with NaOH or HCl, the increment of ionic strength due to the pH-adjusting solution was corrected.

4.2.8. Analytical Methods

The concentrations of phenanthrene were determined with analysis by GC. The GC instrument, a Varian GC 3800-FID system coupled with a Varian 8200 autosampler (CA, USA), was equipped with a 25 m × 0.32 mm ID (DB-5) column with 0.25 μm film thicknesses (J&W Scientific Inc., CA). Helium was used as the carrier gas (1.5 mL/min). The temperature program was as follows: the oven temperature was held at 40 ^{o}C for 1.5 minutes then ramped to 175 ^{o}C at a rate of 50 ^{o}C/min. The temperature was held at 175 ^{o}C for 1 min, then ramped to 220 ^{o}C at 7 ^{o}C/min, and held at this final temperature for 1 minute. The injector temperature was 250 ºC, and the detector temperature was 230 ºC. Injection was made in the split mode with a split ratio of 1:50 (since 1.75 minutes).

4.3. RESULTS AND DISCUSSION

4.3.1. Effect of Biosurfactant on the Phenanthrene Desorption

The effect of rhamnolipid on the desorption of phenanthrene in soil-water system was quantified through measuring the phenanthrene concentration in the bulk after desorption equilibrium. Various biosurfactant concentrations were applied to evaluate the performance of rhamnolipid in removing phenanthrene from the contaminated soil. As Figure 4.2 shows, in the absence of rhamnolipid, the amount of phenanthrene desorbed was 3.37 mg/kg for the under-plant soil with an organic carbon content of 8.84%, and 7.98 mg/kg for the ditch soil with an organic carbon content of 4.57%. The amount of phenanthrene that could be desorbed in ditch soil was greater than that in under-plant soil. In the presence of rhamnolipid biosurfactant, the desorption of phenanthrene by two soils was noticeably affected. The phenanthrene removal amounts were of 8.76 and 12.24

mg/kg with 50 mg/L rhamnolipid for under-plant and ditch soils, respectively. In the presence of 100 and 200 mg/L rhamnolipid solution, the results showed superior desorption efficiency and the desorbed amounts of phenanthrene were 12.05 and 13.12 mg/kg for under-plant, respectively. The increase of rhamnolipid concentration for ditch-soil would result in a similar enhancement of the phenanthrene desorption.

Desorption is the predominant process controlling movement of HOCs through the soil matrix. The less desorbed amount of phenanthrene observed in under-plant soil, which has higher contents of organic matter and lower contents of clay, was due to the stronger binding of phenanthrene to under-plant soil. The removal efficiency often showed great dependence on the soil composition and PAH properties (Zhou and Zhu 2007a). The different performance between these two soils might be attributed mainly to their differences in soil texture and organic contents.

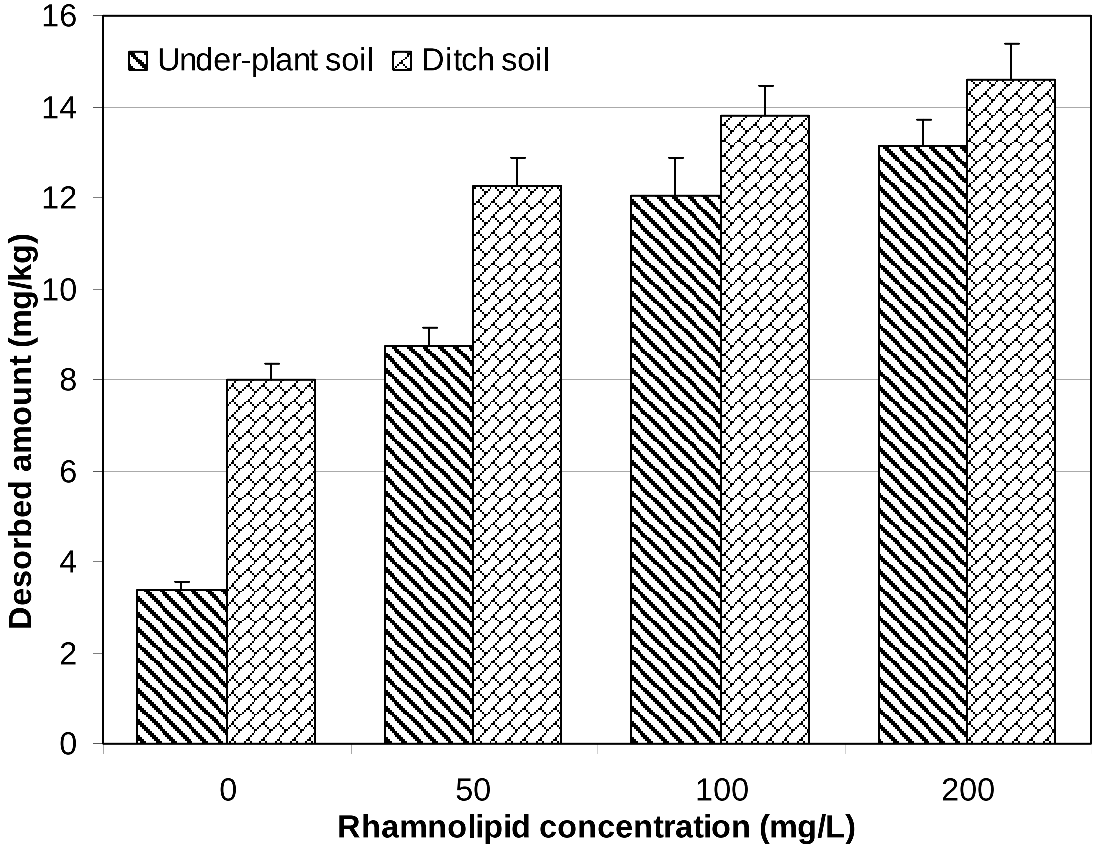


Figure 4.2 Effect of rhamnolipid biosurfactant on the phenanthrene desorption

Biosurfactant concentration is a critical factor for the removal of HOCs from soil. It was observed that increasing the concentration of rhamnolipid could enhance phenanthrene desorption regardless of the soil used (Figure 4.2). At concentrations above the CMC, hydrophobic pollutants can readily partition into the hydrophobic core at the center of the micelle, thus increasing HOC aqueous concentration through micelle solubilization and promoting the desorption of HOCs from soils into aqueous phases (Pennell et al. 1997). In the present study, the rhamnolipid biosurfactant with concentration above 50 mg/L were applied to initiate the onset of micellization and avoid the significant adsorption of biosurfactant (Mata-Sandoval et al. 2002; Cheng et al. 2004). Phenanthrene removed from soil in the presence of 100 and 200 mg/L rhamnolipid could achieve a greater desorption efficiency when compared with that in the presence of 50 mg/L rhamnolipid. The results in this study are similar to previous studies by Lai et al. (Lai et al. 2009) who reported that increasing the concentration of rhamnolipid biosurfactant could enhance the removal of total petroleum hydrocarbons from contaminated soil. However, the excessive biosurfactant addition would make the remediation process less economically feasible. Furthermore, since the biodegradation of biosurfactant could compete with the biodegradation of PAHs, too high concentration of biosurfactant would result in the retardation of contaminant bioremediation (Vipulanandan and Ren 2000). The potential sorption of biosurfactant on soils, which can also show an adverse effect on remediation efficiency, is mainly due to the influence of clays rather than soil organic matters (Ochoa-Loza et al. 2007). Rhamnolipid biosurfactant used in present study could facilitate the phenanthrene removal with high efficiency, thereby being suitable for application for remediation and biostimulation of

PAH-polluted soil.

4.3.2. Effect of SCOAs on the Phenanthrene Desorption by Biosurfactant

The desorption characteristics of phenanthrene by soils were assessed in the presence of rhamnolipid biosurfactant and four SCOAs. Figure 4.3 illustrates the desorbed amount of phenanthrene in the soil-water systems under different combinations of agents. Performance with the combined treatments of rhamnolipid and organic acids exhibited an increase in phenanthrene desorption compared to those that had received a treatment of rhamnolipid alone. The data in Figure 4.3 also indicate that desorption behaviours of phenanthrene in each soil in the presence of different biosurfactant-SCOA combinations are not similar. Among the combined treatments of biosurfactant and SCOAs, the series with rhamnolipid and citric acid exhibited more significant effect on the desorption performance. The maximum removal of phenanthrene was 10.95 and 16.69 mg/kg for the combination of rhamnolipid and citric acid with under-plant soil and ditch soil, respectively.

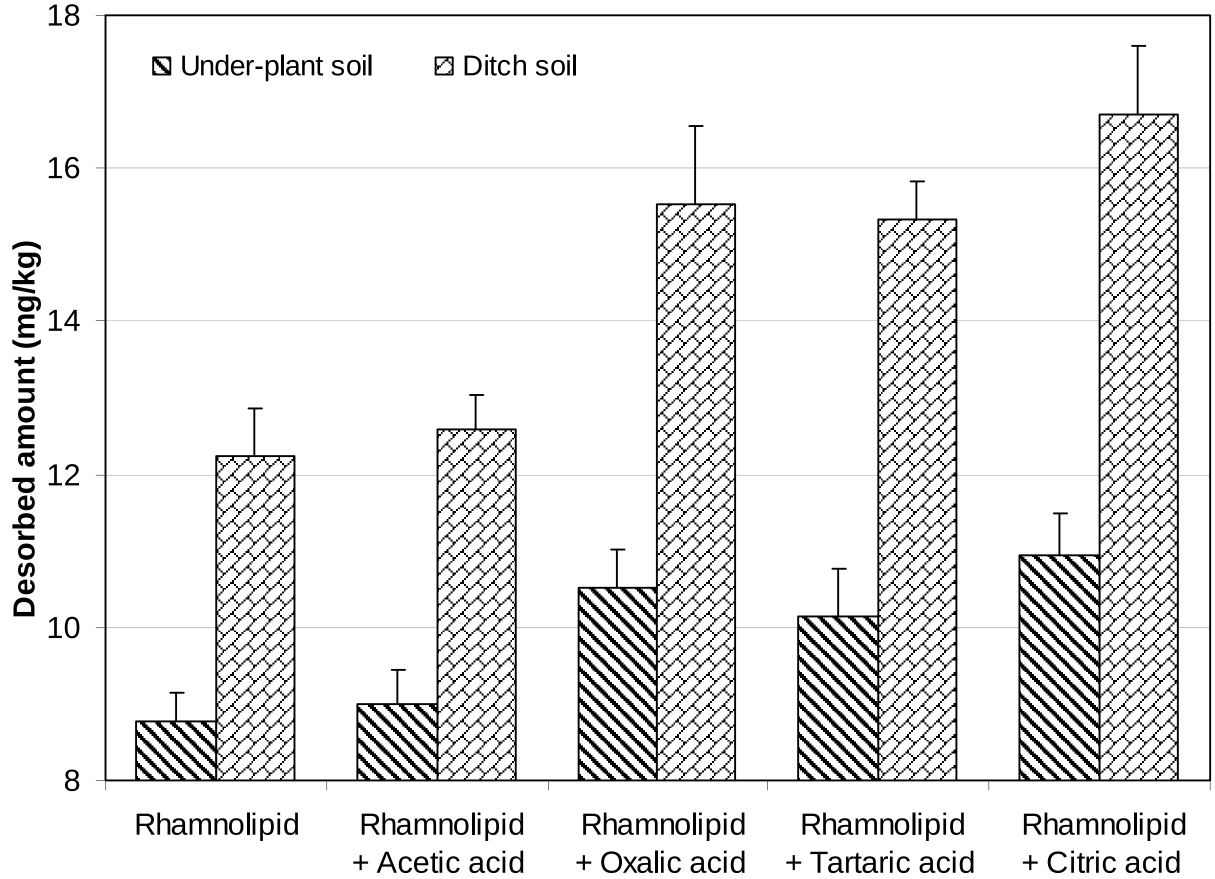


Figure 4.3 Effect of SCOAs on the phenanthrene desorption by biosurfactant

The rhamnolipid biosurfactant was still effective for the significant removal of phenanthrene from the soils in the presence of SCOAs. The result indicates the presence of SCOAs other than rhamnolipid is responsible for the different behaviors of phenanthrene desorption. The mechanism by which rhamnolipid and SCOAs affected the desorption of phenanthrene was complex. SOM functions as an important partition medium in the retaining of HOCs (Rutherford et al. 1992). The organic matter can bond with the metals strongly in the soil through forming surface complexes. The combined treatments with rhamnolipid and citric acid showed better metal extraction performance than individual application of rhamnolipid or citric acid by increasing ligand availability (Gunawardana et al. 2010). In the presence of biosurfactant, therefore, the use of SCOAs might further enhance the release of these metals and disrupt the linkage between organic matter and soil matrix. Phenanthrene may be released from the soil along with the desorbed organic matter. This is in accordance with other studies that the presence of organic acid was correlated with the favorable desorption of organic pollutants (White et al. 2006; Zhang and Dong 2008; An et al. 2010). Moreover, the rhamnolipid biosurfactant could lower the interfacial tension against soil organic fractions in water, facilitating the translocation of organic matter and bounded contaminants into aqueous phase. Then the surfactant molecule could bond with the unbound phenanthrene compounds and dissolve them.

Besides soil organic matter, mineral surfaces also play a role in the distribution of PAHs, especially for the soil with low organic matter content. SCOAs are known to interact with inorganic soil particles via different mechanisms (Jones and Brassington 1998). The adsorption sites on the soil surface might be occupied by organic acids and thus the adsorption of phenanthrene was hindered. In addition, the adsorption of SCOAs could retard the adsorption of the biosurfactant on the soil surface. More surfactant molecules, therefore, will be diffused in the solution and possess a stronger capacity to desorb phenanthrene. Several effects discussed above could all facilitate the desorption process of phenanthrene. Enhanced phenanthrene availability in these combinations could be attributed to the synergistic actions of rhamnolipid and organic acids through potentially different modes of action.

The observed removal efficiencies of phenanthrene from soil were in the order of: rhamnolipid and citric acid > rhamnolipid and oxalic acid > rhamnolipid and tartaric acid > rhamnolipid and acetic acid. The differences are mainly due to different chemical structures and properties of organic acids. Among the SCOAs used, for example, citric acid is a ternary organic acid and can provide more anions for complexing than the other unary or binary acids. Such characteristic could lead to the greater efficacy of citric acid in desorbing metals and SOM from soils, carrying more adsorbed phenanthrene molecules meanwhile. Furthermore, ions of binary and ternary organic acids can form chelates with five- or six-membered ring structure which are more stable (Qin et al. 2004). Thus it can be seen the extent of increment was less for the series with rhamnolipid and acetic acid than that with rhamnolipid and other organic acids. In some other studies, however, it was observed that oxalate acid and acetic acid could enhance more desorption of organic and metal contaminants, respectively (White et al. 2003; Maturi and Reddy 2008). Such difference is perhaps ascribed to the presence of rhamnolipid biosurfactant, as well as the differences of contaminants and soil properties, which need to be elucidated in further research.

4.3.3. Effect of SCOA Concentrations on the Phenanthrene Desorption in the presence of Biosurfactant

The experiments were based on a series of batch tests with same initial concentration of rhamnolipid but different dosages of SCOAs. Considering the conditions in filed applications (Dermont et al. 2008), initial SCOA concentrations ranged from 0 to 300 mmol/L. As shown in Figure 4.4, when rhamnolipid and SCOAs were applied in combination at different ratios, the desorption percentage of phenanthrene were all higher than that where rhamnolipid had been applied alone. It can be seen that the desorbed phenanthrene increased significantly with the increase of SCOA concentration from 0 to 100 mmol/L, and then increased slightly when further increasing the SCOA concentration from 100 to 300 mmol/L in most series. The desorbed amount with under-plant soil reached 9.25, 11.43, 10.89, 11.72 mg/kg in the presence of 100 mg/L rhamnolipid and 300 mmol/L acetic acid, oxalic acid, tartaric acid and citric acid, respectively. A similar trend was also found in other treatments with ditch soils. Additionally, the phenanthrene desorption with the combinations of biosurfactant and different SCOAs showed different increments when organic acid concentrations increased. At the same concentration range of SCOA with ditch soil, the desorbed phenanthrene with acetic acid varied from 12.29 to12.93 mg/kg, which was less remarkable than the series with rhamnolipid and other organic acids.

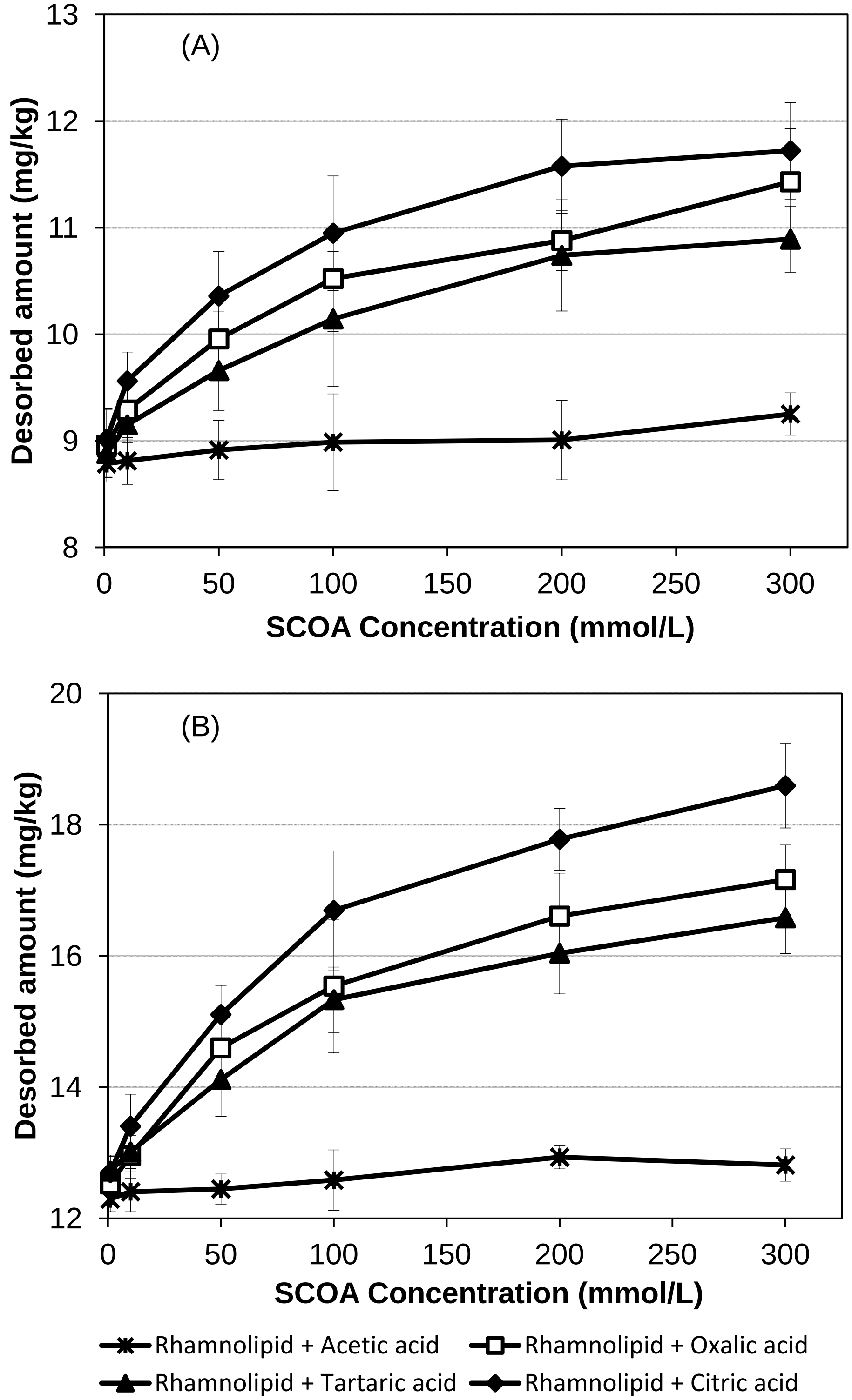


Figure 4.4 Effect of SCOA concentrations on the phenanthrene desorption from (A) under-plant soil and (B) ditch soil in the presence of biosurfactant

It was observed that the removal of phenanthrene using rhamnolipid and SCOAs gradually increased as the SCOA concentration increased up to a concentration of 300 mmol/L. But the relative change in the amount of desorbed phenanthrene in the presence of both biosurfactant and SCOAs decreased with an increase in the concentration of SCOAs. As the concentration of rhamnolipid was fixed, the enhancement was most likely due to the variation of SCOA amount. At low concentration of SCOAs, the effect of organic acids was not significant and there was no obvious difference in the desorption enhancement for various combinations. At this stage, the enhanced desorption of phenanthrene could be mainly ascribed to the performance of rhamnolipid biosurfactant. At higher concentration of SCOAs in the presence of rhamnolipid, organics acids became more available to destroy the barriers within soil matrix that normally functioned to impede the translocation of organic contaminants. More desorbed phenanthrene was observed at high SCOA concentrations, meaning that the SCOA concentrations in the presence of rhamnolipid at fixed concentration were positively correlated to desorbed amount of phenanthrene from soil. In the absence of biosurfactant, it has been previously noted that desorbed norfloxacin increased with increasing concentrations of citric acid, malic acid and salicylic acid (Zhang and Dong 2008). In contrast, it was observed that desorbed *p,p'*-DDE decreased with organic acids above 50 mmol/L (White et al. 2003). Although the increased SCOA concentrations were favorable for the enhanced desorption of phenanthrene, the increments for each SCOA were different, indicating the nature of organic acid is important for this process. When the amount of organic acid was higher than certain value, the low increasing rate of desorption was possibly due to excess quantities of organic acids approaching the maximum effectiveness to dissociate organic matter and desorb contaminant from soil.

4.3.4. Effect of pH on the Phenanthrene Desorption in the presence of Biosurfactant and SCOAs

The effect of pH on the desorption of phenanthrene in the presence of rhamnolipid and SCOAs was studied by conducting batch studies at various pH between 3 and 9. Figure 4.5 depicts the amount of initial PAHs desorbed from soil into aqueous phase. The data indicates that the desorption behavior of phenanthrene in two soils could be affected by the pH conditions in the system. In the presence of biosurfactant and SCOAs, the extent of phenanthrene desorption was relatively lower at low pH range. At pH 3, the desorption amount was from 4.64 to 5.63 mg/kg for different series with under-plant soil. Then the desorption increased sharply from pH 3 to pH 6, but decreased little with the change in pH from pH 6 to pH 9. With the ditch soil, the phenanthrene desorption was also less pronounced at pH 3. Above pH 3, similar trend was observed except that the addition of oxalic, tartaric and citric acids in the presence of rhamnolipid appeared to slightly enhance the desorption of phenanthrene at pH 9 compared with that at pH 6. The amounts of phenanthrene desorbed at pH 9 were 16.34, 15.57, and 17.89 mg/kg in the presence of rhamnolipid along with oxalic, tartaric and citric acids, respectively. At the same pH value, desorption amounts of phenanthrene differentiate for varied combinations. The use of rhamnolipid and citric acid showed better desorption performance than the combinations of rhamnolipid and other organic acids.

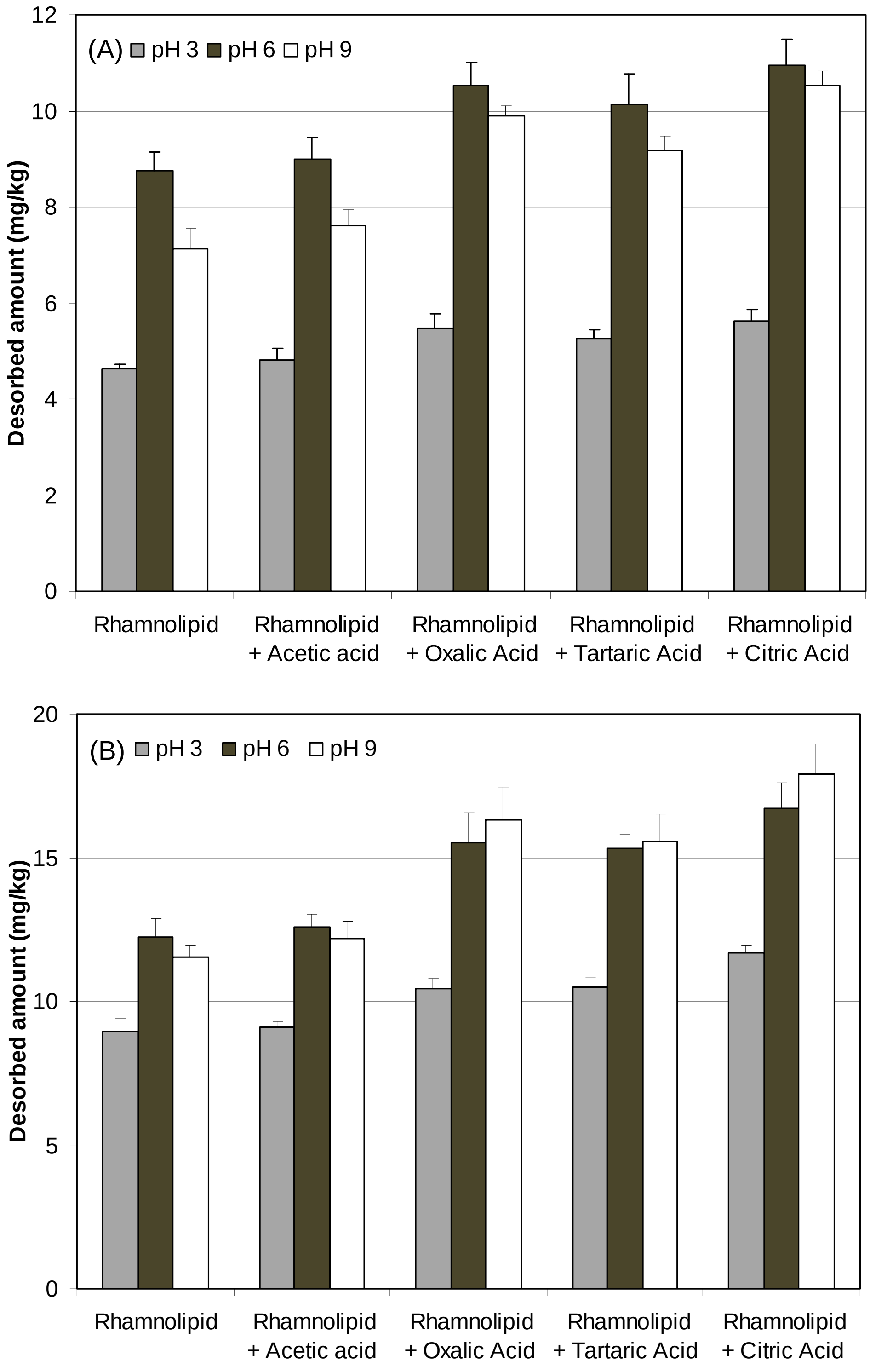


Figure 4.5 Effect of pH on the phenanthrene desorption from (A) under-plant soil and (B) ditch soil in the presence of biosurfactant and SCOAs

The results indicate that pH variation could influence the transfer of phenanthrene from soil to aqueous phase in the presence of surfactant and organic acids. The performance of biosurfactant may be related quantitatively to the surface tension and contaminant solubility, which are pH dependent (Zhang and Miller 1992; Shin et al. 2004). As for the SCOAs, the possible existing forms of organic acids (dissociated and undissociated) are also strongly related to pH conditions (Jones and Brassington 1998). Under the combined application of rhamnolipid and SCOAs, the series at pH 3 could achieve a least desorption of phenanthrene when compared with those at higher pH range. This was mainly due to limited ability of rhamnolipid biosurfactant to enhance surface activity and contaminant solubility at low pH. Also, less organic acids could be dissociated from their protons and existed as organic acid molecules. The maximum desorption was achieved when the solution pH increased to 6. At this pH range, both of the surface activity and contaminant solubility with biosurfactant are near to the optimum conditions. Organic acids could provide more ions, resulting in enhanced complexing tendency (Qin et al. 2004).

Beyond pH 6, the increase of pH would result in a slight decrease for the desorption efficiency of phenanthrene in most tests. Although the individual performance of rhamnolipid could be limited at pH above 6, the removal of phenanthrene still reached more than 7.61 and 12.19 mg/kg with combined use of rhamnolipid and SCOAs in our experiment with under-plant and ditch soil, respectively. The high removal efficiency at high pH could be attributable to facilitation by organic acids. Moreover, the system at high pH might lead to increased polarity of the organic material, showing lower affinity for hydrophobic compounds (Ping et al. 2006). At the same time, increases in pH could be accomplished with increased soil-particle dispersion, as well as more disassociated soil minerals and organic matter (You et al. 1999). These factors will contribute to the strong desorption even at high pH range. Furthermore, since soil is negatively charged at near-neutral or higher pH, rhamnolipid, present in anionic forms, are expected to sorb minimally to the particle surface.

For both under-plant and ditch soils, elevated pH in combination with rhamnolipid and citric acid had the largest removal efficiency. The variations of phenanthrene desorption at different pH might relate to the different dissociation constants of organic acids involved. The complexing ability of organic acid will increase with enhanced pH, especially for the polyprotic weak acid such as citric acid. The different phenanthrene desorption performances at varied pH may be attributed to effects of biosurfactant and organic acids, as well as the soil constitutes and other system conditions. The relative importance of the different mechanisms depends on the physical and chemical properties of the interactive sorbate-sorbent system. Furthermore, based on our results, the optimum pH values for desorption was relatively close to that for microbial growth. It is thus important to also include such environmental concern of pH for in situ application.

4.3.5. Effect of Soil DOM on the Phenanthrene Desorption in the presence of Biosurfactant and SCOAs

The desorption amounts of phenanthrene in the presence of biosurfactant and SCOAs with DOM-removed soils are illustrated in Figure 4.6. When compared with Figure 4.3, the results showed that the phenanthrene desorption differentiated significantly between the treated and untreated soils. In general, the desorbed amounts of phenanthrene for treated soils were less than those for untreated soils. Without the amendments of SCOAs, addition of rhamnolipid enhanced the mobilization of phenanthrene with the desorption of 5.98 and 9.36 mg/kg for DOM-removed under-plant and ditch soils, respectively. The desorption capacities were greater in the presence of both rhamnolipid and SCOAs, irrespective of whether the soil DOM was removed. In the series with rhamnolipid and different organic acids, the desorbed amounts of phenanthrene in the soil-water systems were from 6.13 to 7.66 mg/kg for treated under-plant soils, which were lower than the values of corresponding untreated soils. Similar trend was observed for different combinations of biosurfactant and SCOAs with treated ditch soils, except the phenanthrene desorption was greater in the series with rhamnolipid and tartaric acid as compared with the tests with rhamnolipid and oxalic acid.

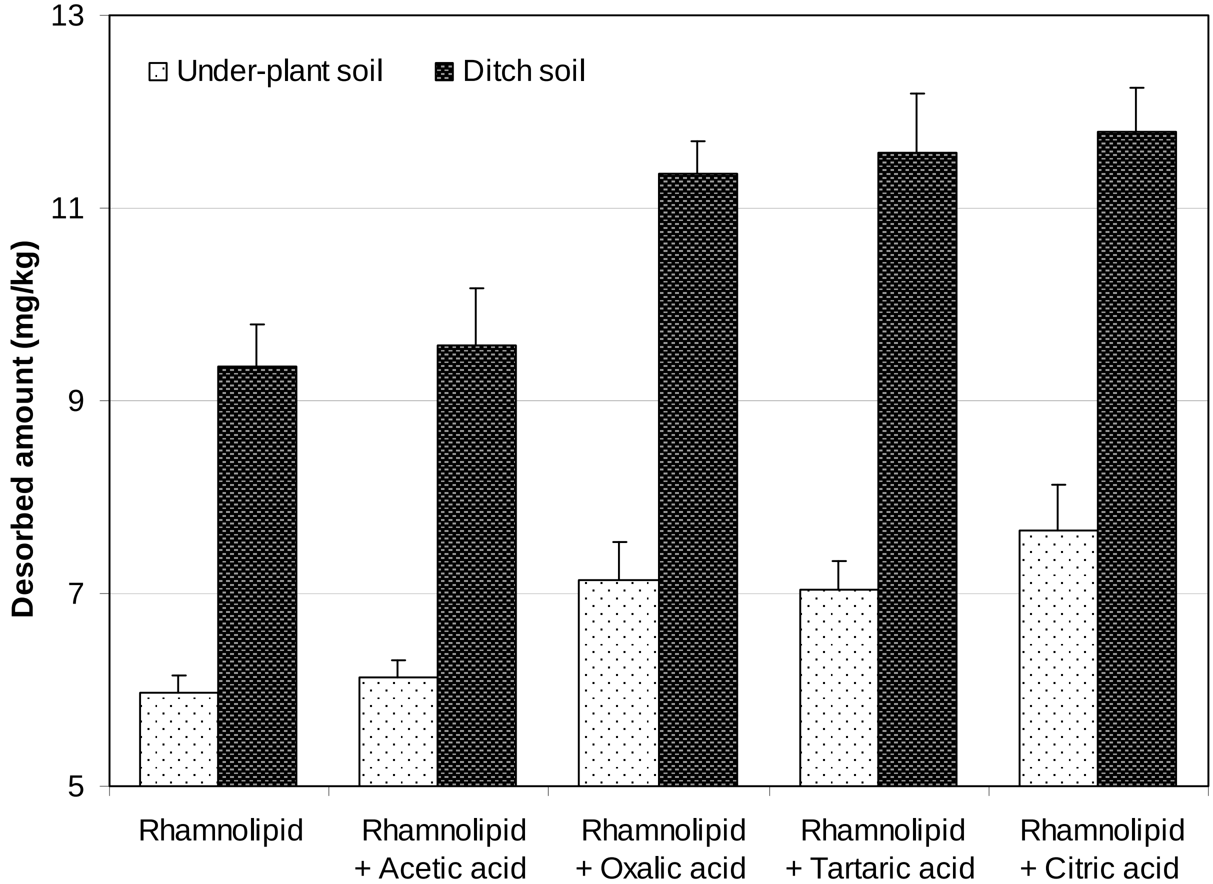


Figure 4.6 Effect of soil DOM on the phenanthrene desorption in the presence of biosurfactant and SCOAs

The desorption of phenanthrene was adversely affected with the use of DOM-removed soil. This difference indicates that some soil properties other than biosurfactant and organic acids can be responsible for the changes of phenanthrene desorption. This result is similar to previous study where adsorption of phenanthrene on soil increased after removal of DOM (Luo et al. 2008). The DOM in soil could exhibit a high affinity for HOCs and enhance the dissolution of organic compounds in soil-water system (Pignatello et al. 2006). With a decreased quantity of DOM in soil, the concentration of DOM in solution decreased so that less phenanthrene was transported into aqueous phase. Binding affinity of organic contaminates to the sediment increased after the removal of soil DOM. In contrast, if all the organic matter is removed, organic contaminants would deposit mainly on mineral surface and exhibits a stronger desorbing capacity (Gao et al. 1998).

Although most DOM has been removed, larger amounts of phenanthrene were desorbed from soil in the soil-water systems containing both rhamnolipid and SCOAs than those from soil in the systems containing only rhamnolipid. This is in part due to the mobilization of phenanthrene by rhamnolipid biosurfactant, but also due to the influence of the organic acids on remaining organo-mineral linkages, all of which operate simultaneously. The variation of desorption percentage with different combinations is closely related to the speciation of the organic acids. The lower increases in phenanthrene desorption with rhamnolipid and acetic acid amendments are possibly due to weak complexing ability of organic acid, restricting the diffusion of resident contaminants in soils. These observations suggested that the soil DOM was a critical factor affecting the desorption processes by biosurfactant in presence of organic acids.

4.3.6. Effect of Ionic Strength on the Phenanthrene Desorption in the presence of Biosurfactant and SCOAs

The phenanthrene desorption influenced by combined use of rhamnolipid and SCOA at different ionic-strength conditions is shown in Figure 4.7. The desorption of phenanthrene in the presence of rhamnolipid and different organic acids decreased with increasing concentrations of the ions. At the ionic strength of 0.3 mol/L, the phenanthrene desorption ranged from 7.92 to 10.16 mg/kg and 10.64 to 14.30 mg/kg for different combinations with under-plant and ditch soils, respectively. Compared with the tests without any amendments, the desorption amount of phenanthrene was also elevated with the addition of biosurfactant and SCOAs at higher ionic-strength range. However, the increase was not very significant as noticed at lower ionic strength. At the ionic strength of 0.4 mol/L NaCl, the phenanthrene desorption efficiency with different combinations was from 6.52 to 9.10 and 8.45 to 13.77 mg/kg for under-plant and ditch soil, respectively. At the same range of NaCl concentration, ditch soil followed by under-plant soil, showed the greater desorption capacities with different combinations of rhamnolipid and SCOAs.

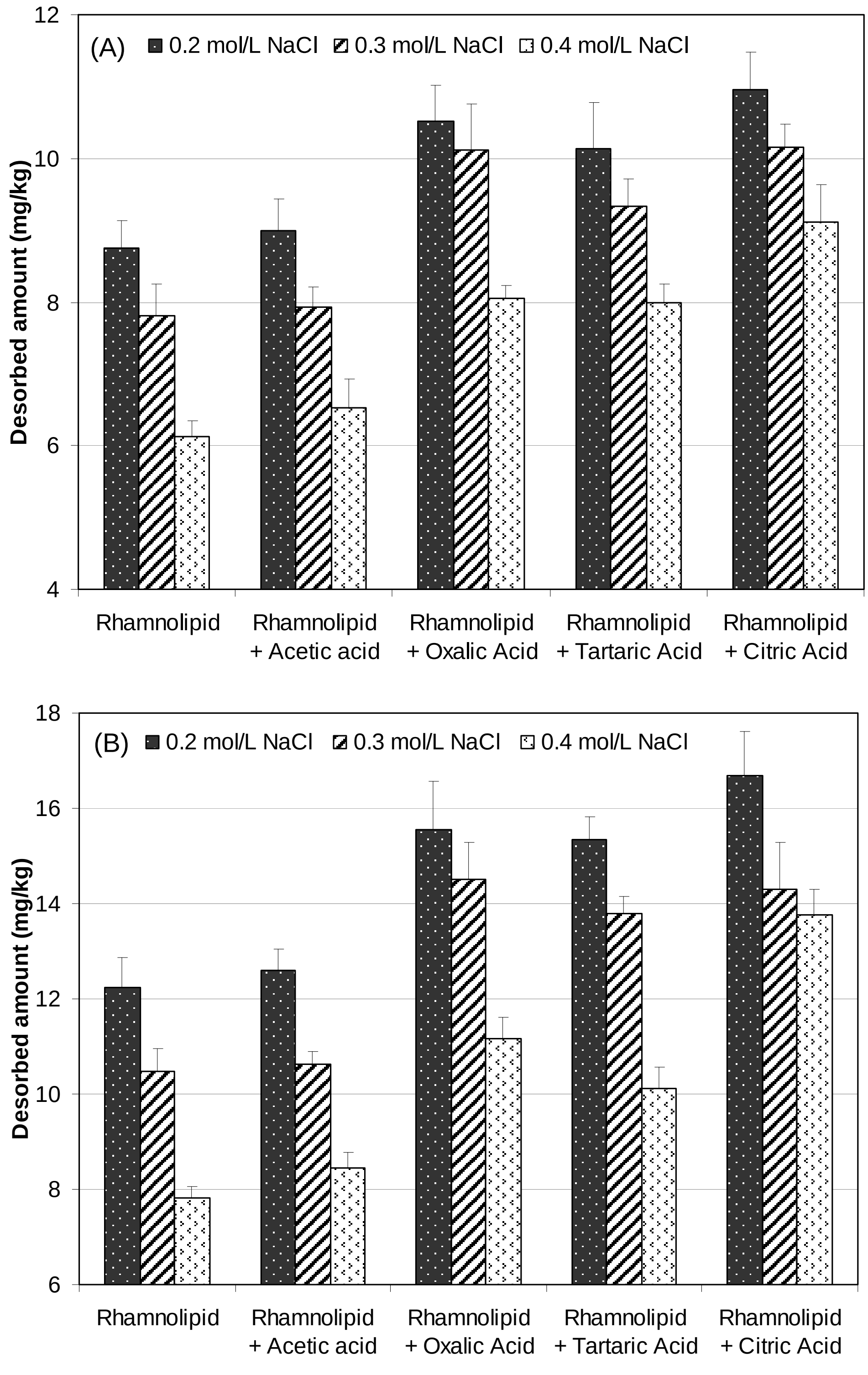


Figure 4.7 Effect of ionic strength on the phenanthrene desorption from (A) under-plant soil and (B) ditch soil in the presence of biosurfactant and SCOAs

Organic acids often coexist with metal ions in natural environment. The above results indicates that the variation of system ionic strength is likely to influence the overall phenanthrene desorption efficiency with the addition of rhamnolipid and SCOAs. A recent study reported that the surface activity of rhamnolipid was not negatively affected to any degree by high salinities (Abdel-Mawgoud et al. 2009). The size of both mono- and dirhamnolipid biosurfactant vesicles were reduced after the addition of NaCl, thereby improving the water solubility of the biosurfactant (Pornsunthorntawee et al. 2009). However, the findings of present study show that the high ionic strength values were correlated with the low mobility of phenanthrene. In the solution with high ionic strength, solubility of HOCs might decrease due to the salt-out effect process (Brunk et al. 1996). It was also postulated that PAHs could be less partitioned to dissolved organic substances in the presence of high-concentration metals (Saison et al. 2004). The presence of more salt ions, therefore, can decrease the diffusion of phenanthrene contaminants from soil into aqueous phase. In addition, certain SCOAs could enhance the removal efficiency for phenanthrene which contains rhamnolipid biosurfactant and NaCl at high concentrations.

The metal ions showed less inhibitory effect on phenanthrene desorption in biosurfactant -enhanced process when the organic acids were amended. This was of special interest for application to in situ soil washing with high salinity level. Among the different combinations at the same ionic strength, the maximum desorption for phenanthrene was observed in the series with rhamnolipid and citric acid. In the presence of NaCl, the desorption of phenanthrene by two soils was still different. Consequently, other factors, like soil fractions and organic acid characteristics, might also be important for deciding the combined role of biosurfactant and SCOAs in contaminant behaviors within metal ion enrichment.

4.4. SUMMARY

The study investigated the effect of SCOAs on the desorption of phenanthrene in the presence of rhamnolipid biosurfactant. The results supported the combined use of biosurfactant and SCOAs could further enhance the desorption of phenanthrene from soil into aqueous phase. The overall desorption behavior of phenanthrene could be assumed to be a sum of a large number of individual desorption events with different mechanisms. Desorption amounts of phenanthrene differentiated for varied combinations, in which the effect of ternary and binary SCOAs were more remarkable. SCOAs at high concentration caused a more significant increase in desorption from the soils with the amendment of biosurfactant. The quantity and species of organic acids could affect the tendency of phenanthrene distribution in the presence of biosurfactant. Furthermore, the phenanthrene desorption was higher in the ditch soil compared with the under-plant soil. The variation of desorption with different combinations was also closely related with the soil DOM.

Soil property might be an important factor influencing the mobility behaviors of phenanthrene with combined use of biosurfactant and organic acids. In addition, adjusting the pH and ionic strength could control the effect of biosurfactant and organic acids, allowing higher remediation efficiency at specific values. The results presented here demonstrated that the effect of SCOAs on the biosurfactant-enhanced desorption might be directly influenced by the solution chemistry. The results suggest that the combined application of rhamnolipid and SCOAs can be regarded as a good alternative for the removal of PAH compounds from contaminated soil. Further study is also needed to help obtain more theoretical foundation for the PAH mobility with additional biosurfactant and organic acids.

CHAPTER 5

STEPWISE ADSORPTION OF PHENANTHRENE AT THE FLY ASH-WATER INTERFACE AS AFFECTED BY SOLUTION CHEMISTRY

5.1. BACKGROUND

Although various renewable energy resources are being promoted internationally, electricity production based on fossil fuels is still dominant in many countries. FA (FA) is generated as a byproduct from coal-fired power plants (Ahmaruzzaman 2009). The production of FA has been more than 600 million tonnes each year worldwide (Nollet et al. 2003). FA can be used as raw material for cement, structural fill, road base, mining, waste stabilization, and many other applications (Burgess et al. 2006). However, less than 25% of produced FA is utilized (Ahmaruzzaman 2009). The production of FA far outweighs consumption (Iyer and Scott 2001). Most of the FA has to be disposed at holding ponds, lagoons, landfills or slag heaps.

PAHs are a group of organic compounds which are toxic to human health, as well as a variety of flora and fauna species (Joner et al. 2001; Fang et al. 2008; An et al. 2010; Wei et al. 2011b; Yu et al. 2011a). These pollutants are frequently found in FA as a result of incomplete combustion (Korfmacher et al. 1980; Drakonaki et al. 1998; Mastral and Callén 2000); a large amount of FA has been dumped into land storage systems, leading to contamination of PAH when it is released to the environment. Due to limited land resources and inefficient management practices, separate disposal of FA cannot always be achieved and, thus, massive quantities of FA often coexist with other industrial and municipal wastes in landfills (Iyer and Scott 2001; Sharholy et al. 2008; An et al. 2012b). PAHs, which can be released from landfill waste or can be the result of transformation processes, have often been characterized as important pollutants in landfill (Gounaris et al. 1993; Wiszniowski et al. 2006). Thus an inevitable consequence of FA disposal is the coexistence of FA with extraneous sources of PAHs in landfill systems. As a result, PAH contamination caused by both intrinsic and extraneous sources at FA disposal sites is of increasing concern. Moreover, as a prominent low-cost adsorbent (Ahmaruzzaman 2010), FA might be useful for the removal of PAHs.

Adsorption is the primary process controlling the transport and fate of many PAHs in the environment. The rates of volatilization, photolysis, hydrolysis, and biodegradation are often dependent upon the extent of adsorption (Minero et al. 1992; Nudelman et al. 2008). The application of FA as a low-cost adsorbent for removing inorganic pollutants, such as toxic metals, phosphate, fluoride, and boron, has been successfully demonstrated in many previous studies (Ahmaruzzaman 2010). Apart from these inorganic pollutants, there has also been continued interest in investigating the adsorption of various organic compounds on FA. Adsorption of dyes and their mixtures from aqueous solutions on FA has been studied (Iyer and Scott 2001; Li et al. 2006; Ahmaruzzaman 2010). Other phenolic and ketone compounds can also adsorb to FA (Kumar et al. 1987; Banerjee et al. 1995). A number of isotherm models have been employed to describe adsorption processes on the surface of FA (Ahmaruzzaman 2009; Andersson et al. 2011). Factors affecting adsorption process were also evaluated (Ahmaruzzaman 2010). However, limited studies have focused on the interactions of

HOCs with FA. Nollet et al. (2003) investigated the adsorption-process kinetics and the factors controlling the rate of adsorption in the removal of polychlorinated biphenyls (PCBs) by FA. Singh (2009) reported that coal FA had high retention capacity for metribuzin, metolachlor, and atrazine, and the Freundlich adsorption isotherm appeared to explain the related process. Although these findings are encouraging, a number of issues about the characteristics of nonionic HOCs on FA surface are poorly understood.

In solid-liquid systems, the mechanism for the distribution and transportation of solute from bulk solution to solid surface is complicated (Moreno-Castilla 2004). The exact process of PAH adsorption on FA is still uncertain and the influencing factors need to be clarified. This research aims to investigate the adsorption process of phenanthrene on FA. This is the first study to our knowledge to explore the interaction between PAHs and FA at the solid-liquid interface, and to discuss the environmental issues related to PAH pollution during FA disposal. A stepwise multisite Langmuir model is developed to simulate the adsorption process. The effects of aqueous chemistry characteristics (i.e., temperature, pH, HA and ionic strength) corresponding to the in situ conditions of disposal sites are also evaluated. The results reveal the migration patterns of PAHs in a FA-water system and can facilitate environmental risk assessment at FA disposal sites.

5.2. MATERIALS AND METHODS

5.2.1. Chemicals

Phenanthrene was selected as a representative PAH because it was commonly found in FA and landfill leachate. Phenanthrene was obtained from Aldrich Chemical Co. (WI, USA) with purity greater than 98%. Sodium salt of HA (38.4% organic carbon), obtained commercially as pure chemical reagents (Sigma Aldrich, MO, USA), was used. High-performance liquid chromatography (HPLC) grade acetonitrile and methanol were obtained from Fisher Scientific (PA, USA). High-purity water used in all experiments was prepared by processing deionized water through a Milli-Q system.

5.2.2. Fly Ash

Two types of dry FA were supplied by coal-based thermal utilities, including Shand Power Station and Boundary Dam Power Station, Saskatchewan, Canada. They are labeled as Shand FA (SFA) and BD FA (BDFA), and are categorized as Class C and Class F FA, respectively. The properties and major constituents of them are summarized in Table 5.1. Prior to experiments, the FA was washed in ultrapure water, by stirring at room temperature for 48 hours, to remove the soluble compounds. FA was also washed with acetone to remove organic compounds. The materials were dried at 105 ± 5 °C overnight, and then bottled and stored in a desiccator.

Table 5.1 Properties of the selected FA

Adsorbents	SFA	BDFA
Physical form	Powder	Powder
SiO_2 (%)	42.5	47.7
Al_2O_3 (%)	18.3	20.1
Fe_2O_3 (%)	3.97	4.25
CaO (%)	20.6	11.2
SO_3 (%)	3.47	0.56
Loss on ignition (%)	1.29	0.19
Type*	Class C	Class F
Density (g/cm^3)	2.62	2.45
pH_{ZPC}	8.4	7.7

*FA classification is according to standard specifications of the American Society for Testing and Materials (ASTM).

5.2.3. Adsorption Studies

First, a stock solution of phenanthrene was prepared by dissolving pure crystals in methanol. Second, 0.2 g FA and 10 mL water were added to 25 mL glass centrifuge tubes with Teflon-lined screw caps. The background solution comprised 0.1 mol/L NaCl. Third, an appropriate volume of phenanthrene methanol stock solution was added to each vial. Fourthly, the centrifuge tubes were vortexed for 20 seconds, and then placed on a reciprocal shaker at a constant temperature and 200 rpm for 24 hours to reach adsorption equilibrium. Preliminary experiments showed that 24 hours were enough for the adsorption process to reach equilibrium. The amount of phenanthrene adsorbed to FA was the difference between the initial amount added and the amount remaining in the solution.

To investigate the influence of temperature, pH, HA and ionic strength, the adsorption experiments were conducted under multiple conditions. These experimental details and analytical methods are shown as follows. All of the tests were conducted in triplicate.

To study the effect of pH on adsorption of phenanthrene, the adsorption behaviors of phenanthrene were carried out at a range from 4 to 10. The pH was adjusted with appropriate HCl and NaOH, and the ion concentration in the system was kept constant. The initial concentrations for phenanthrene were ranging from 0.25 to 1 mg/L. Temperature was kept constant at 20 °C. Batch adsorption experiments were performed in the manner as mentioned above. In addition, we also investigated the potential influence of pH variation on the surface properties of FA samples. 2 g FA was added to the 250 mL Erlenmeyer fasks. 100 mL background solution adjusted to different levels was also included in the flasks. Then sample flasks were mounted on the shaker at 20 °C and at 200 rpm to keep the adsorbent suspended. The tests were conducted in triplicate. The treated FA was dried and samples from parallel flasks were mixed together. The surface area of FA was measured using adsorption of nitrogen gas.

The effect of HAs on the behaviors of phenanthrene was examined in FA-water system. Adsorption experiments were carried in the presence of HA at concentrations ranging from 0 to 50 mg OC/L. An appropriate volume of phenanthrene methanol stock solution was added and the initial concentrations for phenanthrene varied from 0.25 to 1 mg/L. Temperature was kept constant at 20 °C and pH was adjusted to 7. Batch experiments were performed following the adsorption test procedures. Batch experiments for solubilization of phenanthrene in the presence of HA with different concentrations were carried out subsequently. For each batch test, excess amount of phenanthrene was added to each vial containing a series of 10 ml HA solutions to ensure maximum solubility. The sample vials were sealed with a screw cap fitted with Teflon lined septum to prevent any volatilization loss of phenanthrene. Triplicate samples were prepared for each HA concentration. These samples were then equilibrated for a period of 48 hours on a reciprocating shaker maintained at a temperature of 20 °C. Previous experimental results showed 48 hours to be sufficient for reaching solubilization equilibrium under mixing. After this, the samples were subsequently centrifuged at 5000 rpm for 30 minutes to separate the undissolved phenanthrene. An appropriate aliquot of the supernatant was then carefully withdrawn to analyze the phenanthrene concentration by HPLC.

The tests of HA's adsorption onto FA were also conducted. In the experiments, 50 mg FA samples, along with 100 ml solutions of concentrations 0-100 mg OC/L, were put into 250 ml flasks. The temperature was controlled at 20 °C. The tests were conducted in an orbital-shaker at 200 rpm. The samples were separated by filtering and then analyzed by spectrophotometer. The amount of HA adsorbed to FA was the difference between the initial amount added and the amount of HA remaining in solution. In addition, in order to investigate the effect of HA at different pH levels. The adsorption experiments were carried with the initial HA concentrations at 25 and 50 mg OC/L. The initial concentration of phenanthrene was 0.5 mg/L. The medium composition was similar to that in original background solution. The pH was adjusted to the range from 4 to 10 and temperature was kept at 20 °C. The standard batch equilibration method was adopted as described above.

To investigate the influence of ionic strength, the adsorption tests were done in the FA-water system. NaCl was added at different concentrations (0.1 to 1 mol/L). The initial concentrations of phenanthrene were 0.25, 0.5 and 1 mg/L and pH value was 7. The centrifuge tubes were placed on a reciprocal shaker at 20 °C and 200 rpm for 24 hours to reach the adsorption equilibrium.

5.2.4. Analytical Methods

Phenanthrene was analyzed through high-performance liquid chromatography (HPLC), with an Agilent 1260 Infinity LC System (USA) equipped with vacuum degasser, binary pump, autosampler, thermostated column compartment (set to 30 °C), diode array detector (DAD), and ZORBAX Eclipse PAH column (3.5 μm particle size, 4.6 mm × 150 mm ID). A mobile phase consisting of acetonitrile/water (75:25, v/v) was used at a flow rate of 1.0 mL/min. Phenanthrene was monitored with DAD at 250 nm.

Samples were collected via syringe and filtered through sterile, 0.2-μm-pore-size polytetrafluoroethylene (PTFE) filters before injection into HPLC system. The specific surface area of FA was determined at 77 °C with a TriStar II 3020 (Micromeritics, USA) using BET nitrogen gas sorption method. The ash sample was examined by an environmental scanning electron microscopy (ESEM, Quanta 200 FEG, FEI, USA). The pH measurements were taken through a SevenEasy S20K pH meter (Mettler-Toledo, USA). A UV-vis spectrophotometer (Cary 300, Varian, Inc., USA) was used for the determination of HA concentrations at 400 nm.

5.2.5. Data Analysis

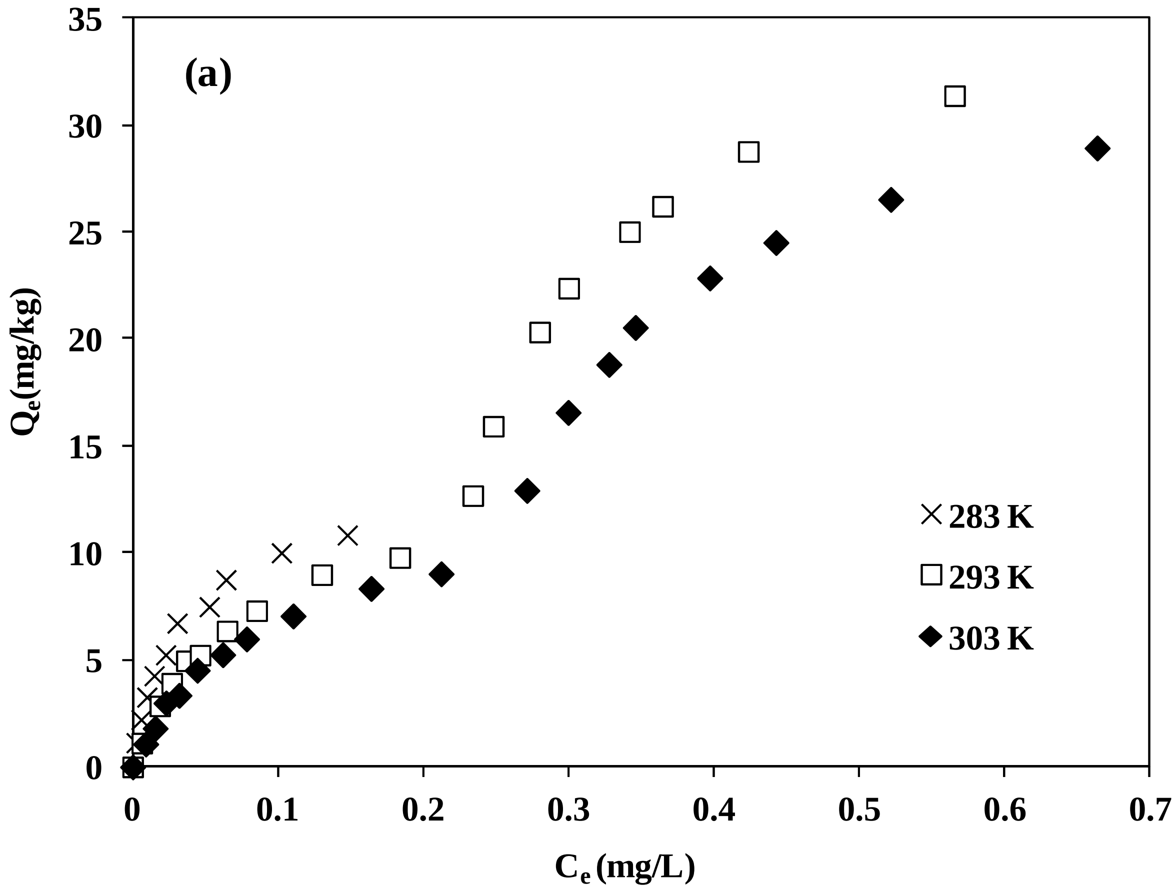
Replicate analyses gave errors of ± 5 to 10%. Adsorption equilibrium data were fitted to the developed model. The data were analyzed through nonlinear regression using SigmaPlot software (Systat Software Inc., CA, USA). Statistical analyses were undertaken through one-way ANOVA and least significant difference (LSD) analysis for comparisons of treatment means with $p < 0.05$.

5.3. RESULTS AND DISCUSSION

5.3.1. Adsorption of Phenanthrene on Fly Ash

The adsorption isotherms of phenanthrene on FA under different temperature levels are shown in Figure 5.1. The selected temperature levels can represent general temperature conditions at FA disposal site. The isotherms exhibit an increasing trend in the adsorbed amounts of phenanthrene, while the stepwise behaviors are apparent and the increasing patterns are significantly different (p < 0.05). The isotherm appears to have one plateau at 10 °C, while two plateaus are observed when the temperature reaches 20 and 30 °C. Due to the solubility limits of phenanthrene at relatively lower temperature, a full range of phenanthrene concentration in aqueous phase cannot be obtained at 10 °C. Thus, a fit at 10 °C would be unable to provide sufficient data for analyzing second plateau. To elucidate the adsorbing mechanism in FA-water system, it is necessary to analyze it over a wide range of phenanthrene concentrations. Thus the following sections focus on the results at 20 and 30 °C.

Visual inspection results indicate pronounced nonlinearity in all of the isotherms. However, traditional nonlinear isotherm models as reviewed by Hinz (2001) cannot fit experimental data of phenanthrene adsorption on FA (data not shown due to poor fitting quality). These mathematical models are not adequate to represent the stepwise-shaped curves. At 20 and 30 °C, the isotherms for both SFA and BDFA samples can be characterized as type IV isotherms according to the classification by Giles et al. (1974). The existence of stepwise isotherms can be attributed to the multisite or multilayer mechanism.


(a)
35
30
25
20
15
10
5
0
Qe(mg/kg)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Ce (mg/L)
283 K
293 K
303 K

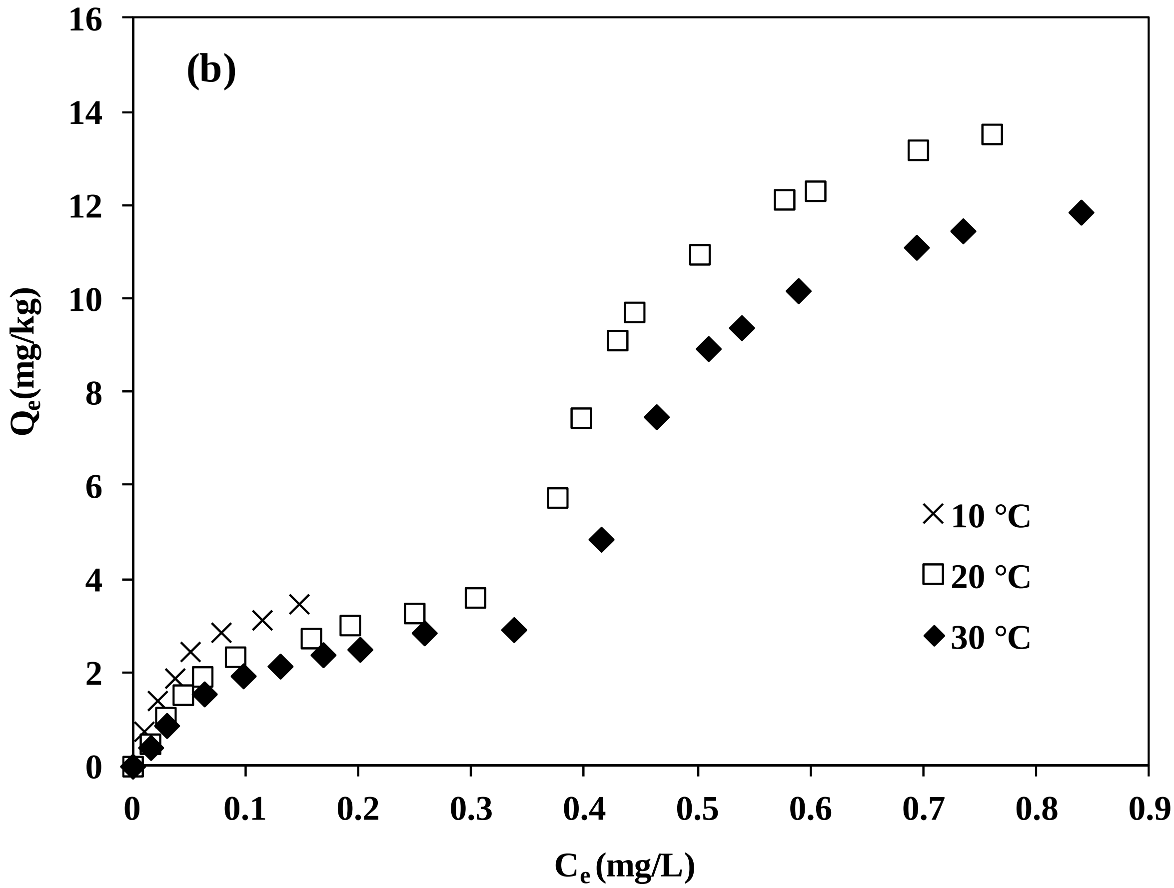


Figure 5.1 Adsorption isotherms of phenanthrene on (a) SFA and (b) BDFA

To characterize the adsorption behavior, the concept of relative surface coverage was adopted to measure the occupied surface area of the adsorbent. The interaction between phenanthrene and FA is one type of surface adsorption phenomenon. Each phenanthrene molecule can take up an area of 198 $Å^2$. The maximum adsorption amounts were 31.39 and 13.53 mg/kg for SFA and BDFA at 20 °C, respectively (Figure 1). This corresponds to surface coverages of 0.20 and 0.09 m^2/g (phenanthrene area per gram of FA). These values were much lower than those of SFA and BDFA that were 7.46 and 5.24 m^2/g derived from BET measurements, respectively. Thus, the total surface area of FA is sufficient for binding the full amount of phenanthrene in any orientation, without the requirement for a multilayer coverage. This indicates that the uptake of phenanthrene on FA surface can take place through monolayer adsorption.

5.3.2. Modeling of the Stepwise Adsorption Process

In previous studies, similar stepwise isotherms were identified for vapor and gas adsorption on solids (Fox and Katz 1961; Malović and Vučelić 1998; Perrin et al. 2004). The pressure and temperature could also have influence on the behaviors of stepwise adsorption. However, the mechanism for adsorption on solid-liquid interface is significantly different, and the stepwise-shaped isotherm in solid-liquid systems has not been systematically investigated. As shown in Figure 5.1, it is interesting to note that the isotherm can be divided into several sets of nonlinear sections. Each section can represent one Langmuir-type isotherm. This is a reasonable assumption based on the monolayer adsorption process. The Langmuir model (LM), which assumes uniform site energy for adsorption sites, is often applied to homogeneous surfaces (Hinz 2001; Choy et al. 2004).

In its general form, multisite Langmuir model (MLM) takes into account several kinds of active sites on the heterogeneous surface of the adsorbent, and is useful for adsorbents with more generally heterogeneous surfaces (Janoš et al. 2003). FA comprises various fine inorganic products; this characteristic is shown in Figure 5.2. The surface of FA is often associated with pits, edges, and other discontinuities (Wang and Wu 2006). It is thus reasonable to assume that not all surface sites on FA are identical. Additionally, a variety of site types might exist, with varying binding energies and affinity scales for the adsorbate.

At a low concentration of phenanthrene adsorbate, it is speculated that all types of unoccupied sites are in excess and the phenanthrene molecule binds preferentially to sites with higher affinity. As the quantity of phenanthrene increases, adsorption to the higher energy sites becomes saturated and excess free phenanthrene molecules are forced to seek other sites with lower affinity. Thus a stepwise isotherm can be obtained and perceived as the sum of multiple adsorbing steps, each describing a group of sorption sites with LM/MLM-type isotherms. In order to better describe the isotherm of phenanthrene adsorption on FA, a stepwise multisite Langmuir model (SMLM) was developed in this study.

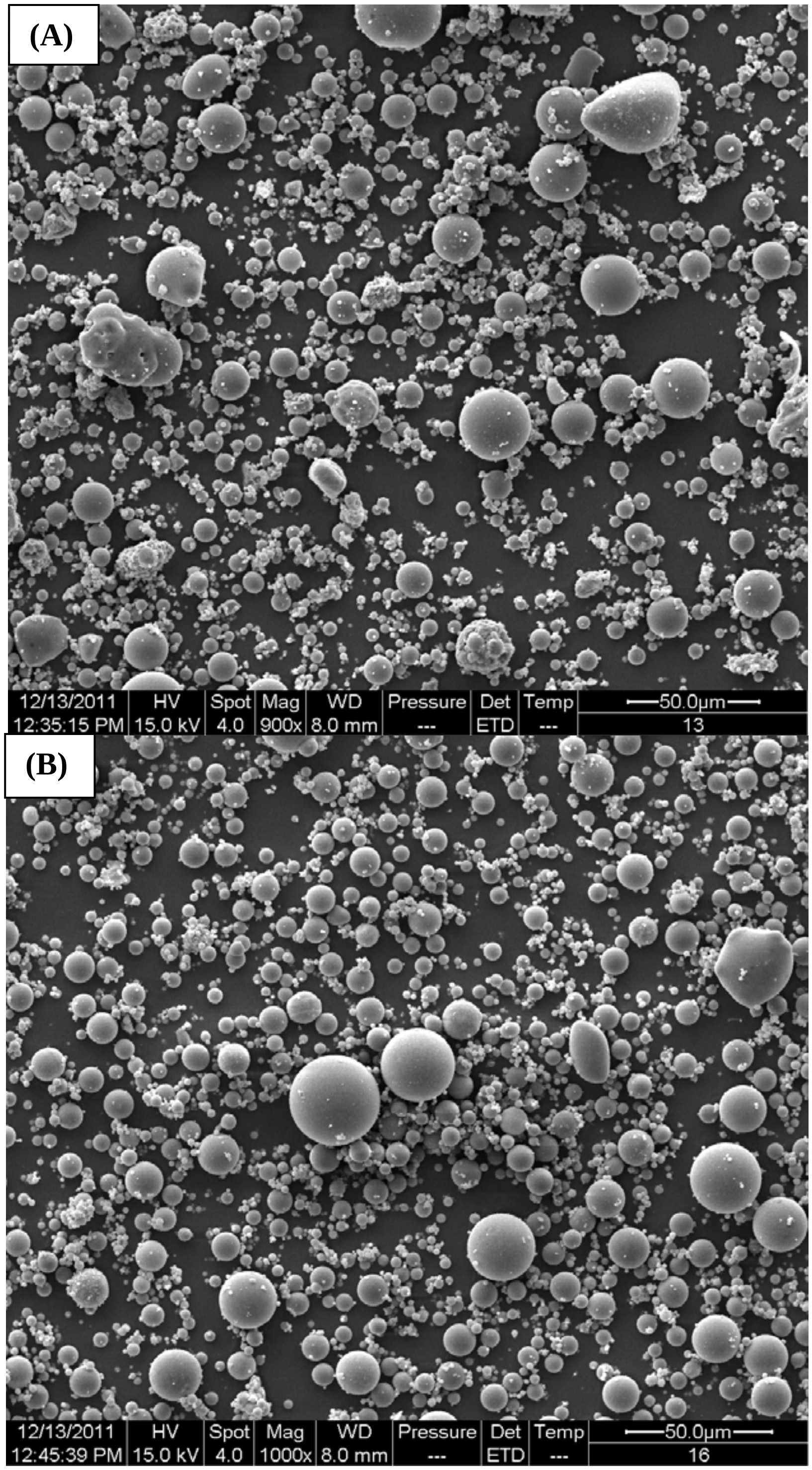


Figure 5.2 ESEM images of (a) SFA and (b) BDFA

The MLM can be written as follows:

$$Q_e = \sum_{j=1}^{n} \frac{Q_{\max j} K_j C_e}{1 + K_j C_e} \tag{5.1}$$

where Q_e is the adsorbed amount of phenanthrene, C_e is the equilibrium concentration of phenanthrene in the solution. $Q_{\max j}$ and K_j are the maximum adsorption capacity and Langmuir affinity constant for site type *j*, *j* = 1, 2, …, n. When $n = 1$, the LM can be obtained. Equation (5.1) is merely applicable to the single-step curves. When more steps are involved, a critical concentration (C_i) is introduced, with subscript *i* denoting the isotherm step. When the concentration of phenanthrene in the solution is above C_i. Equation (5.1) can be modified to the following:

$$Q_e = \sum_{j=1}^{n} \frac{Q_{\max j} K_j (C_e - C_i)}{1 + K_j (C_e - C_i)} \tag{5.2}$$

Equation (5.2) can be used to describe the adsorption behaviors at each step. This equation can only be used when $C_e > C_i$. If $C_e < C_i$, it means that step *i* has not been reached, such that Q_e for step *i* could not be considered and should be equal to zero. Thus Equation (5.2) can be rearranged as follows:

$$Q_e = \sum_{j=1}^{n} \frac{Q_{\max j} K_j [(C_e - C_i) + |C_e - C_i|]}{2 + K_j [(C_e - C_i) + |C_e - C_i|]} \tag{5.3}$$

If $C_e > C_i$, $Q_e = \sum_{j=1}^{n} \frac{Q_{\max j} K_j (C_e - C_i)}{1 + K_j (C_e - C_i)}$

If $C_e < C_i$, $Q_e = 0$

For all of the adsorption steps, the related mathematical expression of SMLM can be given as follows:

$$Q_e = \sum_{i=1}^{m}\sum_{j=1}^{n} \frac{Q_{\max ij} K_{ij} [(C_e - C_i) + |C_e - C_i|]}{2 + K_{ij} [(C_e - C_i) + |C_e - C_i|]} \tag{5.4}$$

The total maximum adsorption capacity is the sum of adsorption capacities from all effective adsorption sites at all steps (Equation 5.5):

$$Q_{\max} = \sum_{i=1}^{m}\sum_{j=1}^{n} Q_{\max ij} \tag{5.5}$$

A schematic illustration of an SMLM is shown in Figure 5.3. For example, if the data can be characterized as a three-step isotherm including a single LM-type isotherm for the first step, a three-site MLM-type isotherm for the second step, and a two-site MLM-type isotherm for the third step, then corresponding SMLM can be described as follows:

$$Q_e = \frac{Q_{\max 1} K_1 C_e}{1 + K_1 C_e} + \frac{Q_{\max 2} K_2 (C_e - C_2)}{1 + K_2 (C_e - C_2)} + \frac{Q_{\max 3} K_3 (C_e - C_2)}{1 + K_3 (C_e - C_2)} + \frac{Q_{\max 4} K_4 (C_e - C_2)}{1 + K_4 (C_e - C_2)}$$
$$+ \frac{Q_{\max 5} K_5 (C_e - C_3)}{1 + K_5 (C_e - C_3)} + \frac{Q_{\max 6} K_6 (C_e - C_3)}{1 + K_6 (C_e - C_3)} \tag{5.6}$$

where $Q_{\max 1}$ and K_1 are LM parameters for single-site adsorption in the first step; $Q_{\max 2}$, $Q_{\max 3}$, $Q_{\max 4}$, K_2, K_3 and K_4 are MLM parameters for three-site adsorption in the second step; $Q_{\max 5}$, $Q_{\max 6}$, K_5 and K_6 are MLM parameters for two-site adsorption in the third step; C_2 and C_3 are critical concentrations for steps 2 and 3, respectively.

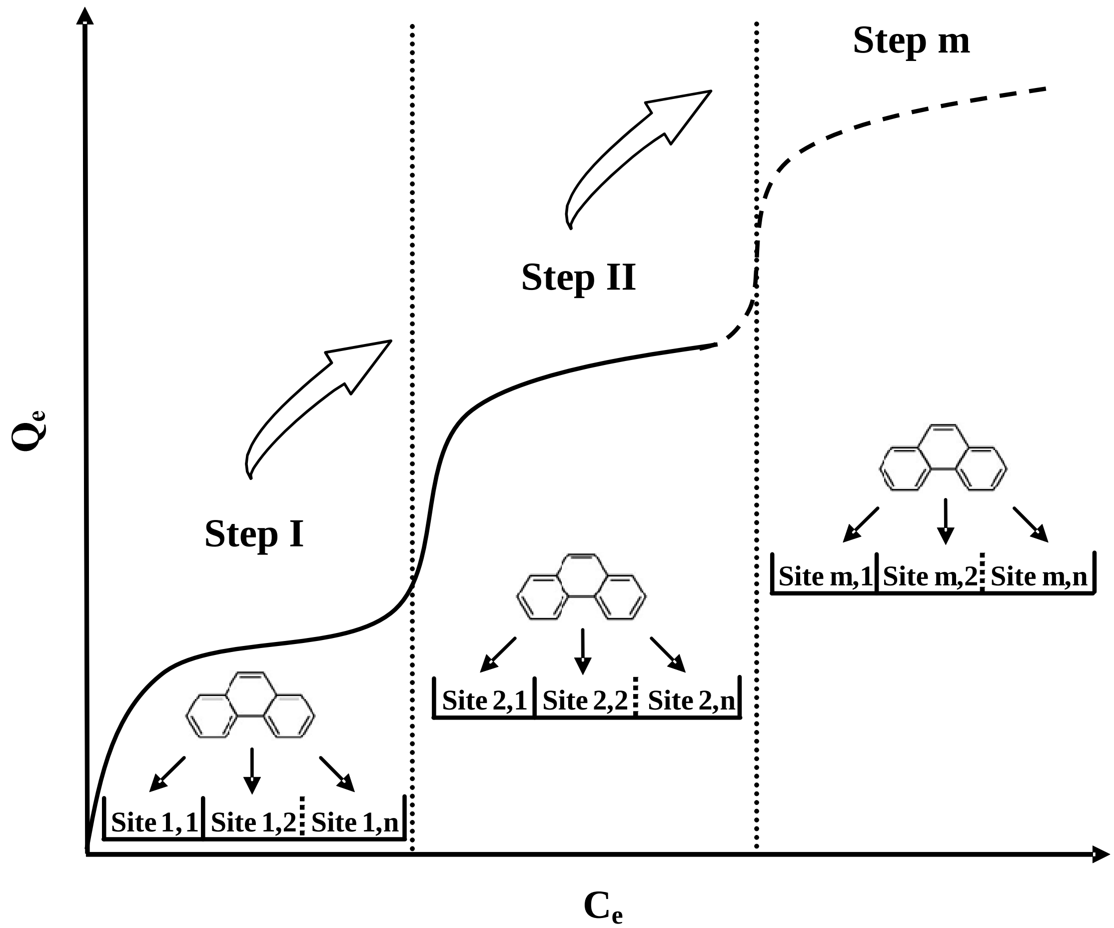


Figure 5.3 A schematic illustration of the SMLM for adsorption of phenanthrene

The developed SMLM was employed to describe phenanthrene adsorption isotherms for the two FA types. The estimated parameters based on experimental data with the aid of nonlinear regression analysis are given in Table 5.2. The results indicate that the surface of FA comprises several distinct site types with various affinities for phenanthrene molecules. The SMLM approach is suitable for both types of SFA and BDFA. Moreover, in the first step for two FA types, the single-site LM can best fit the equilibrium data at both 20 and 30 °C, indicating only one site type for each ash type would interact with the phenanthrene adsorption in this step. Such adsorption sites for FA have higher affinity for the phenanthrene. In the second step, the two-site LM gives a satisfactory fit to experimental data for both SFA and BDFA series. It indicates the existence of two site types on these ash samples. This result is supported by results from two previous studies, by Janoš et al. (2003) and Li et al. (2006), which indicated that the two-site Langmuir isotherm could be used for projecting experimental data from the process of adsorption on FA.

Table 5.2 Parameters of SMLM for phenanthrene adsorption on FA

	Step	Q_{max} (mg/kg)	K (L/mg)	R^2	C_i (mg/L)
SFA					
20 °C	Step 1	$Q_{max\,1}$ = 13.31	K_1 = 14.55	0.996	
	Step 2	$Q_{max\,2}$ = 5.35	K_2 = 28.73	0.992	C_2 = 0.225
		$Q_{max\,3}$ = 19.36	K_3 = 8.96		
30 °C	Step 1	$Q_{max\,1}$ = 12.47	K_1 = 12.07	0.993	
	Step 2	$Q_{max\,2}$ = 4.54	K_2 = 23.97	0.988	C_2 = 0.253
		$Q_{max\,3}$ = 18.02	K_3 = 7.01		
BDFA					
20 °C	Step 1	$Q_{max\,1}$ = 4.45	K_1 = 11.12	0.991	
	Step 2	$Q_{max\,2}$ = 3.81	K_2 = 22.69	0.993	C_2 = 0.358
		$Q_{max\,3}$ = 7.62	K_3 = 9.38		
30 °C	Step 1	$Q_{max\,1}$ = 3.75	K_1 = 10.44	0.987	
	Step 2	$Q_{max\,2}$ = 3.43	K_2 = 21.01	0.992	C_2 = 0.396
		$Q_{max\,3}$ = 6.98	K_3 = 7.69		

The K values for SFA and BDFA vary with each step. This variation can be attributed to the differences of FA properties. It should also be noted that each type of site can include a wide population of sorption sites. However, these sites can be of similar affinities (Quang et al. 1996). The $Q_{\max}$ for SFA is significantly higher ($p < 0.05$) than that for BDFA in each step and site. The total capacities of adsorbing phenanthrene were 38.02 and 15.88 mg/kg for SFA and BDFA at 20 °C, respectively. Thus the total adsorption capacity of the SFA was also higher than that of BDFA. Compared with the other adsorbents, the adsorbing capacity of FA is higher than those of organoclays (El-Nahhal and Safi 2004), but lower than those of natural soils and sediments (van den Heuvel et al. 2005). Moreover, the total adsorbing capacities of phenanthrene in the second step are higher than those in the first step. Thus, different site types at the second step could still contribute a significant amount to the adsorption of phenanthrene on FA, even if the site types in the first step might have higher affinity for phenanthrene.

5.3.3. Thermodynamic Characteristics of the Adsorption Process

As seen in Figure 5.1, temperature has pronounced effects on the adsorption process. A slight decrease in the adsorption capacity was observed as the temperature increased. This trend indicates that the adsorption of phenanthrene from aqueous solution onto FA might be an exothermic process. To better determine the predominant mechanism and driving forces involved in the adsorption process, the related thermodynamic characteristics were further investigated. The high-quality fit of SMLM for the sorption of phenanthrene to FA suggests an assumption that the heat generated from the adsorption is a constant, which is valid at least for the range of conditions used. The changes in Gibbs free energy can be calculated using the following equation:

$$\Delta G = -RT \ln K \tag{5.7}$$

where R is the gas constant, and T is the absolute temperature. The ΔG is also related to ΔH and ΔS, according to the following equation:

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{5.8}$$

$$\Delta G = \Delta H - T\Delta S \tag{5.9}$$

where ΔH is the enthalpy (kJ/mol) and ΔS is the entropy (kJ/(mol·K)). The calculated thermodynamic values of phenanthrene adsorption onto FA are summarized in Table 5.3. For the SFA, the values of ΔG varied between -8.17 and -4.91 during the adsorption process. Negative values of ΔG (from -7.67 to -5.14 kJ/mol) for the adsorption of phenanthrene onto BDFA indicate that sorption of phenanthrene onto FA is spontaneous at all temperatures. The negative value of ΔH in this study is indicative of an exothermic adsorption reaction. Although the thermodynamic parameters for the isotherm at 10 °C are not calculated, it can be observed in Figure 5.1 that more adsorption of phenanthrene occurred at 10 °C for both ash types, confirming an exothermic process in nature.

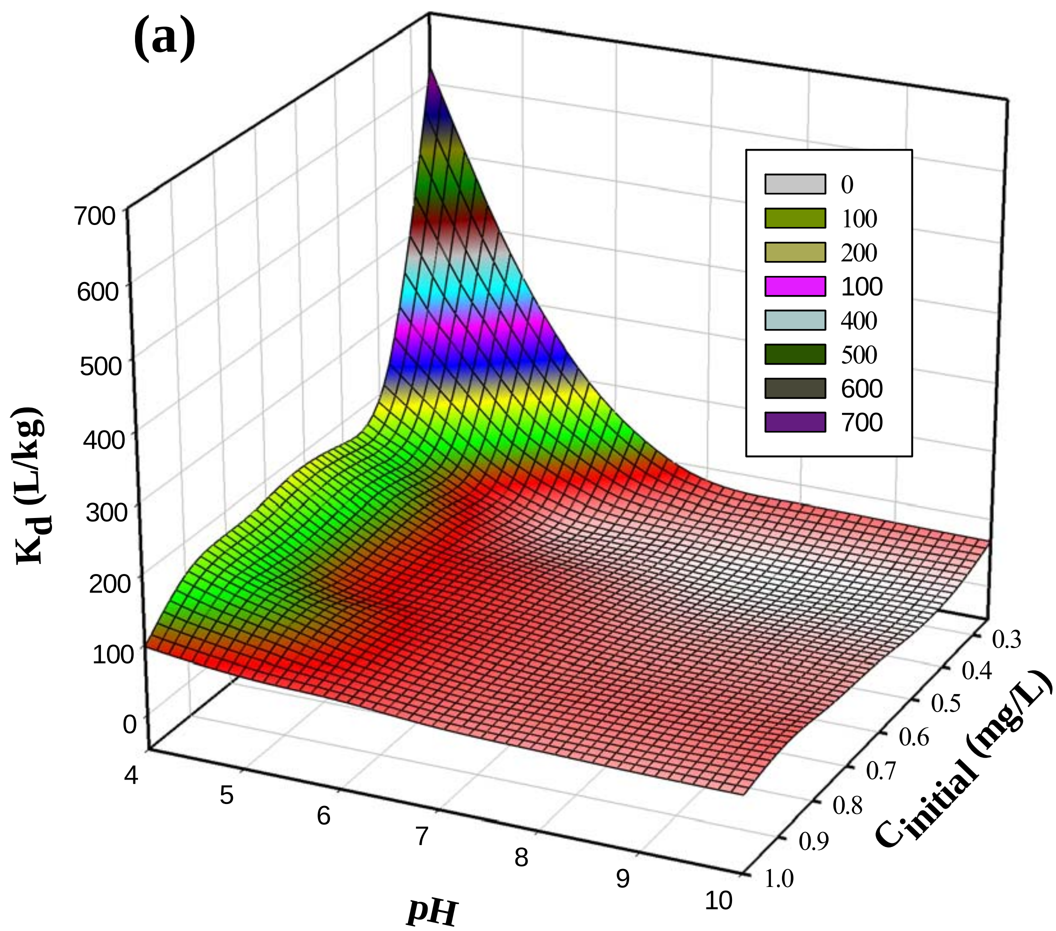
Table 5.3 Thermodynamic parameters calculated for the adsorption of phenanthrene onto FA

	T (°C)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/(mol ·K))
SFA				
Step 1	20	ΔG_1 = -6.52	ΔH_1 = -13.845	ΔS_1 = -0.025
Step 1	30	ΔG_1 = -6.27		
Step 2	20	ΔG_2 = -8.17	ΔH_2 = -13.151	ΔS_2 = -0.017
Step 2	30	ΔG_2 = -8.00		
Step 2	20	ΔG_3 = -5.34	ΔH_3 = -17.939	ΔS_3 = -0.043
Step 2	30	ΔG_3 = -4.91		
BDFA				
Step 1	20	ΔG_1 = -5.87	ΔH_1 = -4.698	ΔS_1 = 0.004
Step 1	30	ΔG_1 = -5.91		
Step 2	20	ΔG_2 = -7.61	ΔH_2 = -5.852	ΔS_2 = 0.006
Step 2	30	ΔG_2 = -7.67		
Step 2	20	ΔG_3 = -5.45	ΔH_3 = -14.533	ΔS_3 = -0.031
Step 2	30	ΔG_3 = -5.14		

Different values of ΔS indicate varying trends of randomness at the solid/liquid interface during the adsorption process. These results are similar to those for the adsorption of other PAHs on minerals such as α-Al_2O_3 and α-Fe_2O_3 (Mader et al. 1997). The relatively low adsorption heat in this study can be explained by weak physical adsorption, such as van der Waals-London (dispersion) forces, predominantly polarizability and dipole interactions (Banerjee et al. 1995). However, the obtained thermodynamic values might be approximate, due to the lack of well-defined system in the adsorption processes.

5.3.4. Effect of pH

Solution chemistry often plays an important role in the distribution of organic compounds in solid-liquid system. Solution chemistry in landfill waste varies significantly with composition, storage time and technology used. Some parameters (e.g., pH, alkalinity, dissolved organic carbon, and metal ions) have been characterized as important factors influencing pollutant behaviors. The effect of pH on the adsorption of phenanthrene onto FA was studied through batch experiments in the range of pH 4 to 10. Since the stepwise pattern was apparent in the adsorption process, a wide range of initial phenanthrene concentrations were necessary to reflect the potential influence of pH. Figure 5.4 depicts the ash-water adsorption coefficients (K_d) under different conditions.


(a)
0
100
200
100
400
500
600
700
Kd (L/kg)
pH
Cinitial (mg/L)
0
100
200
300
400
500
600
700
4
5
6
7
8
9
10
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0

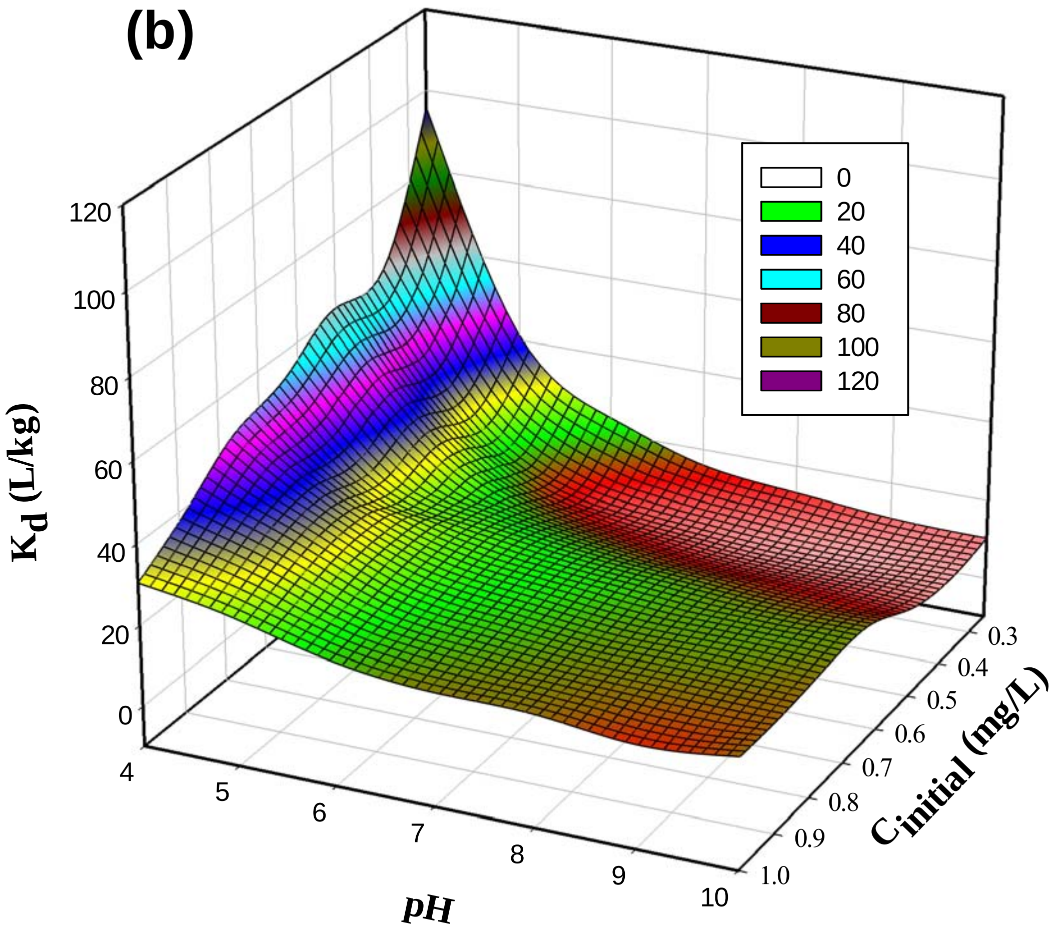


Figure 5.4 Adsorption of phenanthrene on (a) SFA and (b) BDFA at different pH levels

The data show that the adsorption behavior of phenanthrene on the two FA types varied with initial pH and initial phenanthrene concentration. At the same initial concentration of phenanthrene, the K_d values were relatively high at low pH range. At pH 4, K_d ranged from 97.49 to 624.22 L/kg and 30.52 to 95.69 L/kg for SFA and BDFA, respectively. The K_d values gradually decreased from pH 4 to 8, but did not decrease significantly when the pH was 8 to 10. Under the same pH, the use of SFA showed higher K_d values.

Adsorption of solute from aqueous phase is generally influenced by both characteristics of adsorbate and adsorbent, which in turn may be related to pH in the system. The ionic and nonionic organic pollutants in a solution can show different tendencies with regard to the variation of pH. Ionic organic compounds can exist as dissociated or undissociated forms under different pH conditions (Zhang and Dong 2008). Thus the adsorption of such compounds can be significantly influenced by pH. However, pH is not a significant influencing factor for nonionic organic pollutants (Mader et al. 1997). Although phenanthrene is less influenced by pH, interactions between phenanthrene and FA might vary with pH. In a previous study, it was reported that charge density on the surface of FA had significant influence on the sorption of dyes (Janoš et al. 2003). Changes in pH were also found to have different effects on the sorption of phenanthrene by aluminum oxide, iron oxide, kaolinite, quartz, goethite, and so forth (Stauffer and Macintyre 1986; Huang et al. 1996; Mader et al. 1997). The pH-dependent behavior of organic compounds is often explained through charge density and the pH_{PZC} (point of zero charge) of the adsorbent surface. In this study, the pH_{PZC} values of SFA and BDFA were 8.4 and 7.6, respectively. The surface of FA can form aquo complexes with water and develop a charged surface through amphoteric dissociation at varying pH values (Ahmaruzzaman 2009). When the pH is lower than pH_{PZC} of FA, acidic water donates more protons than hydroxide groups, resulting in a positively charged surface on the FA. In an acidic environment, there would exist induced dipole interactions between the charged FA surface and the electron-rich π systems of phenanthrene. Thus, the binding energy of phenanthrene exists and may be increased under low pH.

At the same time, changes in pH may also affect the surface configuration of the adsorbents. The specific surface area of the FA sample was measured to ascertain whether it could vary with pH. The corresponding values are described in Figure 5.5. The results showed that the pH value was negatively correlated with specific surface area of FA (r = -0.976, SFA; r = -0.987, BDFA). The FA under low pH level has a higher specific surface area. This phenomenon might be attributed to the surface modification of the FA particles. Acid pretreatment has been applied to improve the adsorptive capacity of FA for phosphate, dyes and other pollutants (Wang et al. 2005b; Xu et al. 2010). Under acidic conditions, the increase of pore volume and surface area can occur due to partial or complete dissolution of metal constituents in FA. It will facilitate the adsorption of phenanthrene. In addition, there was no obvious variation of surface area under alkaline conditions. Although hydrothermal alkaline treatment of FA can lead to zeolite-like products with high surface area, a high temperature is required for the reaction (Scott et al. 2002). It is reasonable to observe that the influence of alkaline solution on FA properties could be less significant under normal temperature.

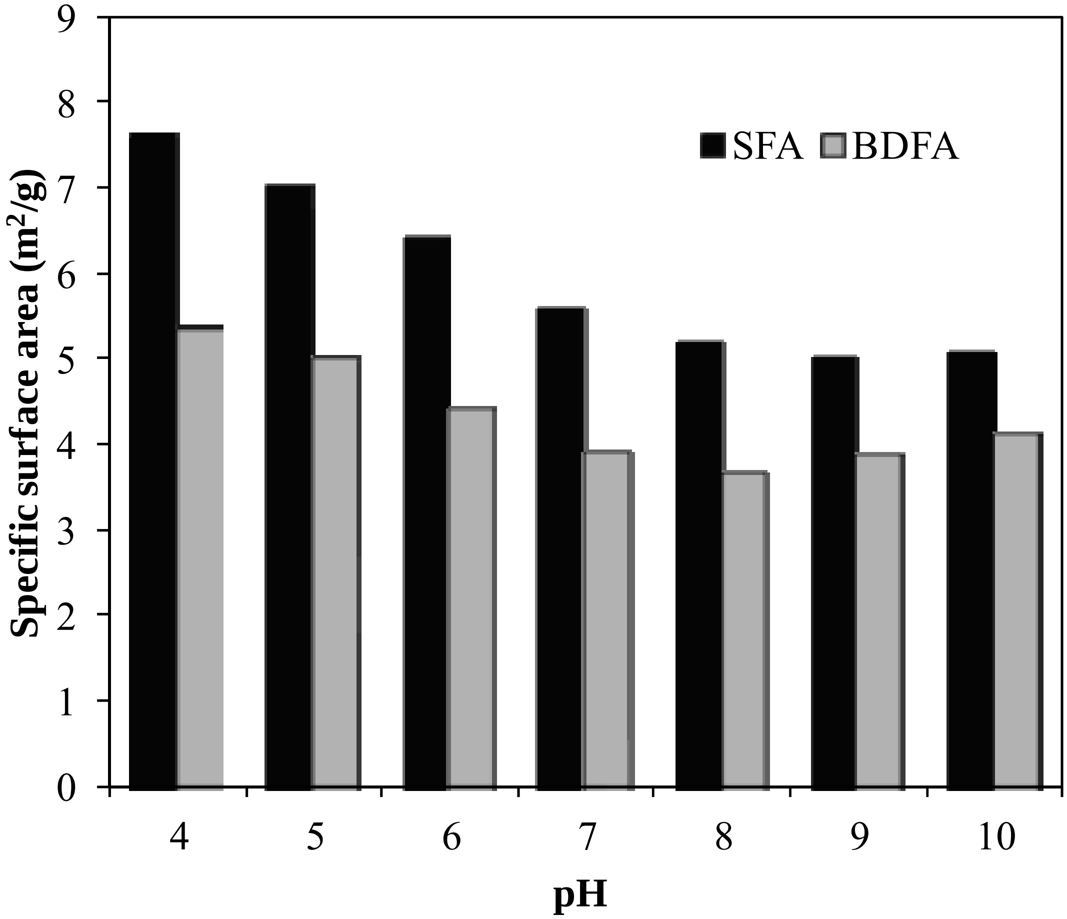
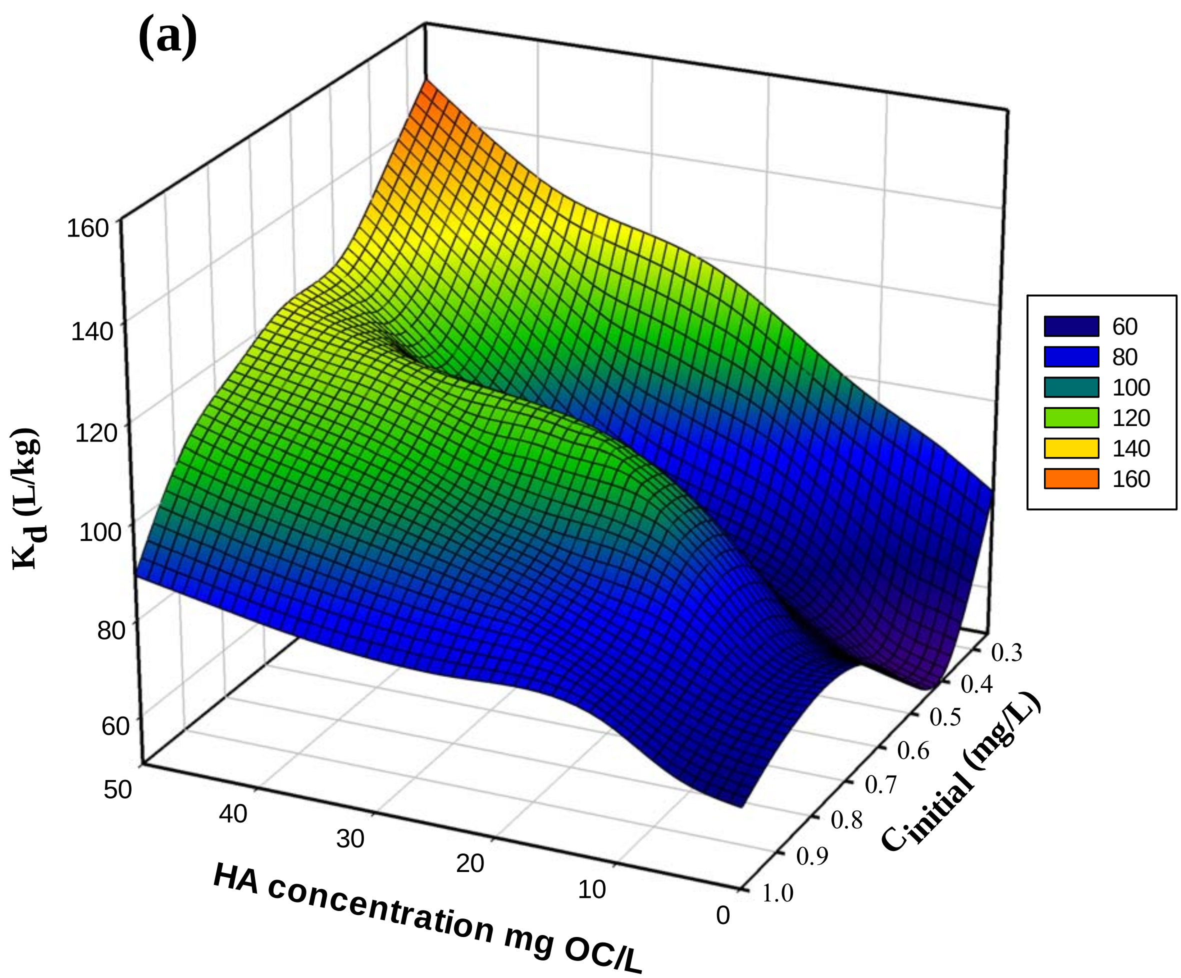


Figure 5.5 Specific surface areas of (a) SFA and (b) BDFA at different pH levels

In the FA-water system, the overall influence of pH on the adsorption of phenanthrene can be considered as an integration of multiple influences. Different phenanthrene adsorption performances under varied pH for the two types of FA may be attributed to the variability in FA constituents. This study suggests that pH can have a measurable influence on the interactions between phenanthrene and FA. The pH may differ temporally and spatially in FA disposal sites (i.e., landfill), due to differences in natural conditions and site-operation patterns. It is important to include such local characteristics in the related in situ assessment.

5.3.5. Effect of Humic Acid

Organic matter in the environment is closely related to the distribution and transportation of HOCs (Salloum et al. 2002; An et al. 2011). HA is recognized as the dominant organic component in natural soil as well as landfill sites (Artiola-Fortuny and Fuller 1982; Kang et al. 2002). HA can show the potential influence on phenanthrene sorption in the FA-water system and thus such effects were investigated in this study. Different K_d values when pH = 7 are illustrated in Figure 5.6. The results showed that the phenanthrene adsorption onto FA in the presence of HA was significantly different from that in the absence of HA. The binding affinity of phenanthrene to the FA increased after the addition of HA. When the concentration of HA was 5 mg organic carbon (OC)/L, the K_d values for the series with SFA varied from 57.14 to 88.89 L/kg. By increasing HA concentration to 50 mg OC/L, the K_d values varied from 89.28 to 148.41 L/kg. Thus, high K_d values were observed under high HA concentrations. A similar trend was also observed for the BDFA.


(a)
160
140
120
100
80
60
50
40
30
20
10
0
Kd (L/kg)
HA concentration mg OC/L
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Cinitial (mg/L)
60
80
100
120
140
160

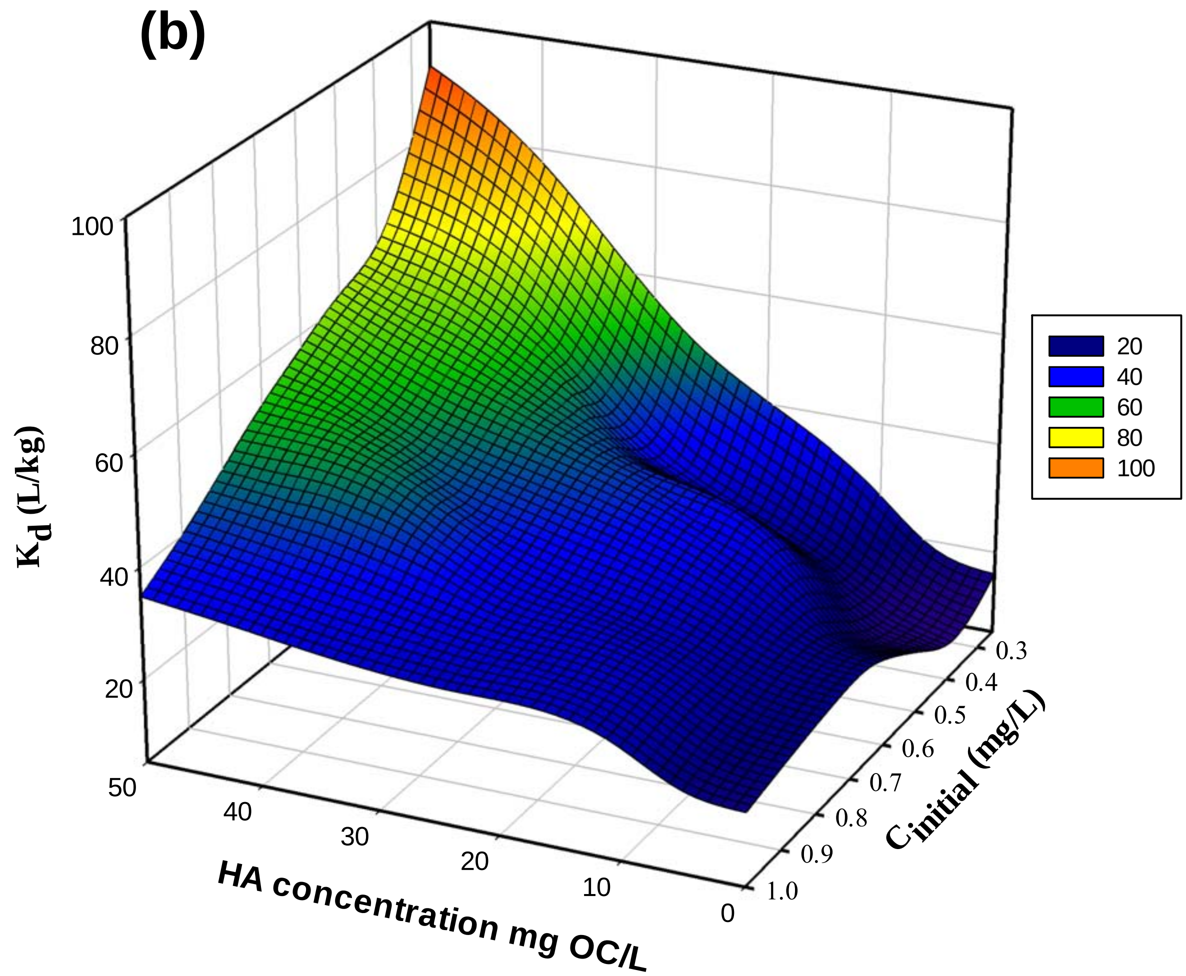


Figure 5.6 Adsorption of phenanthrene on (a) SFA and (b) BDFA in the presence of HA

The presence of dissolved HA can improve the apparent solubility of phenanthrene in aqueous phase (Figure 5.7), which is similar to some previous studies (Chiou et al. 1986; Fukushima et al. 1997). Hydrophobic interaction is mainly responsible for the binding between HA and polar organic compounds, such as PAHs. The π-π interactions between phenanthrene and humic substance acceptor groups in aqueous solvents can also contribute to this process (Wijnja et al. 2004; Zhu et al. 2004). If HA is mainly distributed in aqueous phase with similar function to known surfactants (Wei et al. 2011a; Yu et al. 2011b), then the retention of phenanthrene on FA will be suppressed. However, results of this study suggest that the presence of HA contributes to the uptake of phenanthrene rather than its dissolution or transportation. This may be attributed to the retention of HA along with the combined phenanthrene on FA surface. It was reported that HA can be adsorbed onto clay minerals (Schulthess and Huang 1991; Chang and Juang 2004). The mechanisms such as hydrophobicity, van der Waals forces, and hydrogen bonding might contribute to the adsorption of HA on minerals (Fairhurst et al. 1995). The adsorption of HA on SFA and BDFA was also investigated (the data are shown in Figure 5.8). The results confirm that HA can be adsorbed onto the FA surface. SFA exhibited much greater adsorption of HA than BDFA. Therefore, HA can play an important role in the distribution and transportation of phenanthrene in the FA-water system. This can be attributed to the direct bounding of phenanthrene to HA along with the adsorption of HA onto FA surface.

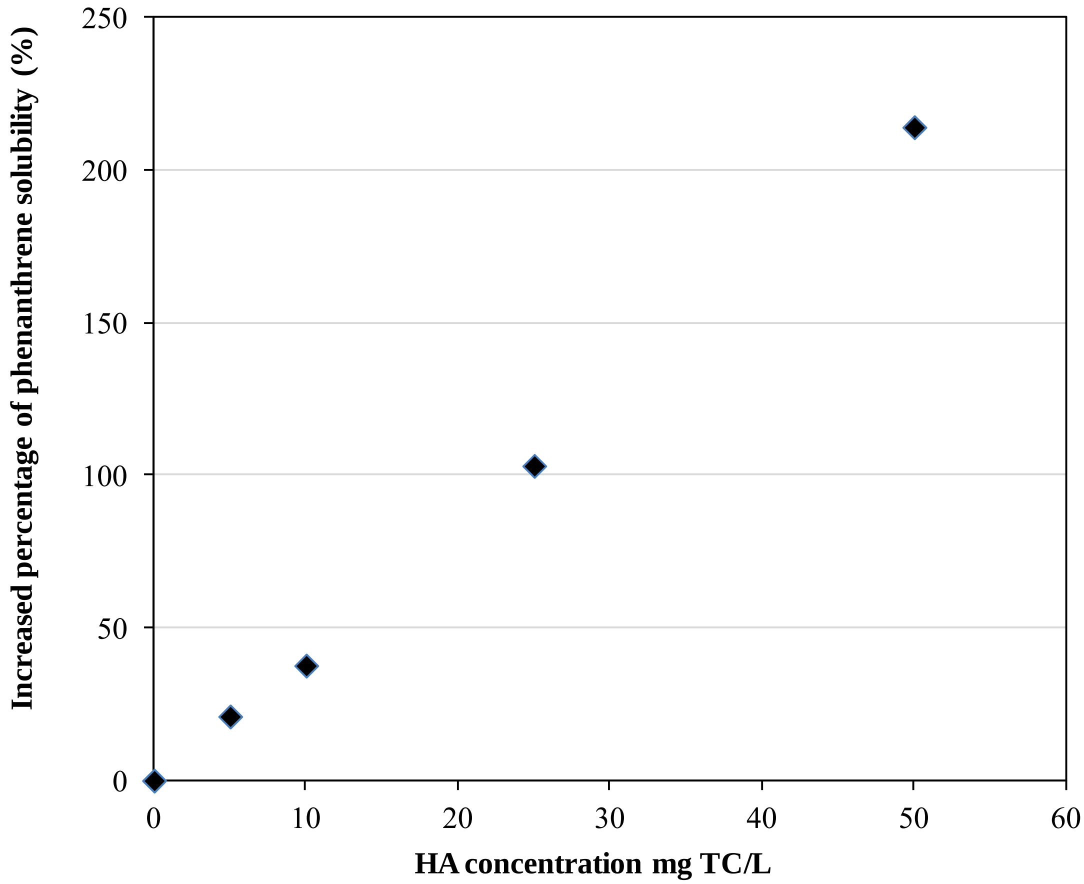


Figure 5.7 Effect of HA substance on the solubility of phenanthrene

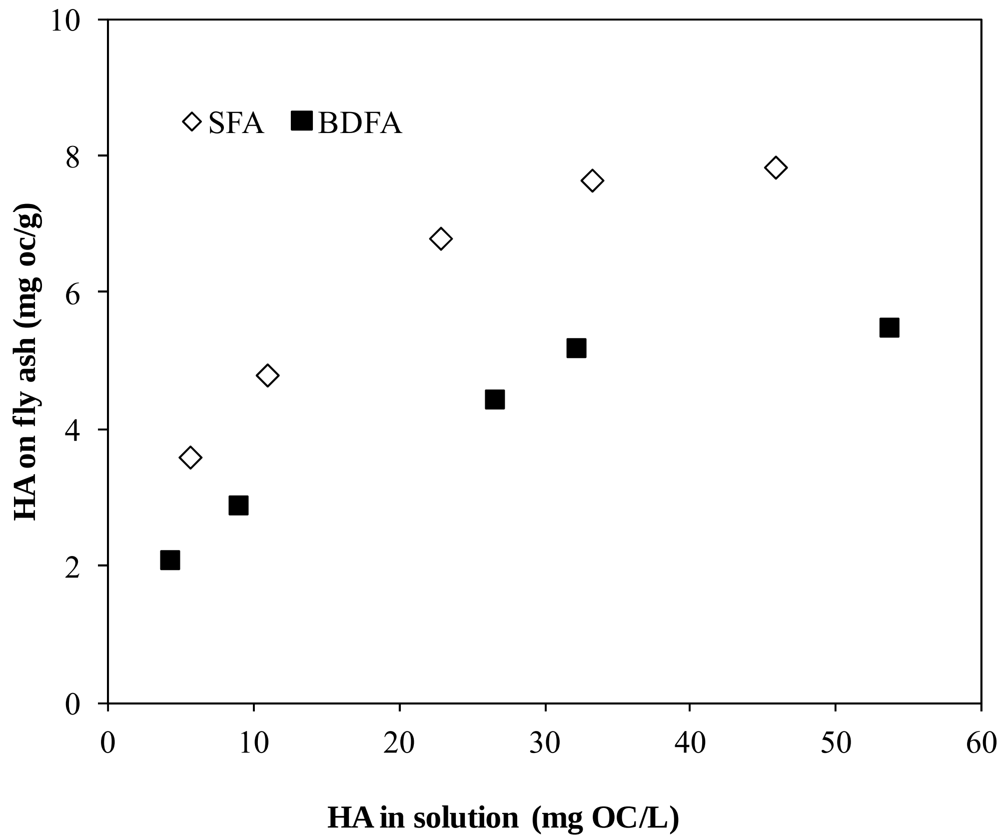
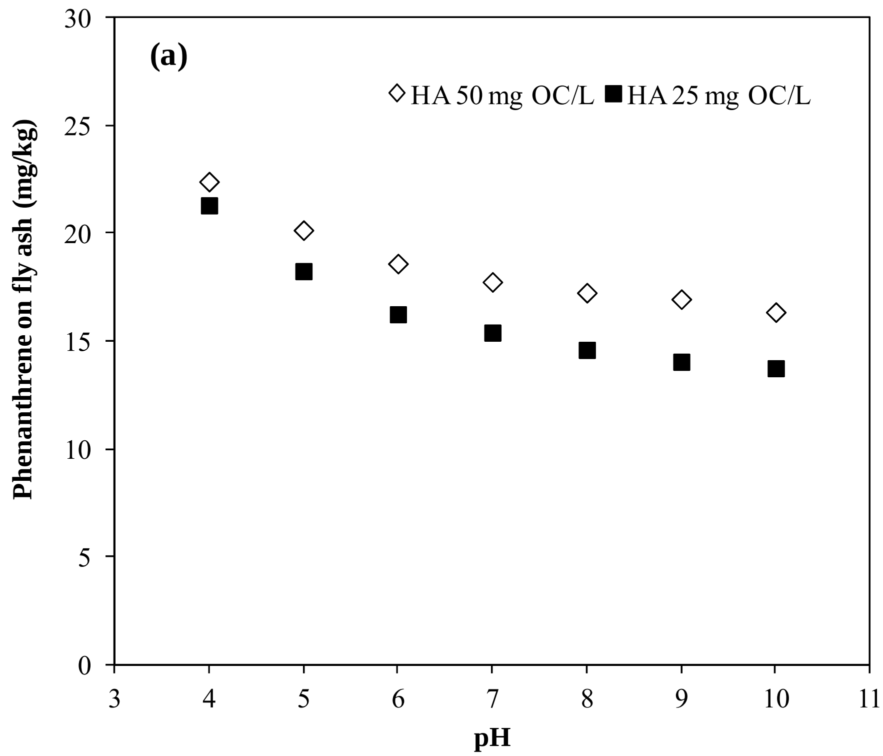


Figure 5.8 Adsorption of HA on (a) SFA and (b) BDFA

Meanwhile, the effects of HA under different pH conditions were investigated (Figure 5.9). Under high pH levels, the effect of HA was less significant than that under low pH. The pH variations also appeared to be responsible for the changes of phenanthrene adsorption on FA in the presence of HA. Many previous studies observed that HA adsorption was highly dependent on the pH of the solution (Murphy et al. 1990; Wan and Liu 2006; Salman et al. 2007). The HA adsorption amount on FA would decrease as pH increased. This influence can be explained by the changes in physicochemical properties of the FA and HA molecules. In the pH range of this study, HA molecules have a negative charge owing to the deprotonation of carboxyl groups or phenolic groups along the HA chain (Fairhurst et al. 1995; Wang et al. 2011a). The pH_{PZC} values of SFA and BDFA were approximately 8. This indicated that the surface of FA may carry positive charges under low pH, resulting in enhanced HA adsorption. Under high pH, the surface of FA would be negatively charged and the bonding between HA and FA surface can become weaker due to the corresponding electrostatic repulsive force. Furthermore, dissociated HA molecules are less hydrophobic and adsorbable under high pH than undissociated ones under low pH. Therefore, high pH can inhibit the adsorption of HA with associated phenanthrene on FA. In addition, the enhanced ionization of HA under high pH would lead to increased solubility of HA. This implied that strong affinity existed between HA and aqueous molecules, and less amount of HA adsorption on mineral surface would thus take place. These observations suggested that HA is a critical factor affecting the process of phenanthrene adsorption onto FA. However, the effects of HA on PAH are also closely related with the species and characteristics of HA compounds.



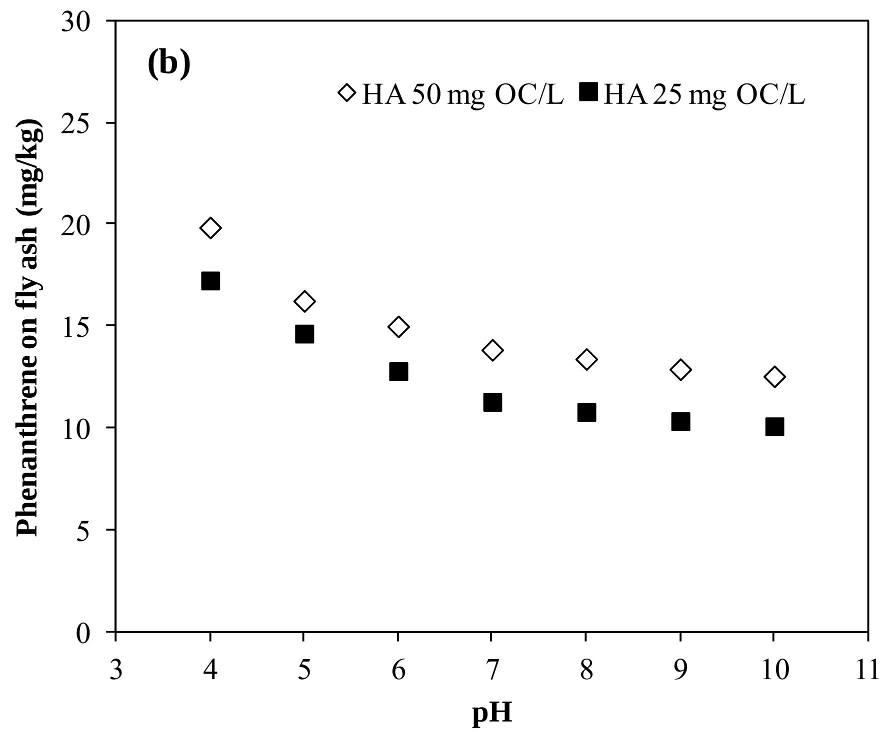
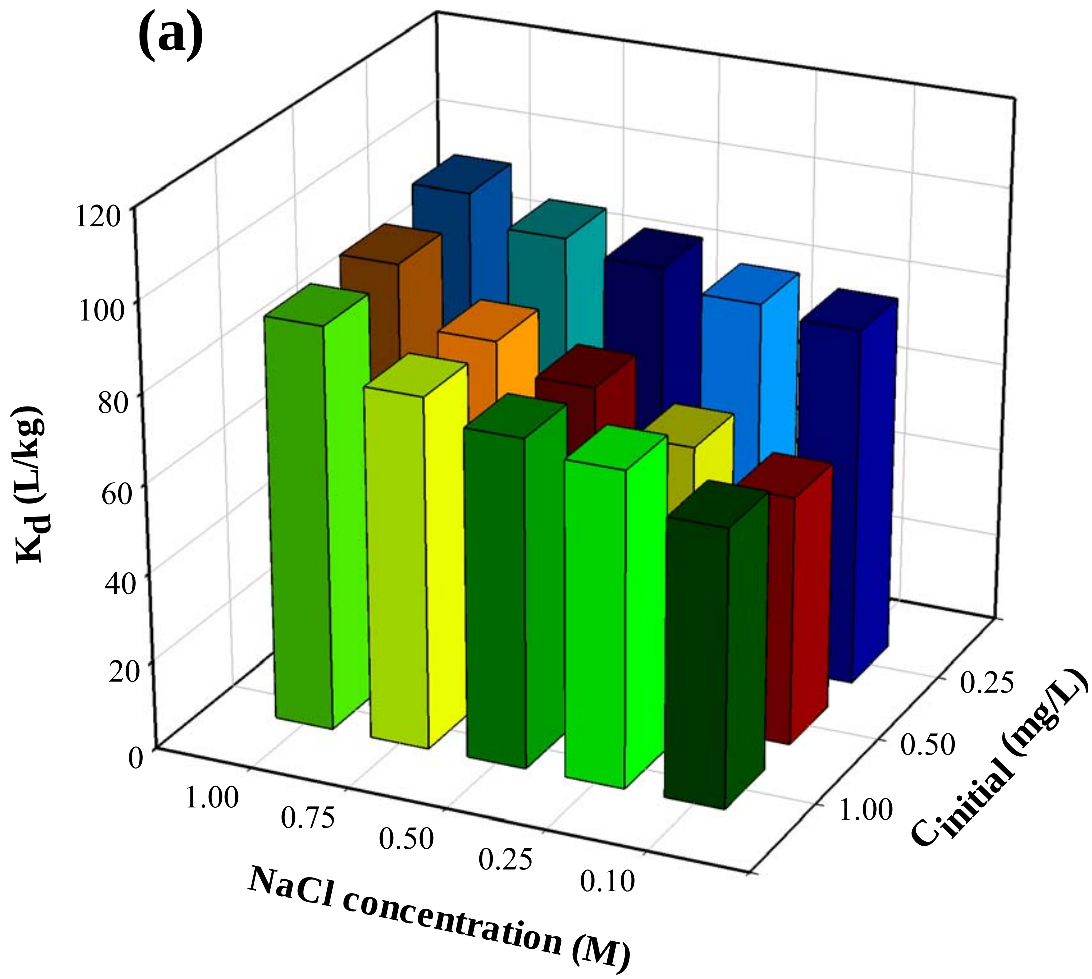


Figure 5.9 Adsorption of phenanthrene on (a) SFA and (b) BDFA in the presence of HA at different pH levels

5.3.6. Effect of Ionic Strength

Metal ions often exist in FA leachate (Reardon et al. 1995). The results show that phenanthrene adsorption onto FA is influenced by ionic-strength conditions (Figure 5.10). Compared with the tests at low ionic strength, the adsorption amounts of phenanthrene were slightly elevated at higher ionic strength. At ionic strength of 0.5 to 1 mol/L, the K_d values would be 72.80 to 97.06 L/kg for SFA, and 20.45 to 53.96 L/kg for BDFA. Within the same range of ionic strength, SFA showed significantly greater adsorption capacities ($p < 0.05$) than BDFA. These results indicate that the variations of ionic strength can influence the overall efficiency of phenanthrene adsorption on FA surface. Mader et al. (1997) observed that ionic strength had little effect on the sorption of PAHs to either α-Al_2O_3 or α-Fe_2O_3, probably due to the low ionic strength. In contrast, when phenanthrene was adsorbed to FA at higher ionic strength, the adsorption improved for both FA types. These findings indicate that high ionic strength is correlated with low mobility of phenanthrene in FA-water system. It was reported that the solubility of HOCs in the solution with high ionic strength might decrease due to the salt-out effect (Brunk et al. 1996). The ionized metal ions can bind tightly with water molecules and increase the electrostriction of the aqueous solutions with low dissolving capacity (El-Nahhal and Safi 2004; Gustafsson and Berggren Kleja 2005). Thus, as the ionic strength increases, the bond between phenanthrene and water molecules might be influenced, leading to reduced aqueous solubility of phenanthrene. It might also increase the retention of phenanthrene in the FA surface. This is of special interest for applications to in situ disposal of FA with high salinity level.



(a)
120
100
80
60
40
20
0
K_d (L/kg)
1.00
0.75
0.50
0.25
0.10
NaCl concentration (M)
0.25
0.50
1.00
Cinitial (mg/L)

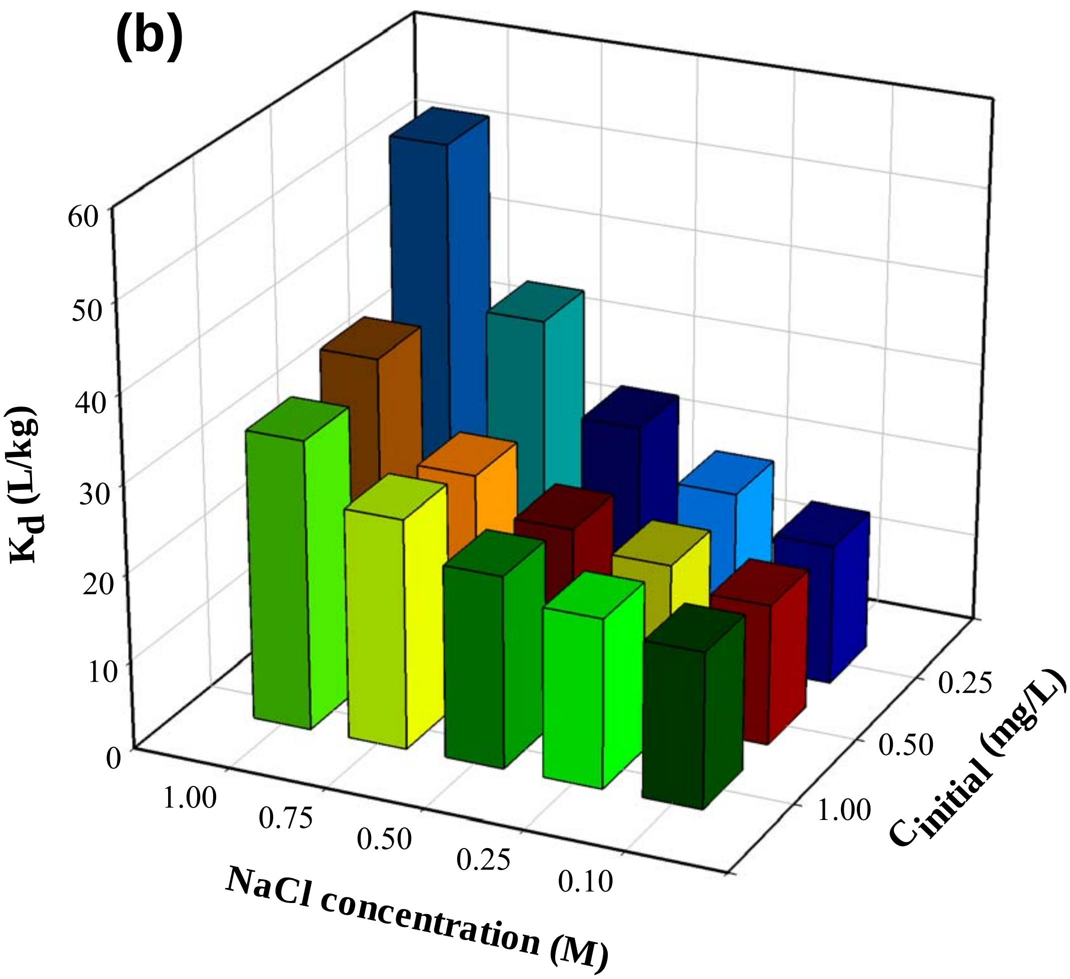


Figure 5.10 Adsorption of phenanthrene on (a) SFA and (b) BDFA at different ionic strength levels

5.4. SUMMARY

The study related to trace organic contamination during FA disposal is an emerging area in environmental research. This study focused on PAH behavior at the FA-water interface, which can help understand migration patterns of complex organic contaminants at FA disposal sites. The adsorption of phenanthrene onto FA showed significant stepwise pattern. As an improved method for adsorption behavior analysis, the developed SMLM can help well simulate the adsorption of PAHs on FA. SMLM can also be applied to other solid-liquid systems as an alternative to describe adsorption on adsorbents with more generally heterogeneous surfaces. In addition, solution chemistry played an important role in the distribution of phenanthrene in FA-water system. Several factors (in particular pH, organic matter and ionic strength) were correlated with the adsorption performances. In the natural environment, the overall influence of various factors on the adsorption of phenanthrene could be an integration of multiple processes. The results of this study have important implications for environmental risk assessment and pollution control at FA disposal sites. Further studies are desired to define the characteristics of FA and other constituents as well as their effects to obtain more theoretical foundation for analyzing PAH mobility in FA-water system.

CHAPTER 6

PERFORMANCE OF IN-VESSEL COMPOSTING OF FOOD WASTE IN THE PRESENCE OF COAL FLY ASH AND URIC ACID

6.1. BACKGROUND

With the rapid development of economy and population, a large amount of solid waste has been generated from domestic, industrial and agricultural activities over the last few decades (Gajalakshmi and Abbasi 2008). Food waste, which can be from various sources such as restaurants, markets, residents and many other food-processing facilities, is one of the most general forms of organic solid waste (Kwon and Lee 2004; An et al. 2012a). In some areas of China and Korea, it can account for approximately more than one quarter of the total solid waste generation (Yuan et al. 2006; Lee et al. 2007). Food waste has been demonstrated to be a threat to human health due to the potentially releasing of nuisance odors and leachate. Inappropriate disposal practice has often resulted in various economic, environmental and biological losses across the world.

Composting has been developed as one of the most promising solid waste disposal methods for safe treatment strategies (Hachicha et al. 2009; Sun et al. 2009; Wang et al. 2011b). During the composting process, the microorganisms decompose the substrate through breaking it down from complex to simpler compounds under aerobic conditions (Bernal et al. 2009; Sayara et al. 2010). Composting can significantly reduce waste volume within various composting systems, such as non-reactor, enclosed reactor and in-vessel systems (Peigné and Girardin 2004). The produced product with humus-like property can be used for stimulating microbial activities and plant growth in various field applications. From the viewpoint of green-recycling in the ecosystem, composting is an environmentally and economically sound manner.

The properties of different solid wastes can be quite variable and this variability could play an important role in the effectiveness of composting. To facilitate the treatment process, pre-separation of organic wastes at source is becoming a more common practice in several European countries (Eklind and Kirchmann 2000). However, it is difficult to achieve such routine classification for many areas due to high cost of operating and maintaining. Massive quantities of food waste often coexist with other agroindustrial and industrial waste. The challenge is especially poignant in many developing countries. Some researches on food waste composting have been reported before, particularly on aspects relating to degradation in simple compost cultures (Smårs et al. 2002; Bernal et al. 2009), investigations on food waste composting in complex multi-source mixtures are relatively limited in scope. To better understand the composting mechanism within real-world applications, there is a need to investigate the interactions among diverse types of materials for the food waste treatment.

FA is the major waste produced by the burning of coal in large quantities by electricity-generating power plants (Trivedi and Sud 2002; An and Huang 2012). The global amount of FA from coal combustion has been estimated to be 500 million tonnes per year (Tanaka et al. 2002). Some FA can be used in cement products, road bases and structural fill; however, more than 70% of the FA is dumped into landfills as waste (Jo et al. 2008). Recently, there have been several reports about the influence of FA on composting. The high porosity and alkali metal oxides in FA might improve the quality of composting substrate. Belyaeva and Haynes (2009) have proved the feasibility of co-composting municipal green waste with additional FA to produce manufactured soil material. They also find the amendment of FA could increase the water holding capacity of the substrate. Koivula et al. (2004) studied the behavior of the organic carbon during the composting of source-separated catering waste mixed with FA. The results showed that the FA could increase the rate of mineralization of compost and the formation of HAs. The quality of compost prepared from coal FA and crop residue have also been assessed by Gaind and Gaur (2003) and the their study showed the compatibility of FA with the microbes. But few efforts have been made to examine the composting of food waste and FA under complicated conditions. As another common solid waste, manure often contains UA as an important bicyclic heterocyclic purine derivative. UA can account for 70% of the total N components in poultry faeces and this proportion is influenced by animal diet (Nahm 2003). Available N supplied from UA could potentially facilitate the microbial activities during the composting. In several previous studies, co-composting of manure and other substrates has also been demonstrated under aerobic conditions. The co-composting of solid swine manure and pine sawdust has been investigated in forced-aeration composting systems (Zhang and He 2006). The biological and thermal kinetics of the process has also been analyzed during the composting of dairy manure and tomato plant residues (Alkoaik and Ghaly 2006). However, very few studies have been conducted to investigate the composting of manure and food waste, despite the prevalence of composting technique. The potential influences and roles of many manure constituents are still not well understood. The coexistence of food waste with agricultural and industrial wastes may be ubiquitous in many areas. Although the study of multi-component waste composting is of great economic and environmental importance, the complexity of their composition makes related study difficult due to the great variety of raw substances. The study in food waste composting in the presence of other components will be helpful for better understanding of this treatment process.

For the experiment of this study, we will evaluate the performance of food waste composting in the presence of FA and UA. Tests will be conducted in the in-vessel composting system. The patterns of food waste composting are compared among various combinations to investigate the influences of FA and UA. The variations of temperature, pH, organic mass reduction rate, O_2 consumption, microbial population and C/N ratio are studied. The results of this study will have important implications for developing appropriate treatment of food waste by composting.

6.2. MATERIAL AND METHODS

6.2.1. In-vessel Composting System

A schematic diagram of the in-vessel composting system in present study is illustrated in Figure 6.1. The cylindrical composting reactor was of acrylic column, with a working volume of 30 L and dimensions of 300 mm × 450 mm × 6 mm (diameter×depth×thickness). To prevent conductive and reflecting heat loss, heavy-duty aluminum foil, foam and fibreglass were employed as three layers of heat-insulating materials, respectively. Two thermometers (Traceable 15-077-9E; Control Company, TX, USA) were used to monitor temperature variation. The upper thermometer located in the middle of the reactor, while the lower one was placed 1 inch above the segmentation plate. The system was aerated by vacuum pump (MOA-P101-AA; GAST Manufacturing Inc., MI, USA). Air was evenly distributed to the waste mixture through a perforated plate at a flow rate of 0.1 vvm (volume of aeration / working volume of reactor / minute). The exhaust gas from the reactor passed through a condensate trap and was discharged to the laboratory ventilation system after analysis.

6.2.2. Composted Wastes

To investigate the performance of food waste composting in the presence of FA and UA, two batch experiments were carried out using in-vessel composting reactors. The composite raw materials could offer an advantage to be duplicated from batch to batch allowing ready comparisons among various tests (Schwab et al. 1994). The composite food waste mixture including potatoes, carrots, steamed rice, meat and leaves was used as the composting raw material. The detailed composition of raw materials for the compositing batch 1 and 2 processes is shown in Table 6.1 and Table 6.2, respectively. The values are the wet weight data of the components. All the raw materials were obtained from a local grocery store. They were minced into pieces with diameter less than 5 mm using food processor and mixed well before the composting reaction began. For Run D and Run E, 4 kg of FA were added to the compost mixture, respectively. The FA was obtained from the Boundary Dam Power Station, which is a coal fired station owned by SaskPower, located near Estevan, Saskatchewan, Canada. For Run E, 84 g of UA ($C_5H_4N_4O_3$, Sigma-Aldrich, MO, USA) were added to the compost mixture. Run C was conducted as a control treatment without FA and UA addition. For each run, a parallel run was conducted simultaneously.

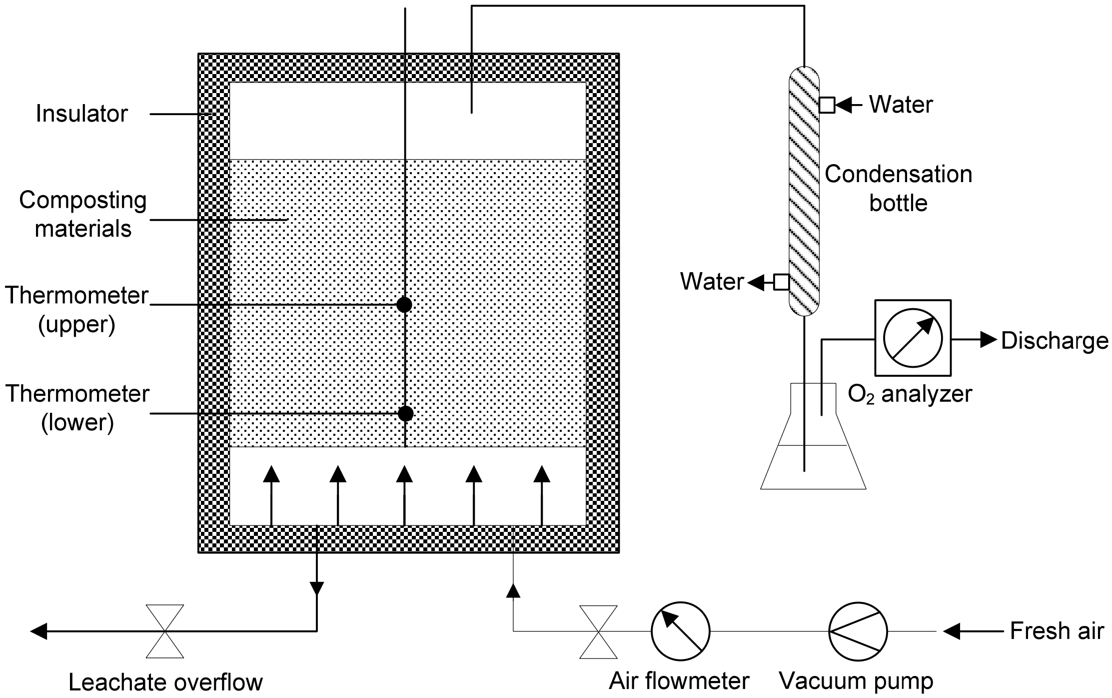


Figure 6.1 Schematic diagram of the composting system

Table 6.1 Composition of raw composting materials in batch 1

Component	Run A	Run B
Potato (kg)	1.27	1.27
Carrot (kg)	1.96	1.96
Steamed rice (kg)	2.01	2.01
Ground pork (kg)	0.35	0.35
Soy bean (kg)	1.96	1.96
Leaves (kg)	0.46	0.46
Seed soil (kg)	2	2
Uric acid (g)	0	168

Table 6.2 Composition of raw composting materials in batch 2

Component	Run C	Run D	Run E
Potato (kg)	1.7	1.7	1.7
Carrot (kg)	2.7	2.7	2.7
Steamed rice (kg)	2.8	2.8	2.8
Meat (kg)	0.5	0.5	0.5
Leaves (kg)	0.6	0.6	0.6
Starting culture (kg)	0.5	0.5	0.5
FA (kg)	0	4	4
Uric acid (g)	0	0	84

6.2.3. Composting Procedure

The composting reactors were run in a laboratory with the ambient temperature at 20 ± 1 °C. The reactors were opened once daily for weighing, turning, observation, and sampling. Before each sampling, the materials in the reactors were stirred well with a shovel to homogenize the mixture. Samples were subsequently taken from different levels of the central reactors. After mixing, subsamples of approximately 50 g were used for the further analysis. For each analysis, three replicates were conducted.

6.2.4. Analytical Methods

Dry weight was determined after drying at 105 °C overnight. Organic matter content was quantified by heating samples at 550 °C for 4 hours. The pH level was measured by a benchtop pH/temperature meter (410A Plus; Thermo Orion, MA, USA) in solution of 5 g compost and 10 mL deionized water. Oxygen in the exhaust gas was tested using an M40 multi-gas monitor (Industrial Scientific Corp., PA, USA). The total carbon (C) and nitrogen (N) contents in the compost were determined by the LECO TruSpec CN determinator (LECO Corporation, MI, USA). A solid sample was acidified by pouring 3 mL 0.1 mol/L H_2SO_4 over the entire sample before drying to avoid ammonium losses, and the dry sample was then ground to a homogeneous powder for analysis. Ammonium nitrogen in solid samples was analyzed using the FIAstar 5000 Analyzer (Foss Analytic AB, Hoeganaes, Sweden). Microbial enumeration was determined using the spread plate counting method (Cheung et al. 2010). The incubation media was 10% tryptic soy broth agar. For each test, 10 g (fresh weight) of compost sample was added into a 250 mL Erlenmeyer flask with 90 mL of 0.85% sterile sodium chloride solution. The flask was capped and placed on a reciprocal shaker at 20 ± 1°C and 200 rpm for 30 minutes. Then certain amount of supernatant was transferred, and diluted it with 0.85% sterilized sodium chloride solution to prepare tenfold serial dilution. The dilution was set to a range from 10^{-2} to 10^{-10}. Four series of dilution where the microorganism can be adequately characterized were selected. 0.1 mL of each series was drawn and spread to a Petri plate containing the required medium. Plates were incubated at 25.0 °C for 7 days to enumerate total mesophilic microorganisms and at 55.0 °C for 2 days to enumerate total thermophilic microorganisms. The unit of microbial populations was colony forming unit (CFU)/g sample in logarithm scale.

6.2.5. Statistical Analyses

Statistical analyses were performed with the use of the Minitab (Minitab Inc., PA, USA) statistical software package. The mean and standard deviation of the tree replicates were reported for all measured parameters. ANOVA and Tukey test were applied to compare differences among means of different treatments. The differences between any pair of treatment means were tested using the least significant difference test with α-value (significance level) at 5%.

6.3. RESULTS AND DISCUSSION

6.3.1. Performance of In-vessel Composting of Food Waste in the presence of Uric Acid

6.3.1.1. Temperature Profile

Temperature range is an important parameter which can reflect the various phases of the composting process (Gao et al. 2010). Figure 6.2 shows the temperature variation of composite food waste inside the reactor during the composting process. The temperature of both of the two reactors rapidly increased to 50-70 °C, indicating the heat could easily be produced during the composting of food waste. Less time was required to reach the maximum temperature in the reactor with UA amendment. The temperature in Run A and Run B reached 62.2 and 70.1 °C after 5 days, respectively. The daily records showed a fluctuation of the temperature. There was no significant difference ($p > 0.05$) between the temperatures in Run A and Run B from day 6 to day 11. During the following 9 days, these high temperatures were eventually decreased to 25.7 and 23.5 °C in Run A and Run B respectively, which close to ambient temperature after 3 weeks of composting.

Both of the two reactors could reach thermophilic phase after 2-3 days of incubation, indicating the presence of sufficient population of indigenous microorganisms in composting system. Different groups of microbial populations would predominate in composting according to the temperature of the mass (Bernal et al. 2009). The maximum temperature in present study was much higher than that in a previous study on composting of a tomato remains wood shavings mixture by Alkoaik and Ghaly (2006). Such difference of the composting process could be affected by the system characteristics.

Three classes of nutrients including protein, fat and carbohydrates could mainly contribute to the energy production in composting system (Alkoaik and Ghaly 2006). The presence of adequate bioavailable carbon source in food waste could help reach the high thermophilic temperature.

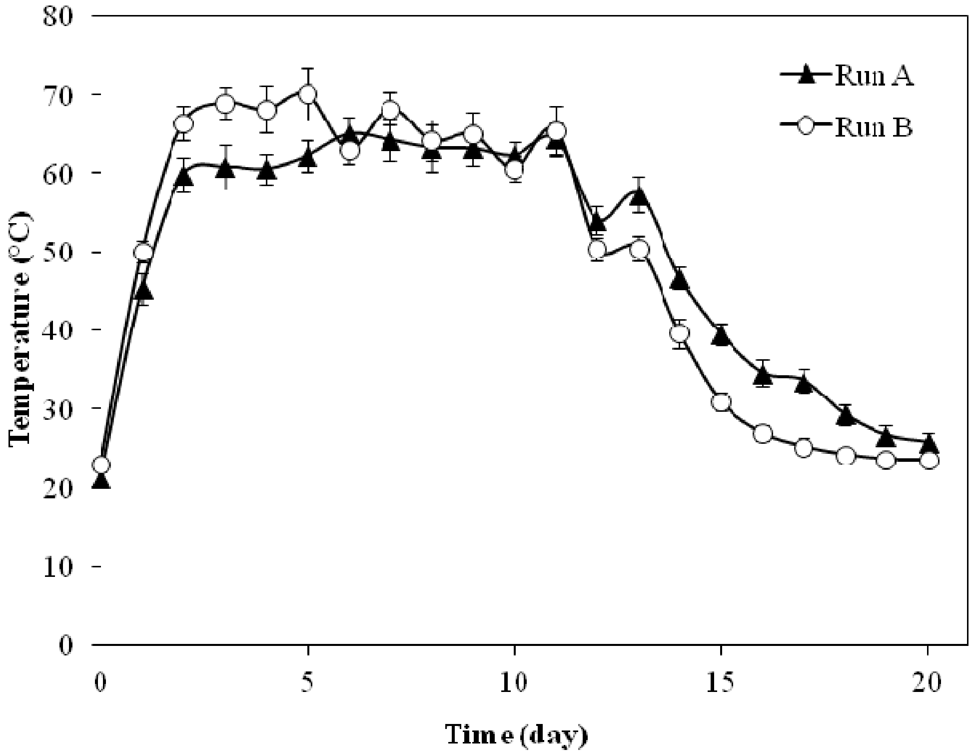


Figure 6.2 Temperature profile in the composting process

The temperature could be also influenced by the amount of oxygen available to the microorganisms in the compost (Imbeah 1998). Continuous aerating in the current in-vessel system could result in more available oxygen than the system without aeration. Compared with the series without UA amendment, the UA-added reactor showed a higher temperature during the initial phase, indicating more heat was generated from the decomposition of the mixture with UA amendment in this stage. The higher temperature in UA-amended series might be due to the enhanced microbial growth and metabolism. The rapid hydrolysis of UA was accompanied by the generation of easily assimilable sources of energy and nitrogen, which can facilitate the microbial growth and the temperature increase.

Within the thermophilic phase ranging from 50 to 70 °C, most of the pathogenic species could be destroyed, which is important for the sufficiently hygienic end-product (Bustamante et al. 2008). It was reported that during composting of municipal solid waste and sludge, the thermophilic stage was quickly achieved but maintained for less time (Gea et al. 2004). This might have been caused by the heat loss/emissions due to absence of efficient insulator in some other systems. The treatment with the UA addition was the first one reaching thermophilic phase, while also entering the cooling phase earlier than that of the UA-free series. During the cooling phase, there was an early decrease of the temperature in the UA-amended reactor due to the reduced microbial activity associated with the limited degradable organic substrates. The reaction temperature decreased rapidly in the cooling stage and then attained the ambient temperature, which was similar to the previous study on the composting of food waste (Jang et al. 2002).

6.3.1.2. Mass Reduction during Composting

The extent of mass reduction was calculated from the degradation percentage of organic matter in compost and shown in Figure 6.3. The mass reduction percentage in two runs was at significantly different level ($p < 0.05$). In the initial stage, the mass reduction for both runs is not obvious. The degradation percentages in Runs A and B were equivalent to 2.40% and 4.96% at day 2, respectively. More intensive processes of food waste mineralisation took place in all of the experimental treatments after the first 2-4 days. The degradation of food waste in Run A lagged behind. During that period, 32.55% of original organic substrate was degraded in Run A at day 10, while the corresponding values for the Run B was 40.57%. The degradation rate was strongly correlated with time ($r = 0.987$, Run A; $r = 0.966$, Run B). During the initial 11 days of the composting, the addition of UA in run B was conducive to faster degradation of the food waste. After day 11, the food waste degradation in Run B was less intense. The degradation of food waste showed a similar pattern in the reactor without UA addition. In the later stage of the composting process (after 14 days), the food waste degradation in Run B got close to that observed in Run A. After 20 days of composting, 53.76% of the total organic matter weight in Run B was lost compared to 51.08% for that of Run A. More than half of the original organic component has been already degraded after 3 weeks of composting.

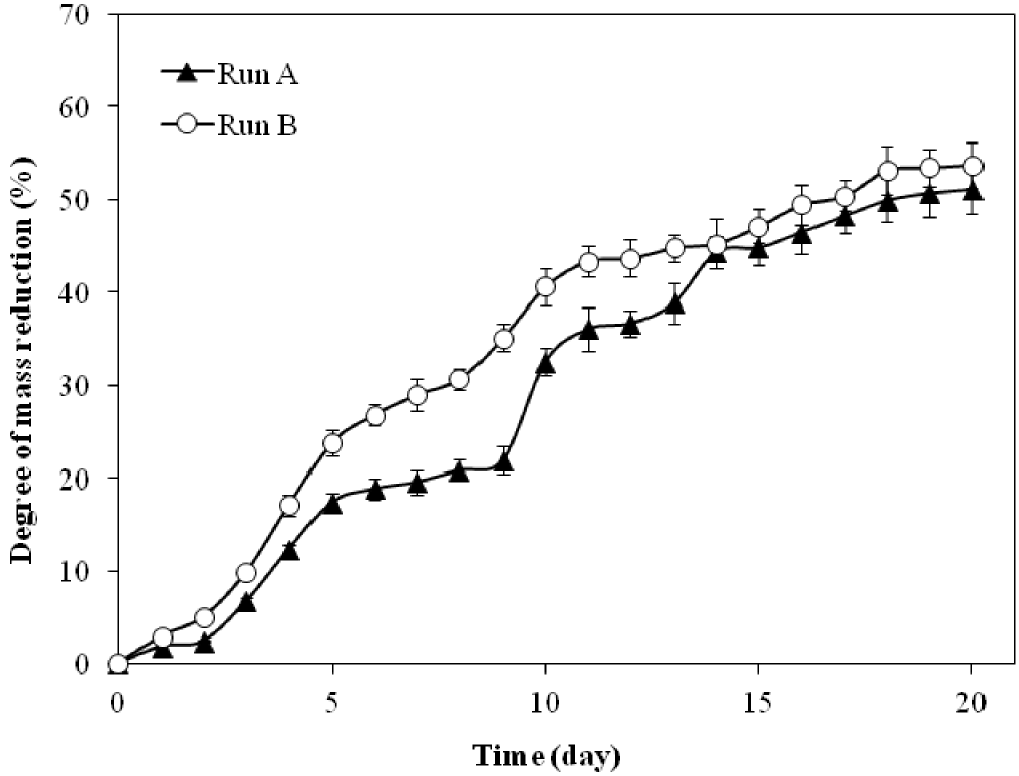


Figure 6.3 Degree of mass reduction in the composting process

The composting process is carried out by many different groups of microbial populations (Sun et al. 2009). The microorganisms within the composting system could degrade the raw organic material to synthesize new biomass and to obtain the energy for related catabolic processes (Alkoaik and Ghaly 2006). The low degradation rate at the first 1-3 days reflected the low microbial activity at the beginning of the process. The higher degradation rate was observed at the following stage and more than 70% of total loss of substrate occurred during the initial 11 days of composting. In the previous studies about composting, a low rate of degradation was often observed due to resistant organic substrates such as cellulose, hemicellulose and lignin in substrate (Bernal et al. 2009). Compared with them, there was a relatively fast substrate transformation rate for the composting process in present study. This was due to the existence of many organic compounds in food waste, such as simple carbohydrates, fats and amino acids, which can be easily degraded and utilized by the composting microorganisms.

The Run B mixture, prepared with UA as the amendment, underwent the more intense degradation, especially during the first 13 days. It indicated that the addition of UA in the composted material showed a positive effect on the degradation in the initial stage of composting. This was likely due to the UA effect which improved the metabolic activity by supplying a suitable amount of nutrient in food waste composting. It has been observed the presence of nitrogenous compounds could favour soil respiration, biomass-C and lipase activity (Margesin et al. 2000). Microbial population could increase dramatically when a nitrogen source was adopted to initiate the composting process (Davis et al. 1992). However, it was reported that the degradation of de-inking paper sludge was not improved by the sequential additions of nitrogen component such as urea during the composting process (Charest and Beauchamp 2002). It could be due to the reduced microbial activity by the producing of excessive free ammonia and soluble salt concentration in composting process. Solid waste like wood fibers that contained relatively difficult-to-biodegrade waste components might also contribute to the insignificant effect in the presence of additional nitrogen component. With more biodegradable waste such as food waste, the reduction could increase considerably in the presence of UA. Available N supplied would increase by the hydrolysis of UA. The existence of UA allowed the action of composting bacteria that transformed the substrate into end products.

Compared with the degradation during the initial 11 days, a lower amount of food waste underwent mineralisation during the subsequent 9 days in the presence of UA. When the large amount of easily assailable organic matter has been degraded, a slow reaction rate was observed in the composting process, which was due to a decrease of the overall microbial activity and the production of end product with high stability. Mature compost with humic characteristics would be produced during the final stabilisation and humification process (Lhadi et al. 2006). These overall variation patterns in present study were congruent with the result of Hu et al. (2009), who depicted the general aerobic composting process of waste materials from the clam processing industry in a in-vessel system. The acceleration of food waste degradation was corresponding to the increase of temperatures in the initial phase. The phase with faster degradation in the presence of UA was also characterised by higher temperatures (Figure 6.2). The increasing temperature facilitated the saprophytic activities that caused the transformation of the material in composting (Sharma et al. 1997). After the peak of degradation of organic matter, the microbial activity decreases, accompanied with the decreasing temperature.

6.3.1.3. pH development during Composting

The pH underwent considerable change during the composting process (Figure 6.4). The original compost of Run A used in this study had a pH value about 5.81. The initial pH of the compost was not significantly changed ($p > 0.05$) when amended with UA in Run B. And significant differences ($p < 0.05$) were evident between the pH levels of UA-free and UA-amended reactors during the first 6 days. The pH of Run A started to decrease at the beginning of the process and remained low for about 4 days. A similar trend of change in pH was also noted for the Run B with UA amendment, except that it had a higher pH at this stage. The pH of Run A and Run B after 2 days of composting were, respectively, 4.69 and 5.02. After this bottom, the pH values for both of the two runs increased rapidly. During the reaction from day 7 to day 11, the pH values were not significantly different for both runs ($p > 0.05$). After that period, the higher pH level was observed in Run B. At the end of composting, the measurements were pH 8.33 in Run A and pH 9.14 in Run B.

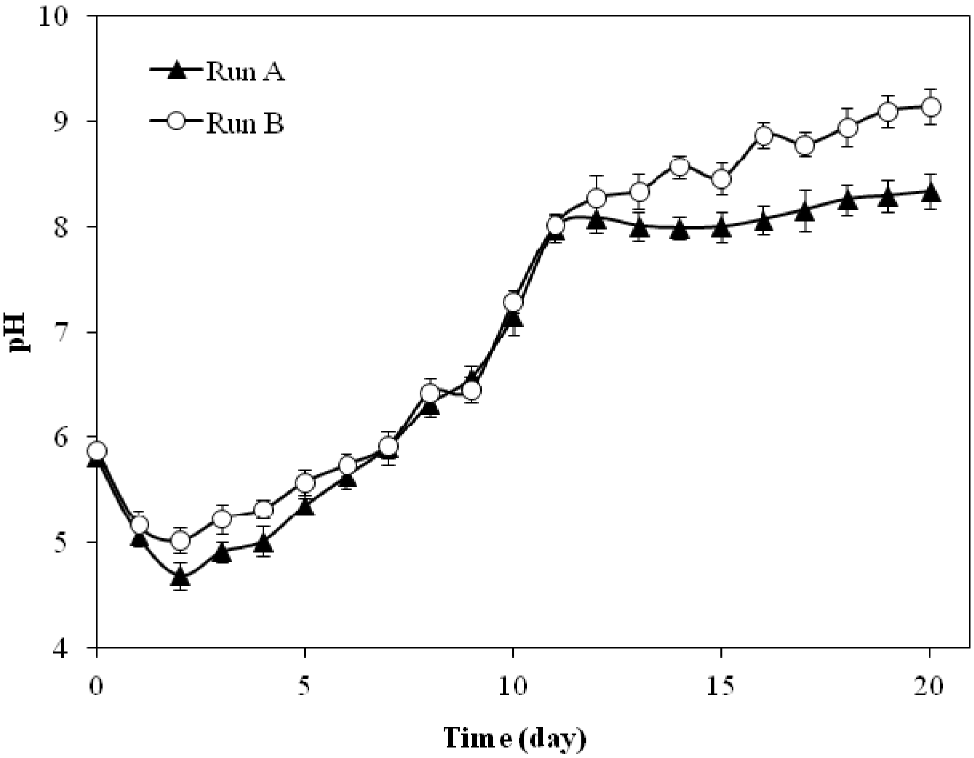


Figure 6.4 pH development in the composting process

The mixture of raw food waste in present study had initial low pH value, which was similar to many other organic household wastes (Smårs et al. 2002). During the composting, a reduction of the pH was noted in the first several days of the treatments, particularly for the series without UA amendment. This trend was also observed in previous reports by Kwon and Lee (2004) and Li et al. (2009) when studying the aerobic composting of food wastes. The decrease of pH could be due to the production of volatile organic acid and the CO_2 that derived from the degradation of the easily biodegradable organic compounds (Tuomela et al. 2000). The amendment of UA could promote the degradation of compost substrate (Figure 6.3). Correspondingly, there might be a more significant drop in pH at the beginning of composting, caused by the microbial production of more volatile fatty acids. However, the subsequent decrease of pH was less than that in UA-free series in present study. The addition of UA could prevent the decrease in pH during the early stage. The raising of pH in compost with UA amendment at the early stage could be explained by the conversion of UA to ammonia, which resulted in an increase in pH. It has been reported that the addition of urea in the composting piles was related to the increase in pH (Ling and Isa 2006). Furthermore, the adequate aeration of in-vessel system could prevent the excess amounts of organic acids produced in anaerobic decomposition and favour the volatilization of volatile acids in system. Addition of lime or buffer agent also could control the reduced pH of the composting mixture in some previous studies (Wong and Fang 2000; Yu and Huang 2009).

The results showed a rise of pH in the following stage of the composting process in all of the runs. The transition from acid phase to alkaline phase was probably related to the proteolytic and ammonification activities as observed in other composting studies (Thambirajah et al. 1995). The pH could also increase with the degradation of organic acids. The pH in UA-amendment series had in general a similar trend but at somewhat higher pH than the corresponding UA-free compost material. Breakdown of UA might contribute to the increase of pH. UA would exists largely in the form of very soluble urates and be utilized at high alkaline condition. During the thermophilic phase, the pH values generally increased as a consequence of intense substrate degradation (Bustamante et al. 2008). Thus the higher pH might be also due to the faster decomposition in the UA-amended compost. The optimum pH range for microorganisms in the composting process is from 7 to 8 (Smårs et al. 2002). However, the suitable pH values may differ for various microbial groups. The pH variation can regulate the equilibrium between ammonium ions and ammonia gas in the pile (Nahm 2005). It could be noted that the pH of the final product were close to the alkaline phase. This has also been observed in other composting studies (Beck-Friis et al. 2001; Gajalakshmi and Abbasi 2008). The addition of UA increased the final pH value as compared with the series without UA amendment.

6.3.1.4. Evolution of O_2-uptake

The O_2-uptake rates at various composting conditions are illustrated in Figure 6.5. At the initial stage, oxygen uptake rates remained at a low level, meaning that oxygen consumption was limited. Then O_2-uptake uptake rates increased quickly and decreased more or less gradually until O_2 uptake was low and experiments were stopped. O_2 uptake took place at various levels of intensity for different reactors. The O_2-uptake peak in Run B was detected at day 4 with a level of 7.34 mg g-dry sample (ds)/h. The O_2-uptake peak in Run A was shown later at day 11 with a level of 6.86 mg g-ds/h. Thereafter, the O_2 uptake rate of both of the two runs showed a decreasing trend. Figure 6.6 presents the cumulative amount of O_2 uptake for the two runs. Significant ($p < 0.05$) differences were observed when comparing the cumulative O_2 uptake amounts of different series. In general, the cumulative O_2 uptake amount in Run B was larger than that in Run A. The most significant difference between the cumulative amounts of O_2 uptake in different runs was observed at day 9, with 1077.54 and 1271.39 mg/g-ds for Run A and Run B, respectively. Such difference became less significant after day 9. The amount of consumed O_2 in each run was similar at the end of the reaction.

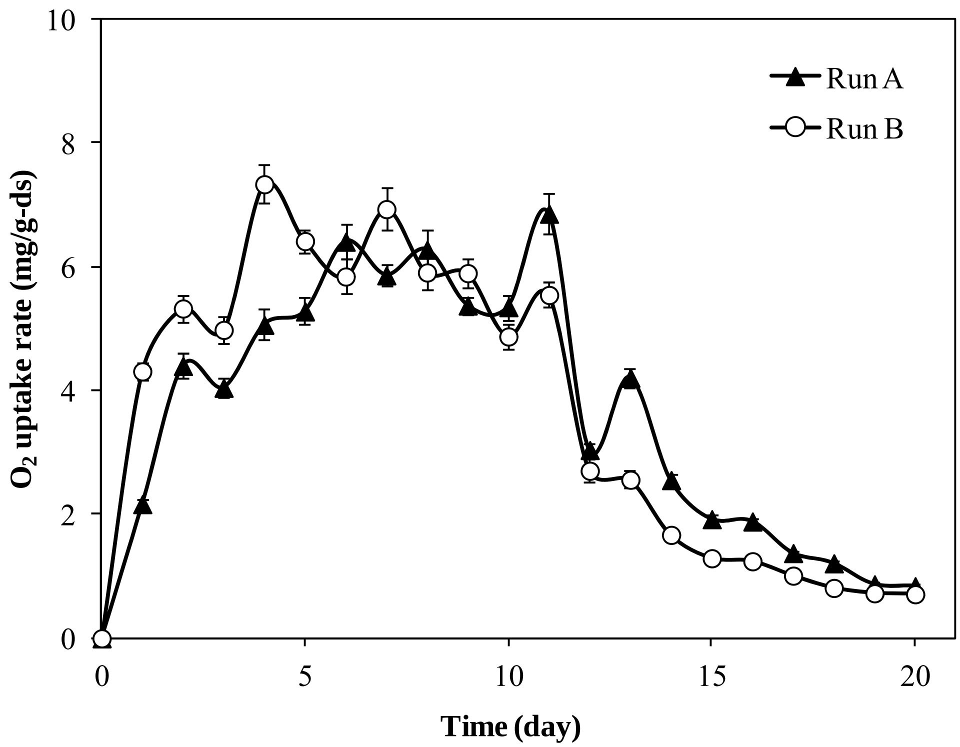


Figure 6.5 Evolution of O_2 uptake rate in the composting process

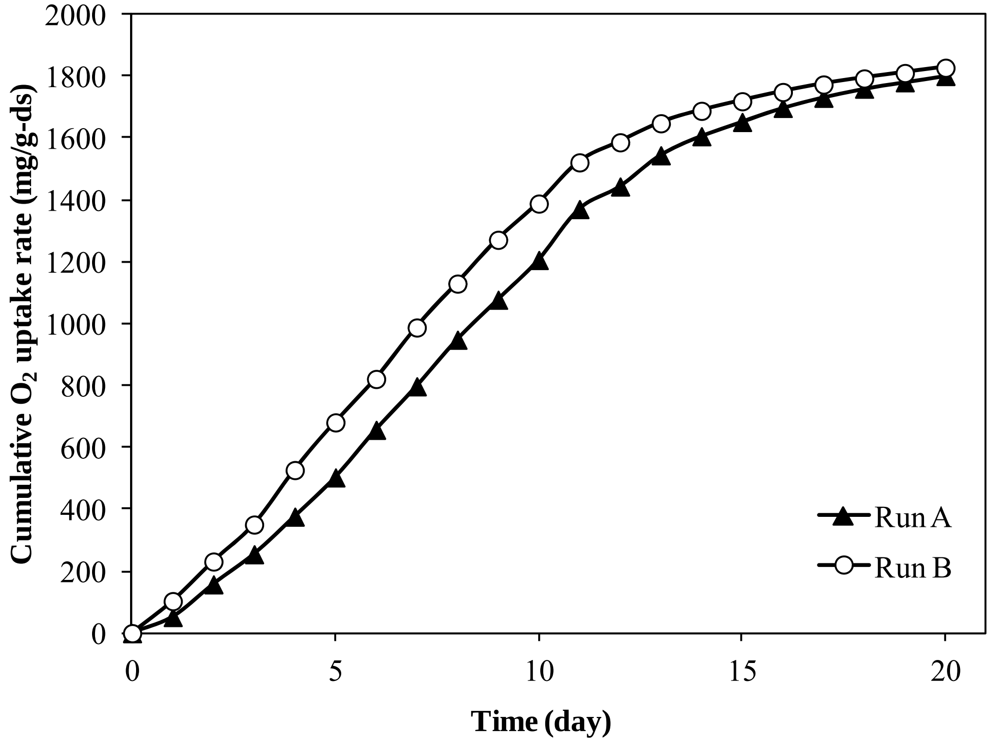


Figure 6.6 Evolution of cumulative amount of O_2 in the composting process

Aeration could provide sufficient O_2 for the biological activities in composting process and take the excess CO_2 away from the system. Insufficient aeration during composting might result in retarded process and poor quality of composts. For food waste composting, An (2006) has compared different aeration rates and recommend an aeration rate of 3 L/min as a suitable rate, based on composting efficiency, agronomic value of final product, air pollution and energy consuming. In the present study, the O_2 uptake showed a strong correlation with the degradation process. During the first half of food waste composting process, the different performances in two series strongly indicated that the variation of O_2 uptake was correlated to the amendment of UA. Under aerobic conditions, the organic compounds are degraded to CO_2 and NH_3 with the consumption of O_2, through different steps of the biodegradation phase (Bernal et al. 2009). The presence of oxygen could also play an important role in the degradation of UA as well as other undigested proteins (Nahm 2005).

The microorganisms in the pile showed intense activity due to the relative abundance of easily biodegradable compounds in the system. In the presence of UA, the more oxygen consumptions in the pile were observed, due to the stronger demand for O_2 by microorganisms. But when most of the food waste degradation had already taken place during the later stage, less significant O_2 demands were shown in UA-amended series because the reduced substrate and biological activity had become the limiting factors in the oxygen consumption. At the final maturation phase, values of O_2 uptake in all cases were relatively similar and no significant variation was detected after 18 days of composting. In addition, when the system temperature increased, not only the degradation rate, but also the O_2 uptake increased. The peak of O_2 uptake (Figure 6.5) was observed close to the peak of temperature, which was similar to previous results from Tiquia et al. (1996) and Lu et al. (2005). But when the compost pH was decreased in the early stage of each run, O_2 uptake rate was not significantly influenced.

6.3.1.5. Variations of C/N ratio

The changes of C/N ratio obtained in these experiments are presented in Figure 6.7. The C/N ratio changed during all the composting reactors, but the C/N-time profile of UA-free series differed significantly ($p < 0.05$) from that of UA-amended series. For the raw composting substrate, the C/N ratios of Run A and Run B were 17.72 and 11.93, respectively. The correlation analysis showed a negative correlation ($r = -0.965$, Run A; $r = -0.923$, Run B) between the time and C/N levels. As the composting process proceeds, a decreasing trend in C/N ratio was observed in Run A. By day 11, its C/N ratio had decreased to 11.81. Similarly, there was also a decrease of C/N ratio in Run B with UA amendment, where the lower C/N ratio at 8.97 was observed after 11 days of composting. The C/N ratios of both runs did not change significantly during the subsequent stage of composting. After 20 days of composting, the C:N ratio of Run B reached 8.56 compared to 10.38 for the ratio of Run A.

The C/N ratio of solid waste from many industrial sources could reach 20 or higher (Charest and Beauchamp 2002). The raw food waste in present study, however, was characterized by the relatively low C/N ratio. The UA-abundant manure often has more lower C/N ratio (Huang et al. 2004). Thus the low C/N ration would also be a characteristic for the unseparated mixture of organic food waste and manure.

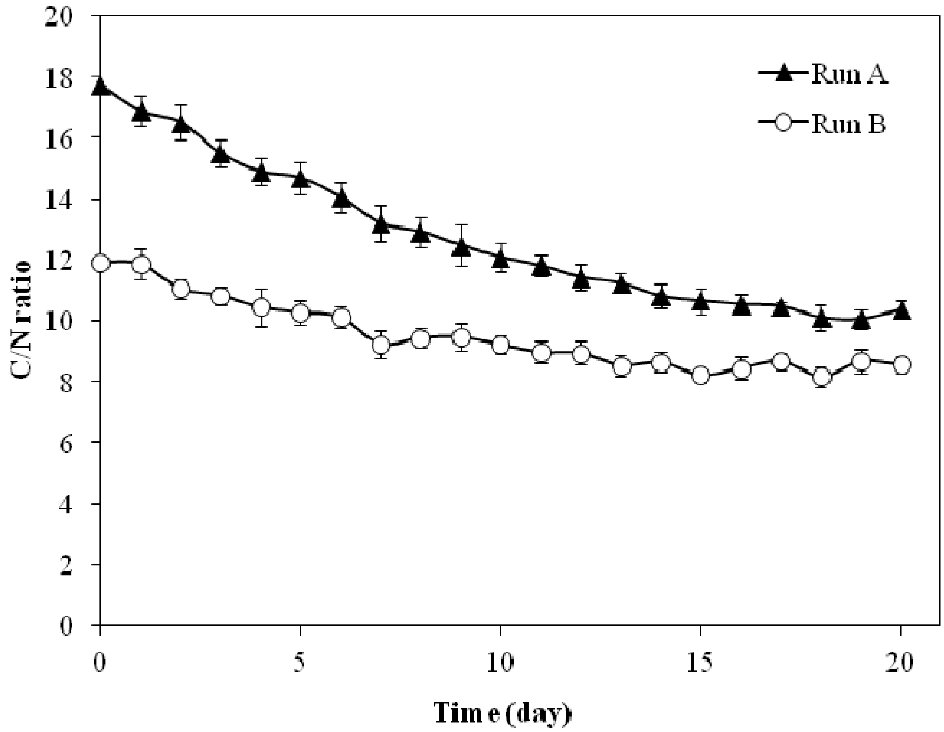


Figure 6.7 Variations of C/N ratio in the composting process

It has been reported the C/N ratio around 30 was optimal for microbiological activity since that ratio was close to the constituents of microorganisms (Zenjari et al. 2006). The compost materials with low C/N ratio have the potential to lose nitrogen through ammonia volatilisation, which could reduce the fertilizer potential and economic value of the end product. But C/N ratio at high level may lead to the retardation of maturation phase (Sharma et al. 1997).

During the decomposition of the organic matter, the C content gradually decreased over time, leading to a low C/N ratio. This can be linked to microbial degradation of carbon source. The addition of UA as readily bioavailable form of nitrogen could favour the microbial activity as well as the degradation of substrate (El Hajjouji et al. 2008). As seen in Figure 6.3, the UA-amended series showed an intense degradation during the first 13 days. Correspondingly, there was significant decrease in C/N ratio for food waste composting with the addition of UA during the early stage. Total N concentration in compost might increase due to the concentration effect when carbon was biodegraded and liberated through CO_2 (Bernal et al. 2009). It could also contribute to the decrease of C/N ratio during the process.

In the subsequent stage of composting, the C/N ratio changes in UA-amended treatment were similar to that in UA-free treatment. The variation of C/N ratio decreased gradually because of the reduction of composting progress and the limited nutrient sources for microorganisms in the later stage. It has been reported that the addition of urea to municipal solid wastes could lead to increased loss of nitrogen (Drozd et al. 2008). There was a slight increase in C/N ratio for the series with UA amendment, which was possibly due to the loss of nitrogen in this phase. This trend has also been noted during many other treatments following decomposition of the organic matter by microorganisms (Silva et al. 2009). The maturation process would lead to the synthesis of new complex and polymerised organic compounds with high stability. Eventually, there was a low C/N ratio for both of the two runs. The product was of good quality for the application because the addition of materials with C/N ratio lower than 15 may not alter the microbiological equilibrium of the soil (Iglesias Jiménez and Pérez García 1992).

6.3.1.6. Changes of NH_4^+-N in Compost

Figure 6.8 illustrates the test results about NH_4^+-N concentration of compost under different conditions. The NH_4^+-N concentration of Run A was significantly ($p < 0.05$) different from that of Run B. Only minor NH_4^+-N was detected during the initial several days of composting, even in mixtures prepared with uric amendment. By comparison, the NH_4^+-N content of Run A was slightly lower than that of Run B till day 5 before increasing further. During the following stage of composting, there was an increase in NH_4^+-N concentration for all the experimental treatments. The highest NH_4^+-N concentration reached 20.81 mg/g at Run A on the day 11. Then NH_4^+ concentration slowly decreased during the subsequent phase. In Run B, the NH_4^+-N concentration reached 17.54 mg/g after 11 days of composting. Afterwards, a general increase was observed in the level of NH_4^+-N concentration for Run B from day 12 to day 20. After 20 days of composting, NH_4^+-N concentrations were 13.25 and 34.47 in the Run A and Run B, respectively. More NH_4^+-N was retained in Run B than in Run A compost.

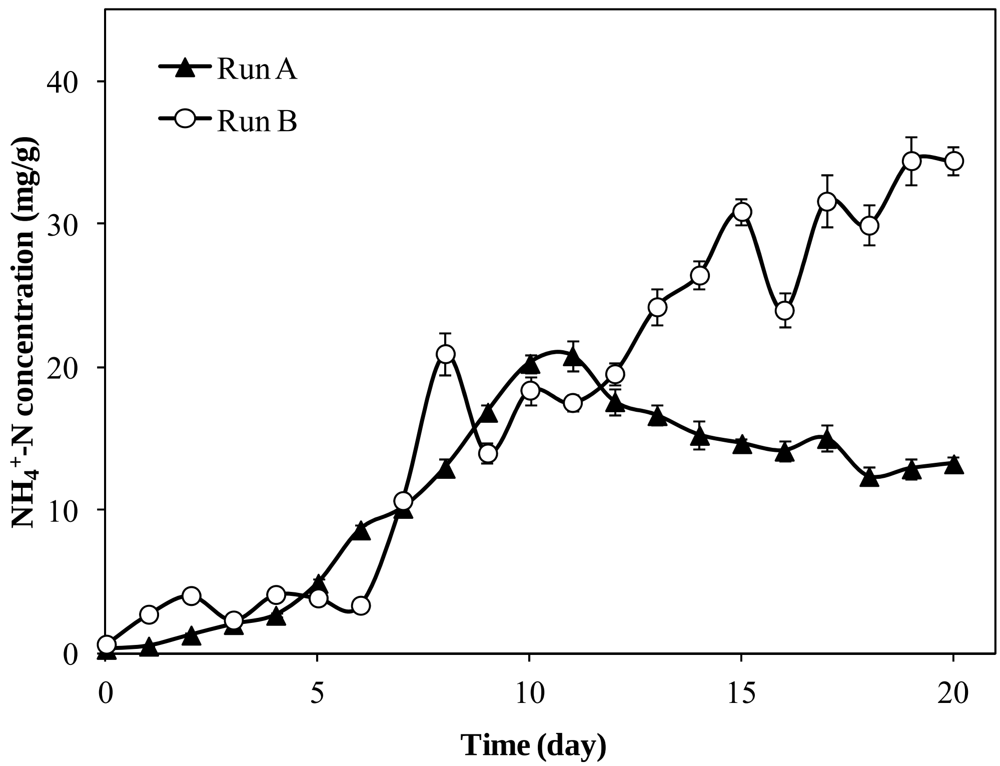


Figure 6.8 Changes of NH_4^+-N in compost

Ammonium could be generated from the ammonification processes when organic matter in compost was degraded (Sánchez-Monedero et al. 2001). The concentration of NH_4^+-N observed in the mixtures could reflect the transformation of the N forms. At the start of all experiments, NH_4^+-N concentration was at the low level. The low degradation rate of food waste during composting limited the transformation processes of nitrogen. During the following several days, a pronounced increase in NH_4^+-N content was noted in composts of both runs. However, the addition of UA didn't increase the amount of NH_4^+-N available in the piles. When the reaction reached the thermophilic phase, there was active mineralisation of the organic compounds, which could lead to the increase in NH_4^+-N. This increasing trend has also been observed in many other composting processes (Charest and Beauchamp 2002).

NH_4^+-N concentration peaked at day 11 and then showed a decline as the process progresses in the UA-free system. The decreased content of NH_4^+-N in the compost might coincide with more immobilization of NH_4^+-N, resulting in a low NH_3 loss even at high pH. This was in agreement with previous study in the composting of distillery wastes and animal manures (Bustamante et al. 2008). But the findings in the reactor with UA amendment were different. The addition of UA in food waste created an increase in NH_4^+-N after day 11. Also, the final composting mixtures containing UA exhibited higher NH_4^+-N than that in UA-free substrate. It indicated the compost was undertaking the further transformation and the NH_4^+-N as substantial amount of N increased during this stage. Degradation of UA could also produce ammonium ion (Gajalakshmi and Abbasi 2008). The ammonia could form in different processes depending on the condition of composting mixture. On the one hand, it can exist as ammonium and then immobilized by the microorganisms for synthesis activity. On the other hand, it might be given off under the condition of high temperature and high pH (Vinnerås 2007).

As seen from the results in Figure 6.4, the pH value in the UA-amended series was kept at a relatively high level at the later stage. Although the pile has been in a cooling stage with decreasing temperature, the alkaline pH values of food waste composting piles could favour the transformation of the soluble ammonium into ammonia. Thus the increased NH_4^+-N content observed in the treated material with UA amendment might lead to a risk for ammonia emissions during the following storage and field application. Moreover, since compost containing high amounts of NH_4^+-N was unstable, the addition of UA to composting possibly caused high losses in total nitrogen content, leading to a slight increase of C/N ratio in the later phase (Figure 6.7). But plenty of NH_4^+-N could play an important role in the formation of NO_3^--N and nitrogen immobilization by nitrifying bacteria (Bernal et al. 2009). The risk can also be managed by controlling of pH level or covering the manure storage pit.

6.3.2. Performance of In-vessel Composting of Food Waste in the presence of Fly Ash and Uric Acid

6.3.2.1. Temperature and pH Profiles

The profile of temperature is shown in Figure 6.9. In all the reactors, the temperature increased quickly during the first several days. Run D could reach 62.4°C within 2 days. The temperature variation of Run E also showed a similar pattern at this stage. But the temperature of Run E was significantly higher that of Run D ($p < 0.05$) during the first 3 days. Although Run C also showed an increasing temperature in the initial stage, the temperature level was lower than that observed in Run D and Run E. The rapid increase of reaction temperature during the early stage was mainly due to the microbiological metabolism. Easily biodegradable fractions in food waste such as sugars, proteins and amino acids were present in this stage. Suitable bacteria and fungi could degrade these simple compounds and generate heat. Similar high temperature has been often observed during composting of organic wastes, especially for easily degraded and energy-rich materials like household waste (Gajalakshmi and Abbasi 2008).

During the following experimental period, the temperature of Run D and Run E remained at a high level for several days. Then the temperature of Run D began to decrease after day 11, while the temperature of Run E began to decrease after day 10. The temperature of Run C fluctuated around 45 °C. At day 23, the temperature of Run C, Run D and Run E were 46.3, 23.8 and 21.4 °C, respectively. The high temperature range observed in present study is close to the range for thermophilic bacteria and fungi to colonize and degrade the substrate (Mbuligwe et al. 2002). A temperature above 55 °C could ensure the destruction of pathogenic organisms within a compost pile, which can create favorable conditions for further application (Gajalakshmi and Abbasi 2008). The later drop off of the temperature reflected the depletion of readily biodegradable components. In the case of both Run D and Run E, there was a mesophilic phase (up to 45°C) before the temperature decreased spontaneously to ambient temperature for both Run D and Run E. But the short mesophilic period was shown in Run D and Run E. This trend was also similar to that observed in other composting processes (Thambirajah et al. 1995).

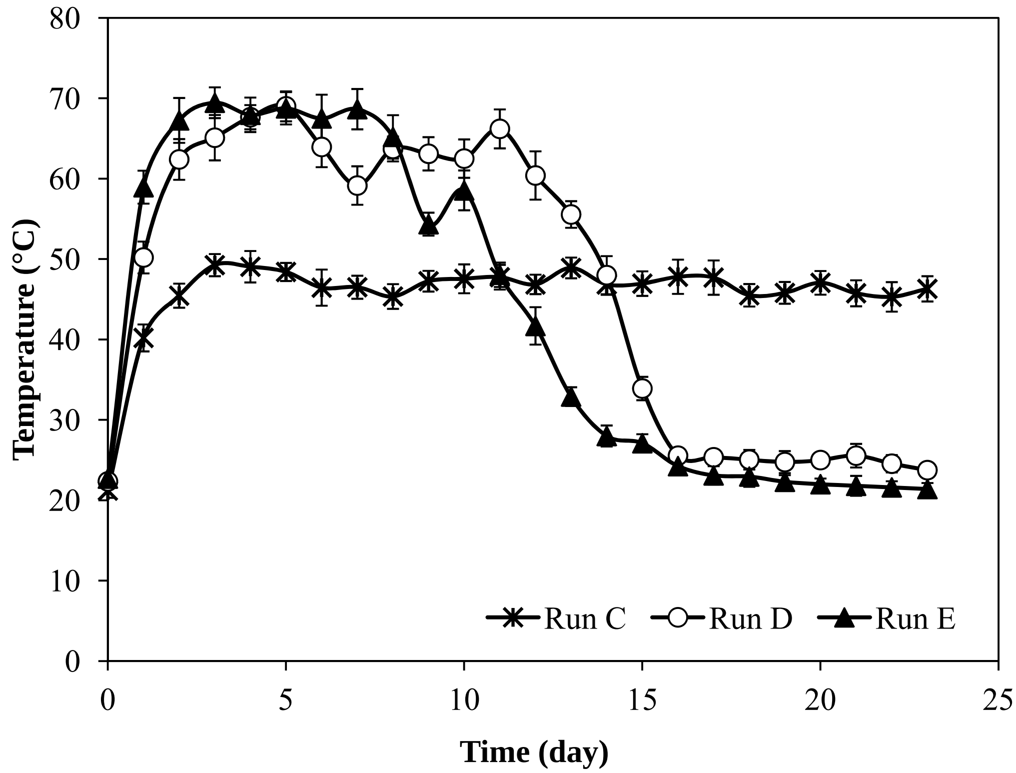


Figure 6.9 Temperature profile during the composting process

It is apparent that the compost of Run D and Run E was stabilized after 23 days of composting. The temperature profile of Run C did not evolve strictly around the constant temperature. Instead, the downward trend for Run C was also observed after 32 days of composting and the temperature of Run C could be close to the ambient environment after 39 days of composting (data not shown).

The temperature changes could reflect the microbial activity and the evolution of the composting process. Aeration plays an important role in the maintenance of high temperature during composting. Previous studies suggested that FA would be a suitable bulking agent for composting process (Kitano et al. 1998). Thus the enhanced porosity by FA amendments allows plenty of air to be trapped and utilized for metabolic heat generation by aerobic organisms, leading to a higher temperature. Furthermore, the enzyme-catalyzed hydrolysis of UA often accompanied with the generation of easily assimilable sources of nitrogen and energy, which can facilitate the microbial growth (Adrizal et al. 2011). The higher temperature observed in UA-amended series during the initial stage might be due to the enhanced intensity of aerobic microbial action.

As depicted in Fig 6.10, the changes in pH during composting process were not uniform for different reactors. The initial pH of Run C, Run D and Run E were 5.79, 6.02 and 6.07, respectively. Unlike many other solid wastes, the raw household waste such as food waste was often characterized by a low pH (Smårs et al. 2002). The initial pH level was slightly higher in Run D and Run E. This was due to the enhanced alkalinity by the amendment of FA. But there was no significant difference for the pH level between Run D and Run E. Addition of UA did not further increase the initial pH of the composting mixture.

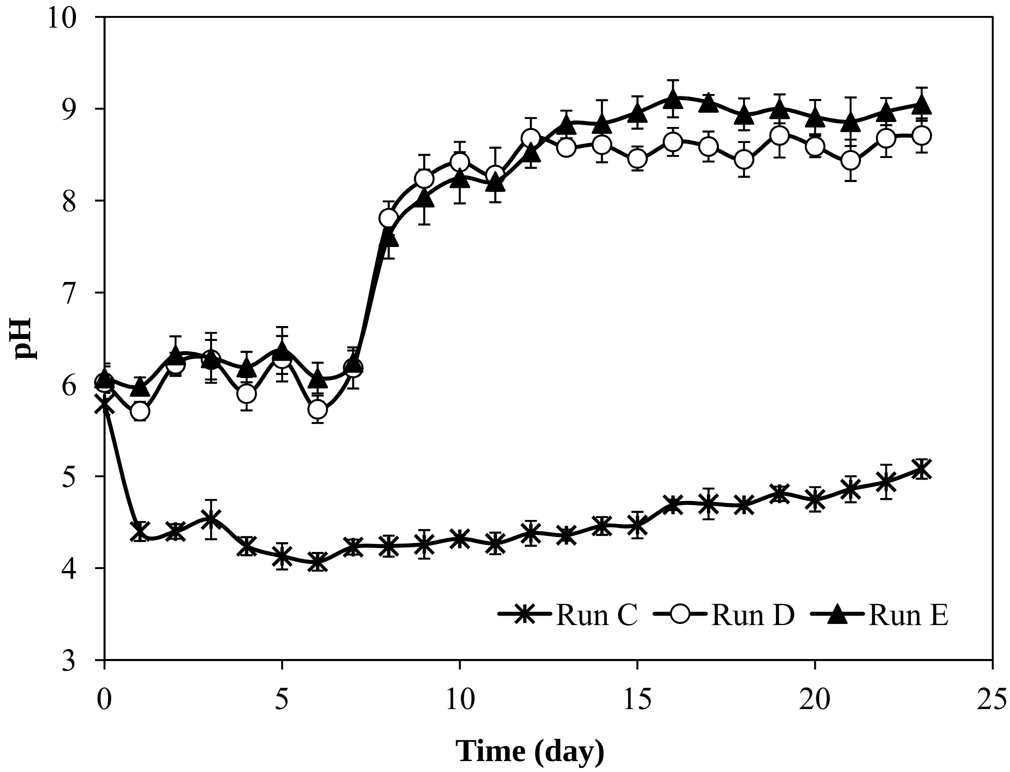


Figure 6.10 pH variation during the composting process

In the beginning, the pH in Run C decreased and reached a minimum of 4.07 at day 6. The significant drop in pH for treatment without any amendment may be due to the formation of carbon dioxide and organic acids (El Hajjouji et al. 2008). The abundant organic components and microbiological activities within food waste compost could lead to the generation of secondary acidic metabolites, which make a significant contribution to lowering the pH**.** Similar acidic environment has also been observed in previous studies about composting (Nakasaki et al. 1993; Smårs et al. 2002). By contrast, a significant decrease of pH was not observed in Run D. The pH of Run D fluctuated from 5.71 to 6.18 from day 1 to day 7. The alkaline components such as alkali metal oxides in FA could buffer the acidity of the composting mixture in this stage. A slightly higher pH level was shown in Run E during this stage, which was due to the addition of UA in food waste. It has been also noted the sequential addition of urea could lead to alkalinization (Charest and Beauchamp 2002). Breakdown of UA and undigested protein in the mixture could all contribute to the increased pH.

As the process proceeds, the compost pH of Run C increased slowly. In comparison, both of Run D and Run E were undertaking a rapid increase of pH after day 7. But the increasing trend became less significant at a later stage. There was no significant difference ($p > 0.05$) between the pH values in Run D and Run E from day 6 to day 11; however, the pH of Run E was significantly higher that of Run D ($p < 0.05$) after day 13.

At the end of composting, the pH values for Run D and Run E were 8.71 and 9.05, respectively. The decomposition of proteins, ammonification, and elimination of the carbon dioxide can all contribute to the pH increase (Thambirajah et al. 1995; Sharma et al. 1997). But the high level of pH observed during the final stage might pose potential risk for ammonia emission. The slightly higher pH in Run E might be due to the faster decomposition of substrate and breakdown of UA in the UA-amended reactor. In contrast, when the sewage sludge was amended with coal FA in a previous study, it was observed the pH could increase as time went on, but followed by a drop of pH later (Fang and Wong 2000). Such difference is perhaps ascribed to the different FA dosage and composting substrate properties.

6.3.2.2. Organic Matter Reduction during Composting

The extent of organic matter reduction is calculated from the degradation percentage of organic mass in compost and shown in Figure 6.11. In the initial stage, the degradation of organic matter in Run C increased slowly and only 7.93% of initial organic matter was reduced till day 10. During composting, transformations of substrates involved various biochemical reactions. The low activity in Run C was corresponding to a decrease in the pH values measured in this pile, compared to the reactors prepared with other amendments. This low pH level of in the initial stage is likely to be an important factor inhibiting the composting process. In the Run D and Run E, the degradation was undertaking a rapid increase after the lag of one day, but the increasing patterns were significantly different ($p < 0.05$). The degradation percentages in Runs B and C were equivalent to 48.35% and 55.97% at day 10, respectively. The amendment of FA showed better degrading performance than that in the control.

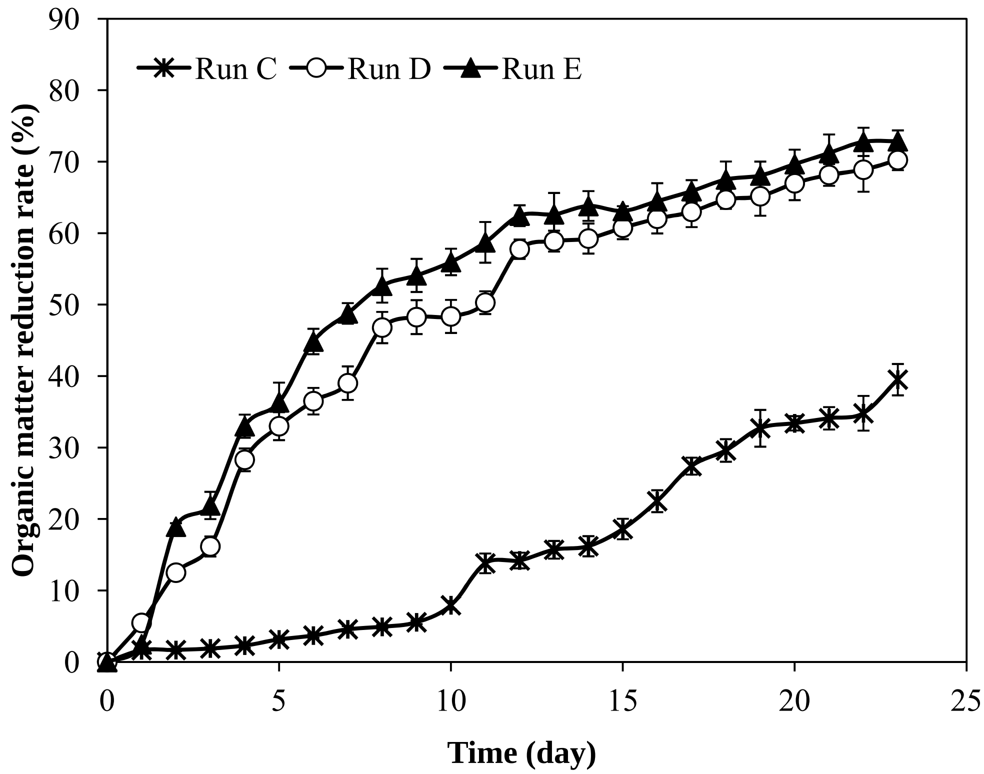


Figure 6.11 Organic matter reduction in the composting process

It has been also observed that the degradation rate of organic matter under appropriate pH control, such as liming and adding sodium acetate, was faster than that in the experiment without any adjustment (Nakasaki et al. 1993; Yu and Huang 2009). Compared with the amendment of FA only, the degradation of food waste mixture was further increased with an addition of both FA and UA, which caused a higher metabolic activity in the treatment.

The intensity of degradation in Run C was enhanced during the late stage. After 23 days of composting, 39.51% of the total organic matter weight in Run C was lost. As for the Run D and Run E, the significant change in degradation of organic matter occurred during the first 12 days, while a slower rate of organic matter losses was observed compared in the successive 11 days. The degradation process almost stopped when readily biotransformed material was fully consumed. At the end of the composting, 70.24% of original organic substrate was degraded in Run D at day 23, while the corresponding values for the Run E was 72.87%.

Mineralization and humification during composting are the main processes causing the transformation of organic waste (Gajalakshmi and Abbasi 2008). The organic waste can be converted into stabilized product with humus-like property, along with the emission of some other metabolic products like inorganic elements, volatile organic compounds and biomass (Mao et al. 2006). Processes with the composting of some organic wastes showed the limited total weight losses, which were often due to the presence of resistant organic substrates such as cellulose, hemicellulose and lignin in substrate (Bernal et al. 2009). However, the mixture in present study showed a high degradation rate. Food waste is generally characterized by abundant assailable organic matter, resulting in more intensive process of mineralization by microorganisms. It has been reported the low microbial activity in low pH range was probably related to a lag phase of composting (Nakasaki et al. 1993). Fang and Wong (2000) reported that the amendment of coal FA might had the adverse effect on the decomposition activity in sludge compost. Compared with the pH level in their study, a much lower pH level was observed in present experiment. Thus the addition of FA could neutralize the acidity and facilitate the degradation of organic compost. This also indicates the influence of FA is highly correlated with the characteristic of composting substrate. When amended with both FA and UA, degradation intensity and temperature would further increase especially in the early stage. The presence of UA might supply a suitable amount of nutrient. The metabolic activity could be improved, resulting more transformation from substrate into end products. But the results also showed that such influence became less significant during the final phase.

6.3.2.3. Variations of O_2 Uptake during Composting

The O_2 uptake rate underwent considerable change during the composting process (Figure 6.12). In Run C, the O_2 uptake rate was below 2.43 mg/(g-dry solid·h) before day 15, which was significantly lower ($p < 0.05$) than O_2 uptake rate observed in Run D or Run E. The O_2 uptake rate of Run E fluctuated between 3.27 and 5.95 mg/(g-ds·h) from day 1 to day 13. The O_2 uptake rate in Run E was significantly higher ($p < 0.05$) than that in Run D in the first 10 days. Run D reached its maximum O_2 uptake rate of 5.33 mg/(g-ds·h) at day 5. The aerobic consumption rate can be selected as a suitable indicator to assess composting performance and end-product stability (Bernal et al. 2009). Aeration is important for the success of any composting procedure, particularly for the in-vessel composting system. In our previous study, different aeration rates have been compared, based on the composting efficiency, end-product quality, air pollution and energy consuming (An 2006). An aeration rate of 0.1 vvm was recommended as a suitable rate for food waste composting in this system. The microorganisms could degrade the organic matter in food waste to CO_2 and NH_3 with the consumption of O_2. The low O_2 uptake amount in the unamended series was mainly correlated with the limited degradation of food waste. When the FA was added, more intense degradation might need more O_2 for bio-chemical reaction within the pile. Also, the presence of FA could improve the porosity of the food waste compost, resulting that more O_2 would be retained and utilized during composting. As for the series with FA and UA, besides the degradation of food waste, the transformation and utilization of UA could also contribute to the consumption of oxygen (Nahm 2005).

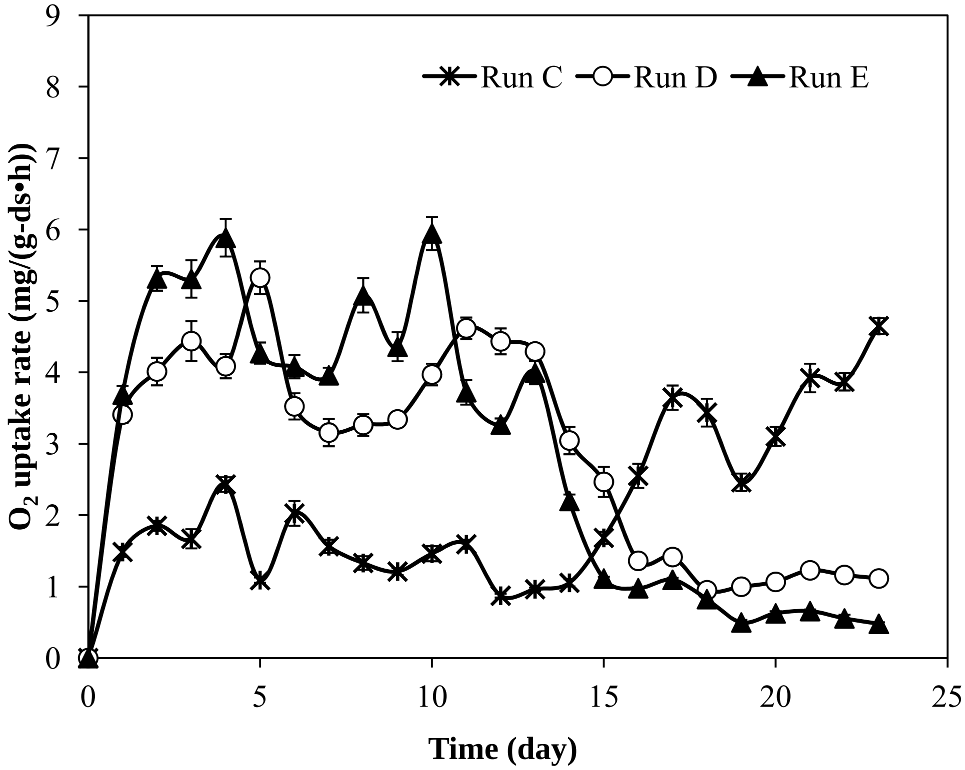


Figure 6.12 Variations of O_2 uptake rate during composting

The plots of the cumulative O_2 versus time showed an increase of O_2 during the composting process (Figure 6.13). As the degradation of compost increased, O_2 uptake was more rapid. Cumulative amounts of O_2 uptake in Run C were 386.91 mg/g-ds after 10 days, 924.69 mg/g-ds in Run D and 1149.52 mg/g-ds in Run E. The cumulative amount of O_2 uptake in Run C was significantly less ($p < 0.05$) than that of Run D or Run E within these 23 days. The cumulative O_2 uptake amounts at day 12 were equivalent to 71.35% and 80.82% of total O_2 uptake amounts after the experimental time of 23 days in Run D and Run E, respectively. It indicated the O_2 consumption mainly occurred during the first half of the process for these two series. During the late phase of composting, the reaction was less intensive and O_2 uptake increased less significantly. The higher O_2 uptake amount was observed in the presence of FA and UA than with FA only, which was due to the stronger demand for O_2 by microorganisms. After 23 days of composting, the increase of O_2 uptake amount ceased for Run D and Run E. The transformation of most biodegradable compounds had already taken place and thus no more significant O_2 demands were shown due to the reduced substrate and biological activity in these piles. As compared with Figure 6.8, the O_2 uptake evolution patterns in the compost reactor could also coincide with the changes in the temperature. These patterns were in accordance with those observed during the other aerobic composting processes (Yu and Huang 2009).

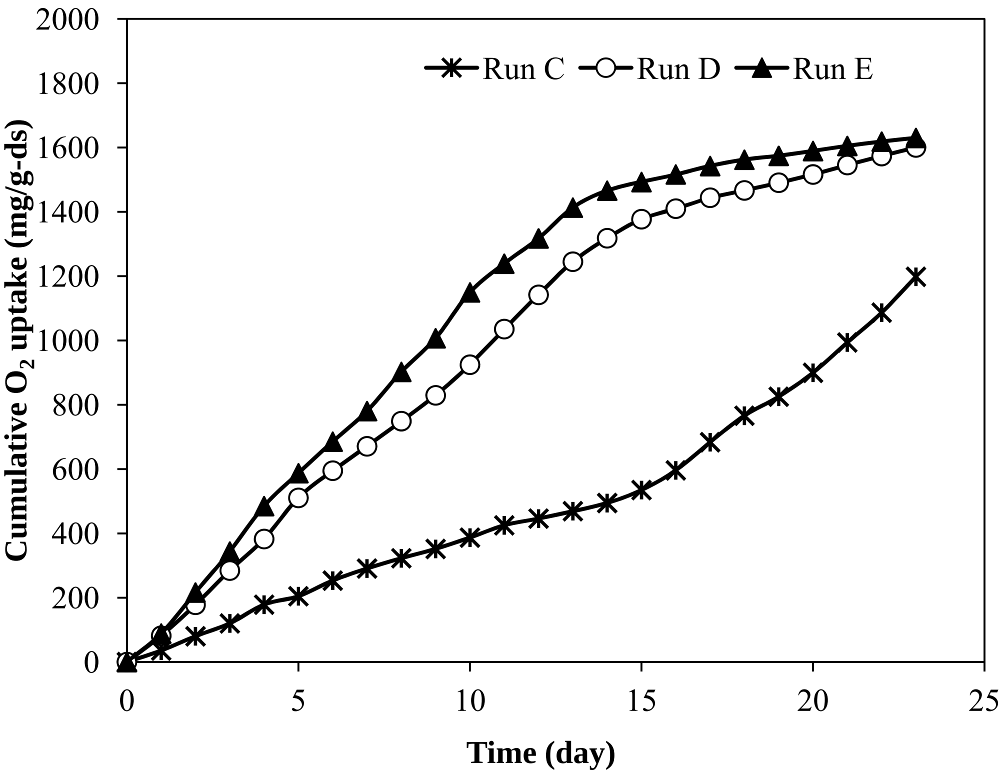


Figure 6.13 Variations of cumulative amount of O_2 during composting

6.3.2.4. Evolution of Microbial Population

The decomposition of food waste is carried out by various groups of microbial populations, which can utilize various complex organic materials in substrates. The microorganisms in the compost would develop according to the temperature of the mass. The succession of microorganism communities might also have a potential influence on the biodegradation capabilities and oxygen consumption requirements of the composting process (Ma et al. 2003). Figure 6.14 depicts the changes in thermophilic microorganism population of all treatments. At the beginning of composting, the population of thermophilic microorganisms in Run C was 3.63 $\log_{10}$ CFU/g. Run D and Run E with FA amendment had a slightly lower number of thermophilic microorganisms than that of Run C. This might be due to the adverse influence of salinity and alkalinity natures of FA (Chen and Li 2006). The initial thermophilic microorganism quantities did not differ significantly between Runs B and Run E. As the process proceeds, the microorganisms within the compost seemed to tolerate and adapt to the environment quickly. All observed thermophilic microorganisms increased, but with different patterns in these reactors.

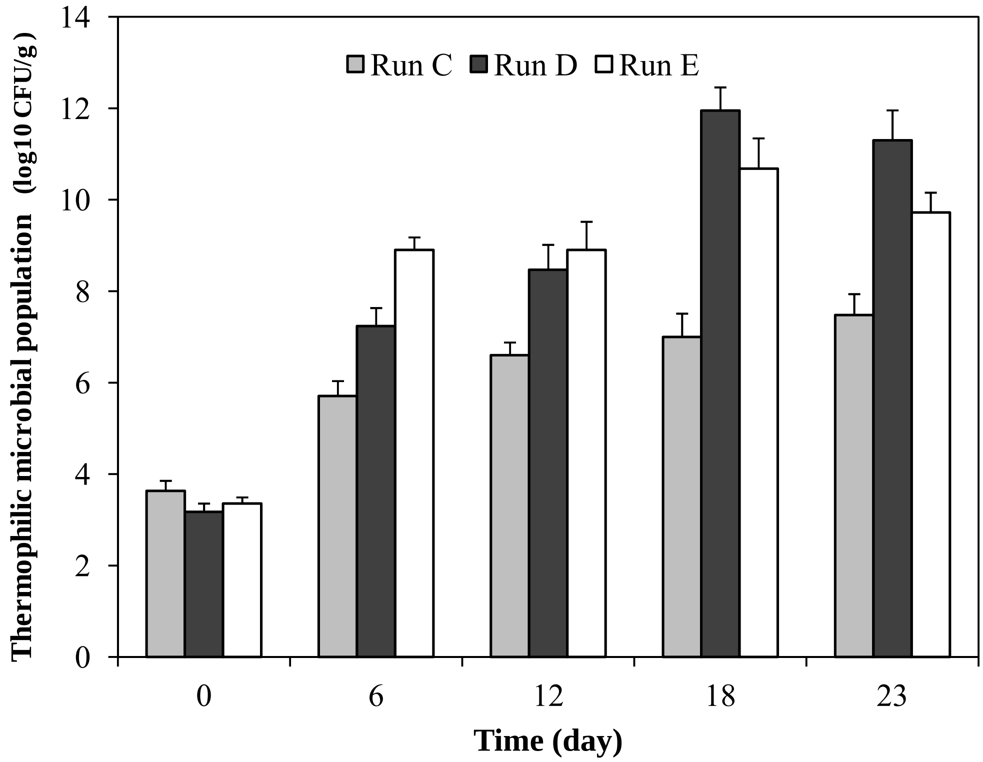


Figure 6.14 Evolution of thermophilic microbial population during composting

At day 6, the population of thermophilic microorganisms in Run C, Run D and Run E was 5.71, 7.24 and 8.90 log_{10} CFU/g, respectively. The population of thermophilic microorganisms with FA amendment outnumbered that without FA amendment during the initial stage. This is in contrast to Fang et al. (1998), who found thermophilic microorganism population could be significantly inhibited in the sewage sludge compost with coal FA amendment. Such difference could be mainly ascribed to the differences of waste properties. The low pH level in composting of food waste might lead to the limited proliferation of microorganisms. The addition of FA could neutralize the acidic environment, which would be favourable for the microbial activities. Correspondingly, the higher temperature and faster degradation could be achieved in FA-amended series during this stage (Figures 6.8 and 6.9). In addition, a higher population of thermophilic microorganisms in Run E was noticed at day 6 and day 12. It suggested that the coexistence of FA and UA might further facilitate the enhancement of microbial population. Microbial numbers can significantly increase when a nitrogen source is used to initiate composting (Davis et al. 1992). Moreover, the rapid increase of thermophilic microorganism population is often accompanied with the high level of urease, which could facilitate the transformation of UA as well as other nitrogen components (Díaz-Burgos et al. 1993). That also might lead to the more intense composting process with the addition of both FA and UA in this stage.

In spite of the decreased temperature, the thermophilic microbial population still increased at day 18, representing an extension of the active phase. After that, there was still an increase about the population of thermophilic microorganisms in Run C, while the population of thermophilic microorganisms in Run D and Run E began to decrease. At day 23, the population of thermophilic microorganisms in Run D and Run E was 11.30 and 9.72 log_{10} CFU/g, respectively. The lower amount of microorganisms was observed in series with both FA and UA. It indicated the additional amendment of UA showed the inhibitory effect on the population of thermophilic bacteria at the final stage of composting. This might be related to the higher level of pH and ammonia emission, which were potentially detrimental to the microorganisms.

As for the mesophilic microorganism during the composting process, the results showed that mesophilic microorganisms were present throughout the composting period. The initial populations of mesophilic microorganism in Run D and Run E were 5.76 and 5.95 log_{10} CFU/g, respectively (Figure 6.15). The amendment of FA still showed a little adverse effect on the microorganisms. Then the composting mixture of Run D and Run E showed a decrease of mesophilic microorganism when entering thermophilic phase. This was similar to the results of some previous studies (Thambirajah et al. 1995). The addition of lime has been reported to pose adverse effect on the mesophilic microorganism population development (Wong and Fang 2000). In present study, however, the mesophilic microorganism showed better development in FA-amended series than that in FA-free series after day 6. Since the thermophilic phase was corresponding with significant mass degradation and high oxygen consumption (Figures 6.11, 6.12 and 6.13), thermophilic bacteria might play a more important role in decomposition of food waste than mesophilic bacteria. Mesophilic bacteria often showed limited degrading activity for organic matter during this stage (Nakasaki et al. 1985).

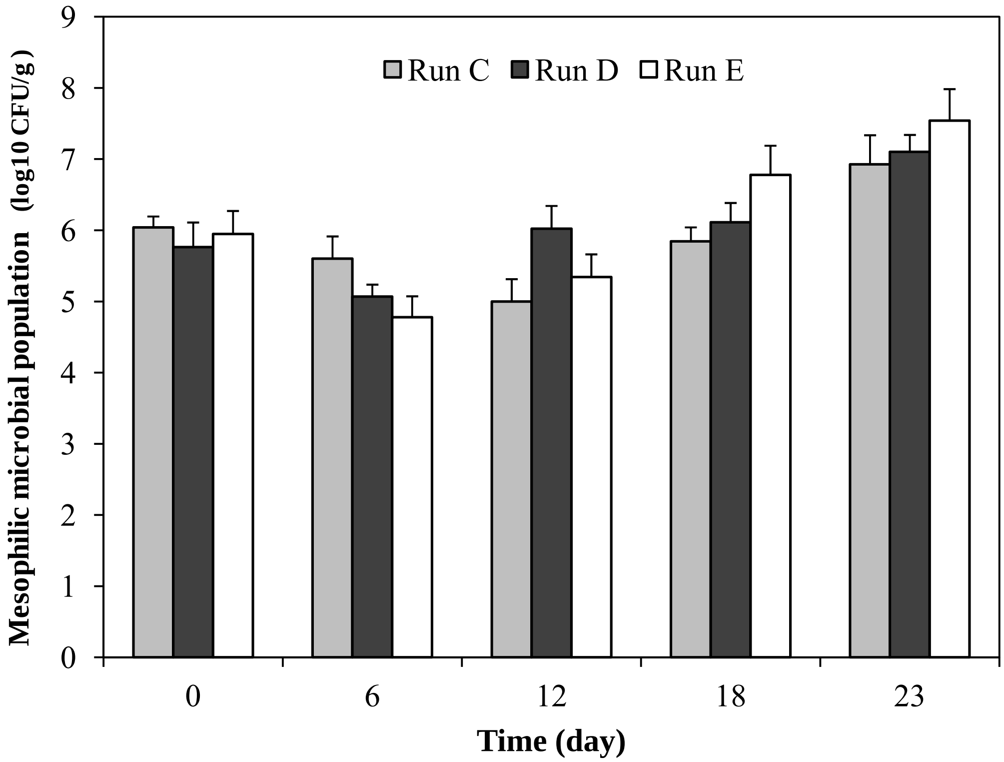


Figure 6.15 Evolution of mesophilic microbial population during composting

At day 12, the populations of mesophilic microorganism in Run D and Run E were to 6.02 and 5.34 log_{10} CFU/g. Less mesophilic microorganisms were observed in Run C, which also reflects the lower microbial activity of the mixture at that time. When temperature declined later, mesophilic microorganism population increased again. And then there was no further decline during the following stage.

6.3.2.5. Changes of C/N Ratio

The variations of C/N ratios obtained in these experiments are presented in Figure 6.16. The initial C/N ratios in the substrates of Run C, Run D and Run E are 32.46, 34.39 and 18.22, respectively. The C/N ratio in the range 25-35 has been reported to be adequate for composting, because the microorganisms require 30 parts of C per unit of N during metabolism (Bernal et al. 2009). In present study, the slightly higher C/N ratio in Run D may be attributed to the amendment of FA in which unburned carbon often exists (Bai et al. 2008). But the nitrogen content in added UA could lead to the relatively lower initial C/N ratio in Run E. This scenario could reflect the reality that food waste in composting mixture coexists with other manure wastes, which are often characterized by the low C/N ratio (Gajalakshmi and Abbasi 2008). The C/N ratio of all treatments generally decreased over time, except there was a slight increase in Run D at early stage. A major portion of the carbon is used by the microorganisms as the energy source and released as carbon dioxide, whereas the nitrogen is partially used for synthesis of proteins. Thus more significant loss of carbon could occur in compost, leading to the decrease of C/N ratio.

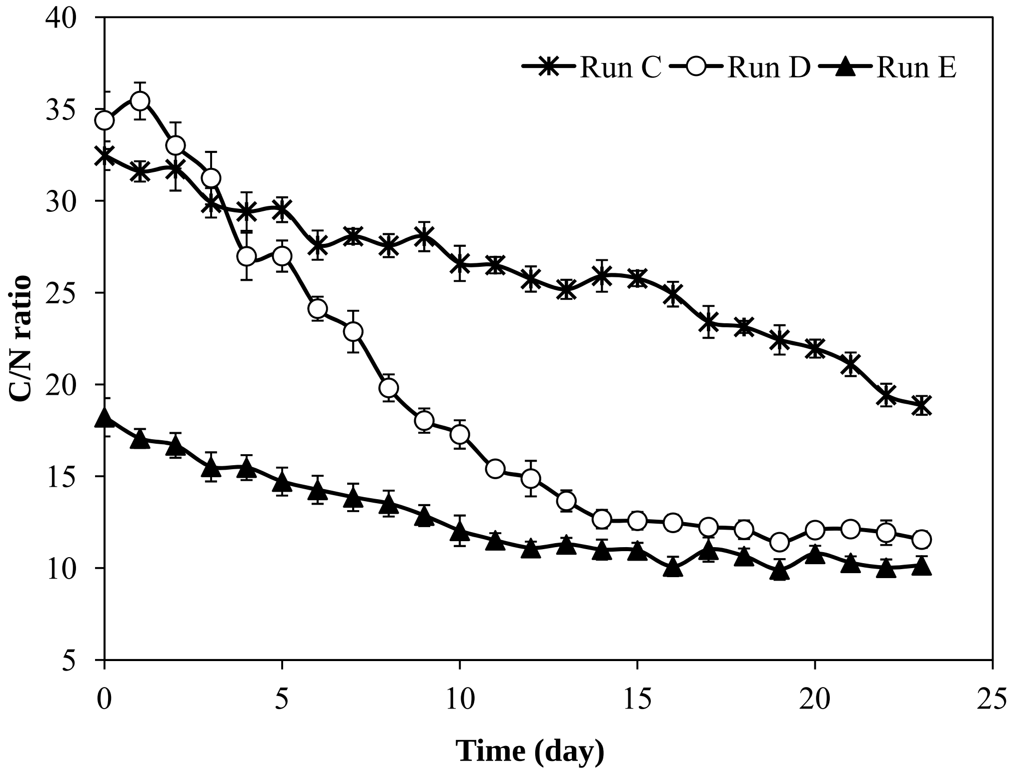


Figure 6.16 Changes of C/N ratio in compost

The C/N variation of different reactors showed different trends. Although Run C and Run D had a close C/N ratio initially, there was a more significant decrease of C/N ratio in Run D subsequently. At day 4, the C/N ratios for Run C and Run D were 29.42 and 26.98, respectively. Then C/N ratio of Run D remained significantly lower ($p < 0.05$) than that of Run C during all the following process. The slower descending trend of C/N ratio in Run C might be due to the lower degradation rate of food waste during composting. The good quality compost is often characterized by a C/N ratio lower than 20 (Sharma et al. 1997; Gajalakshmi and Abbasi 2008). By day 23, the C/N ratios of Run C and Run D had decreased to 18.87 and 11.56, respectively. Additionally, a decreasing trend of C/N ratio was also observed in Run E. But there was obvious fluctuation of C/N ratio during the later stage. Similar variation of C/N has been also observed in previous study about manure composting (Silva et al. 2009). In the coexistence of FA and UA, the compost showed a high pH level within the last period. The intermittent increases in C/N ratio suggested that N was possibly lost through ammonia volatilization. The nitrogen immobilization by nitrogen-fixing bacteria during the mesophilic period of composting might also contribute to this effect (Charest and Beauchamp 2002).

6.4. SUMMARY

The study investigated the influence of UA amendment on the in-vessel composting of composite food waste. UA amendment caused a more significant increase in temperature, particularly in the first half of the process. The addition of UA in the composted material showed a positive effect on the degradation of food waste in the initial stage of composting, while such effect would become less significant in the later stage. The amendment of UA could increase the pH level at the early stage of food waste composting, which would alleviate the inhibitory effect caused by acid environments. But the high level of pH observed the final stage in presence of UA might pose potential risk for ammonia emission. Addition of other agents would help control the pH condition of the composting mixture. Furthermore, changes in oxygen consumption in the treatments suggested that biological activity was more intense with the amendment of UA. The raw food waste in present study was characterized by the relatively low C/N ratio. In the presence of UA, the C/N ratio of food waste was undertaking a similar decreasing trend, while the C/N level was lower than that of UA-free series. Low C/N ratios observed in the coexistence of food waste and manure can be corrected by adding some bulking agents to provide more degradable organic carbon. The results also indicated the presence of UA could facilitate the further transformation into NH_4^+-N as substantial amount of N during the later stage of food waste composting. The present study supported that the performance of food waste composting significantly differentiated between the system with UA amendment and that without UA amendment.

The influence of FA and UA amendment on the in-vessel composting of composite food waste was also investigated. The results showed that the amendment of FA and UA could cause a more significant increase in temperature, particularly in the first half of the process. The alkaline components in FA could buffer the acidity of the composting mixture, while a slightly higher pH level was shown in the series with both FA and UA. When amended with FA and UA, degradation intensity would further increase especially in the early stage. The higher O_2 uptake amount was observed in the presence of FA and UA than with FA only, which was due to the stronger demand for O_2

by microorganisms. Both thermophilic and mesophilic microorganisms were present throughout the composting period. But different trend was observed in the series with both FA and UA. In the presence of FA and UA, the C/N ratio of food waste was undertaking a similar decreasing trend, while the C/N level was lower than that of UA-free series. The results imply that the coexistence of manure and some particular industrial waste might pose both positive and potentially negative effect on food waste composting. The overall effect of UA and FA can be assumed to be a sum of a large number of individual events with different mechanisms. Appropriate strategies could be applied to adjust the composting process, mediating both positive and negative effects in coexistence of food waste and UA as well as FA. Further study is needed to investigate the influences of other components in manure and industrial waste composting as well as the dynamic correlation of various process indictors to get better quality product.

CHAPTER 7

CONCLUSIONS

7.1. SUMMARY

In this dissertation research, several mechanisms have been proposed to explain the fate and transport of PAH in solid-liquid system. In addition, the physiochemical and biological processes in biosurfactant-enhanced remediation and composting have been investigated. A brief summary of this research is given as follow:

(1) The effects of SCOAs on the behaviors of PAHs in soil-water system were systemically investigated. The amendment of SCOAs could influence the behaviors of PAHs in soil-water system. In the presence of SCOAs, adsorption of the pyrene was significantly inhibited while desorption was promoted. The mobility of phenanthrene in soil could be enhanced by introducing organic acids. SCOAs could alter the association of PAHs and other soil constituents, and affect the mobility of PAHs in the soil-water system. Among different organic acids tested, ternary SCOA showed stronger effects than other acids. Since solution pH could determine the SCOA species available for a surface reaction, the effects of SCOAs on adsorption of PAHs were also pH dependent. More PAH compounds could be released into solution with increasing organic acid concentration. Pyrene adsorption performances also decreased in the presence of SCOAs for DOM-free soils. The existence of NaCl at high ionic strength condition could become a rate limiting factor for the transport of PAH in the presence of SCOAs.

(2) The biosurfactant-enhanced remediation of PAH-contaminated soil in the presence of SCOAs was studied. The results supported the combined use of biosurfactant and SCOAs could further enhance the desorption of phenanthrene from soil into aqueous phase. Desorption amounts of phenanthrene differentiated for varied combinations, in which the effect of ternary and binary SCOAs were more remarkable. SCOAs at high concentration caused a more significant increase in desorption from the soils with the amendment of biosurfactant. The quantity and species of organic acids could affect the tendency of phenanthrene distribution in the presence of biosurfactant. The variation of desorption with different combinations was also closely related with the soil DOM. In addition, adjusting the pH and ionic strength could control the effect of biosurfactant and organic acids, allowing higher remediation efficiency at specific values.

(3) The adsorption of phenanthrene on FA in solid-liquid system was investigated. The adsorption of phenanthrene onto FA showed significant stepwise pattern. As an improved method for adsorption behavior analysis, the developed SMLM could help well simulate the adsorption of PAHs on FA. The thermodynamic results indicated that the adsorption was an exothermic process. The adsorption capacity gradually decreased as pH increased from 4 to 8; however, this trend became less significant when pH was changed from 8 to 10. In addition, solution chemistry played an important role in the distribution of phenanthrene in FA-water system. The binding affinity of phenanthrene to FA increased after the addition of HA. The pH variation was also responsible for the changes of phenanthrene adsorption on FA in the presence of HA. High ionic strength corresponded to low mobility of phenanthrene in the FA-water system.

(4) The performance of food waste composting in the presence of FA and UA was investigated. In the presence of UA, UA amendment caused a more significant increase in temperature, degradation of food waste and the pH level in the initial stage of composting. The C/N ratio of food waste was undertaking a similar decreasing trend, while the C/N level was lower than that of UA-free series. In the presence of both UA and FA, the alkaline components in FA could buffer the acidity of the composting mixture, while a slightly higher pH level was shown in the series with both FA and UA. Different trends of degradation intensity, O_2 uptake amount, microbial population and C/N ratio were observed in the series with both FA and UA. The overall effect of UA and FA can be assumed to be a sum of a large number of individual events with different mechanisms.

7.2. RESEARCH ACHIEVEMENTS

(1) This research is the first attempt to investigate the effects of SCOAs on the behaviors of PAHs in soil-water system. The quantity and species of organic acids, as well as the properties of media and sorbents could all affect the fate of PAHs in soil-water system. The results of present study can potentially be applied to the application and optimization of remediation system for facilitating contaminant mobility in contaminated soils.

(2) This research is the first attempt to study the influence of SCOAs on the biosurfactant-enhanced remediation of PAH-contaminated soil. The results indicated the combined use of biosurfactant and SCOAs could further enhance the desorption of

contaminants from soil into aqueous phase. This approach can be regarded as a good alternative for the removal of PAH compounds from contaminated soil in application.

(3) The study related to trace organic contamination during FA disposal is an emerging area in environmental research. This is the first study to explore the interaction between PAHs and FA at the solid-liquid interface, and to discuss the environmental issues related to PAH pollution during FA disposal. As an improved method for adsorption behavior analysis, the developed SMLM can help well simulate the adsorption of PAHs on FA. SMLM can also be applied to other solid-liquid systems as an alternative to describe adsorption on adsorbents with more generally heterogeneous surfaces. The results of this study have important implications for environmental risk assessment and pollution control at FA disposal sites.

(4) This research has successfully evaluated the influence of FA and UA amendment on the in-vessel composting of food waste. The results imply that the coexistence of certain constituents from manure and industrial waste might pose both positive and potentially negative effect on food waste composting. Appropriate strategies should be applied to adjust the composting process under such complex environment.

7.3. RECOMMENDATIONS FOR FUTURE RESEARCH

Based on the research presented in this dissertation, further studies are suggested in the following areas:

(1) In the present study, only batch experiments were conducted to investigate the effects of SCOAs on the behaviors of PAHs. To better simulate the transporting process

in real world, a two- or three- dimensional experimental approach can be considered. The results can be used to support flow simulation at contaminated site.

(2) The present study focused on the combined application of rhamnolipid and SCOAs. In the future, the potential combination of SCOAs with other extracting solutions can be investigated. In addition, compared with using single surfactant, previous studies have shown that using certain mixed surfactants could be more effective for the removal of HOCs from soils. Therefore, it will be also interesting to study the combined application of SCOAs and mixed surfactants.

(3) FA samples were used in present study. In the future study, FA from coal-fired power plants can be separated into different components. It will be interesting to explore the correlation of contaminants and different constituents in FA. The results will help define the roles of each component in adsorption process.

(4) In the present study, the results imply that the coexistence of UA and FA could pose both positive and potentially negative effect on food waste composting. Further study is suggested to develop appropriate strategies to mediating both positive and negative effects.

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