การตรวจหาและการบำบัดสารอินทรีย์อันตรายในน้ำเสียจากโรงงานยางพาราทางภาคใต้ของประเทศไทยด้วยปฏิกิริยาเฟนตัน

นายวรวิทย์ วงศ์นิรามัยกุล

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต
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ปีการศึกษา 2549

CHARACTERIZATION AND FENTON TREATMENT OF HAZARDOUS ORGANIC SUBSTANCES IN PARA RUBBER INDUSTRIAL WASTEWATER IN SOUTHERN THAILAND

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A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy Program in Environmental Management
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Thesis Title	CHARACTERIZATION AND FENTON TREATMENT OF HAZARDOUS ORGANIC SUBSTANCES IN PARA RUBBER INDUSTRIAL WASTEWATER IN SOUTHERN THAILAND
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วรวิทย์ วงศ์นิรามัยกุล : การตรวจหาและการบำบัดสารอินทรีย์อันตรายในน้ำเสียจากโรงงานยางพาราทางภาคใต้ของประเทศไทยด้วยปฏิกิริยาเฟนตัน (CHARACTERIZATION AND FENTON TREATMENT OF HAZARDOUS ORGANIC SUBSTANCES IN PARA RUBBER INDUSTRIAL WASTEWATER IN SOUTHERN THAILAND) อ. ที่ปรึกษา: รศ. ดร. เพริศพิชญ์ คณาธารณา, อ. ที่ปรึกษาร่วม: PROF. CHIH-HSIANG LIAO, Ph.D. 206 หน้า.

งานวิจัยนี้เน้นถึงการตรวจหาและบำบัดสารเคมีอันตรายในน้ำเสียจากโรงงานน้ำยางข้น (*Hevea brasiliensis*) ในส่วนของการตรวจหาสารเคมีอันตรายในน้ำนั้น น้ำเสียจะถูกสกัดโดยวิธีสกัดด้วยของเหลว (liquid-liquid extraction) และการสกัดด้วยเฟสของแข็ง (solid-phase extraction) ก่อนที่จะถูกแยกออกเป็นส่วนย่อยหลายส่วนและระบุชนิดของสารด้วยเครื่องโครมาโตกราฟชนิดแยกสารตามขนาดโมเลกุล (size exclusion chromatography) และเครื่องก๊าซโครมาโตกราฟแมสสเปกโตรมิเตอร์ (GC-MS) ตามลำดับ น้ำเสียก่อนและหลังบำบัดด้วยระบบบำบัดของโรงงานจะถูกติดตามตรวจสอบเป็นระยะเวลา 6 เดือน โดยครอบคลุมทั้งฤดูเก็บเกี่ยวและฤดูยางผลัดใบ จากผลการทดลองพบว่า น้ำเสียประกอบด้วยสารเคมี 7 กลุ่มหลัก คือ acid, indoles, phthalates, alcohols และ phenols, thiazoles, thiocabarmates และ กลุ่มสารอื่นๆ สารสองอันดับแรกที่มีปริมาณมากที่สุดคือ 3-methylindole (3MI) และ diisobutyl phthalate (DIBP) โดยที่ 3MI จะเป็นสารที่มีกลิ่นเหม็น ขณะที่ DIBP เป็นสารที่ไม่สามารถย่อยสลายได้ด้วยวิธีทางชีวภาพ ทำให้น้ำเสียที่ผ่านการบำบัดแล้วของโรงงานยังคงมีค่า COD เกินค่ามาตรฐานน้ำทิ้ง ดังนั้นการบำบัดน้ำเสียด้วยวิธีเฟนตัน (Fenton's treatment) จึงถูกนำเสนอในงานวิจัยนี้ น้ำเสียสังเคราะห์ของ 3MI และ DIBP ถูกเตรียมและหาสภาวะที่เหมาะสมของการบำบัด จากผลการทดลองพบว่า สภาวะที่เหมาะสมของ DIBP และ 3MI คือ 5:5:1 และ 1:1.5:1 $[H_2O_2]:[Fe^{2+}]$:[สาร] และ pH 3 อย่างไรก็ตาม เมื่อนำสภาวะที่ได้จากน้ำเสียสังเคราะห์ไปทดสอบกับน้ำเสียจากโรงงานอุตสาหกรรมจริงพบว่า %การย่อยสลายที่ได้จากน้ำเสียจริงน้อยกว่าน้ำเสียสังเคราะห์มาก ดังนั้นจึงได้ทำการกำหนดหาสภาวะที่เหมาะสมในการดำเนินการใหม่สำหรับน้ำเสียจากโรงงานจริง จากผลการทดลองพบว่า สภาวะที่เหมาะสมสำหรับน้ำเสียก่อนเข้าระบบบำบัดของโรงงานคือ 20:10:1 $[H_2O_2]:[Fe^{2+}]$:[3MI] ให้ %การย่อยสลาย 3MI เกือบ 100% ในเวลา 180 นาที และยังเพิ่มค่า biodegradability index ขึ้นประมาณ 0.1 ดังนั้นจึงสรุปได้ว่า การบำบัดด้วยวิธีเฟนตันเหมาะสำหรับใช้เป็นระบบบำบัดเบื้องต้นก่อนเข้าสู่ระบบบำบัดแบบชีวภาพ สำหรับน้ำเสียที่ผ่านการบำบัดด้วยระบบบำบัดของโรงงานนั้นจะมีสภาวะที่เหมาะสมสำหรับเฟนตัน คือ 617 mg L^{-1} $[H_2O_2]$, 70 mg L^{-1} $[Fe^{2+}]$ และ pH 3 โดยบำบัด DIBP และ COD ได้ 90% และ 48% ตามลำดับนอกจากนี้ยังได้มีการกำหนดสมการทางจลนพลศาสตร์ของการบำบัดโดยวิธีเฟนตันเพื่อเป็นประโยชน์ต่อไป

สาขาวิชา การจัดการสิ่งแวดล้อม (สหสาขา)
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ลายมือชื่อนิสิต..
ลายมือชื่ออาจารย์ที่ปรึกษา...........................
ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.......................

4589675020 : MAJOR ENVIRONMENTAL MANAGEMENT
KEY WORD: PARA RUBBER / CONCENTRATED LATEX / CHARACTERIZATION/ WASTEWATER / FENTON TREATMENT

WORAWIT WONGNIRAMAIKUL: CHARACTERIZATION AND FENTON TREATMENT OF HAZARDOUS ORGANIC SUBSTANCES IN PARA RUBBER INDUSTRIAL WASTEWATER IN SOUTHERN THAILAND. THESIS ADVISOR: ASSOC. PROF. PROESPICHAYA KANATHARANA, Ph.D., THESIS CO-ADVISOR: PROF. CHIH-HSIANG LIAO, Ph.D., 206 pp.

This study focuses on the characterization and treatment of the hazardous organic substances in rubber latex *(Hevea brasiliensis)* wastewater. In the characterization part, the organic substances in wastewater were extracted by liquid-liquid extraction (LLE) and solid-phase extraction (SPE) their separation and identification by size exclusion chromatography (SEC) and GC-MS, respectively. The variations of the raw and treated wastewater quality were monitored for 6 months, covering the cropping and leave shedding season. According to the monitoring results, there are 7 organic groups contained in the raw wastewater such as acids, indoles, phthalates, alcohols and phenols, thiazoles, thiocarbamates and the others. Two dominant species in the raw wastewater were 3-methylindole (3MI) and diisobutyl phthalate (DIBP). The first compound, 3MI, belongs to the category of bad smelling property, while the second is recalcitrant to biodegrade. Both cause the problems the para rubber industry suffers frequently, including the malodor and the effluent COD exceeding the standard value. Because of this, Fenton's treatment was proposed in this study. The synthetic wastewater of each compound was prepared and treated by Fenton's reagent. The optimum operating conditions were determined. The results show that the optimal molar ratio of [H_2O_2]: [Fe^{2+}]: [DIBP or 3MI] is 5:5:1 for DIBP, and 1:1.5:1 for 3MI, given the pH of 3. With such information available, the optimum conditions were applied to the industrial wastewater, and the results of which were compared with those of the synthetic wastewater. According to the experimental results, there were significant differences in %degradation between the synthetic and the real wastewater. Consequently, the operating condition of both industrial raw and treated wastewater were re-optimized. The results show that the optimum condition for the raw wastewater was 20:10:1 for 3MI at pH 3, while the optimum values for treated wastewater were 617 mg H_2O_2 L^{-1} and 70 mg Fe^{2+} L^{-1} at pH 3. Under these conditions, the 3MI in the raw wastewater could be removed nearly 100% in 180 min, and the biodegradability index was increased by 0.1, approximately. Therefore, the Fenton's oxidation is recommended as pretreatment system for the subsequent industrial biological treatment. The DIBP and COD in the treated wastewater could be removed by 90% and 48%, respectively under the optimum condition. These are enough to meet the discharge. In addition, the empirical kinetic equations with respect to Fenton treatment were also determined for further application.

Field of study Environmental Management	Student's signature ....Worawit W..........
(Inter-Department)	Advisor's signature ....
Academic year 2006	Co-advisor's signature

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NOMENCLATURES

3MI	3-methylindole
[3MI]	Concentration of 3-methylindole
A	Accidental compound (appeared <80% of analyzed samples)
AOPs	Advanced Oxidation Processes
AU	Absorbance Unit
BOD_5	Biochemical oxygen demand
CO_2	Carbon dioxide
COD	Chemical oxygen demand
CZE	Capillary zone electrophoresis
C	Chronic compound (appeared >80% of analyzed samples)
$C_{3MI,0}$	Initial concentration of 3-methyl phthalate
$C_{Fe2+,0}$	Initial concentration of ferrous ion
$C_{DIBP,0}$	Initial concentration of diisobutyl phthalate
$C_{H2O2,0}$	Initial concentration of hydrogen peroxide
CH_2Cl_2	Dichloromethane
Cs	Analyte concentration in the extract solvent
C_w	Analyte concentration in aqueous phase
^{O}C	Degree Celsius
D	Partition coefficient
DCM	Dichloromethane
DIBP	Diisobutyl phthalate
[DIBP]	Concentration of diisobutyl phthalate
DEP	Diethyl phthalate
DMP	Dimethyl phthalate

$\left(\frac{d[DIBP]}{dt}\right)_{initial}$	Initial reaction rate of diisobutyl phthalate
$\left(\frac{d[3MI]}{dt}\right)_{initial}$	Initial reaction rate of 3-methylindole
E	Extraction efficiency
EPA	Environmental protection agency
F	Frequency compound (appeared 50-80% of analyzed samples)
Fe^{2+}	Ferrous ion
$[Fe^{2+}]$	Concentration of ferrous ion
Fe^{3+}	Ferric ion
$[Fe^{3+}HO_2]^{2+}$	Peroxo complexes
$Fe(OH)_3$	Ferric hydroxide
GC	Gas chromatography
GC-ECD	Gas chromatography coupled with electron capture detector
GC-MS	Gas chromatography coupled with mass spectrometry
H^+	Hydrogen ion
H_2SO_4	Sulfuric acid
H_2O_2	Hydrogen peroxide
$[H_2O_2]$	Concentration of hydrogen peroxide
HCl	Hydrochloric acid
He	Helium
HO_2^-	Perhydroxyl ion
L	Tubular length
m^3 ton production^{-1}	Cubic meter per ton of production
mg L^{-1}	Milligram per litter
nm	Nanometer
O_2	Oxygen

$\bullet OH$	Hydroxyl radical
$HO_2\bullet$	Hydroperoxyl radical
H_2O	Water
H_2O_2/UV	Hydrogen peroxide combined with ultraviolet
HPLC	High performance liquid chromatography
in. Hg	Inch of mercury
k	overall rate constant
k_{3MI}	apparent rate constant depending on initial 3MI concentration
k_{DIBP}	apparent rate constant depending on initial DIBP concentration
k_{Fe2+}	apparent rate constant depending on Fe^{2+} concentration
k_{H2O2}	apparent rate constant depending on H_2O_2 concentration
km^2	Square kilometer
LC-MS	Liquid chromatography coupled with mass spectrometry
LLE	Liquid-liquid extraction
NaOH	Sodium hydroxide
OH^-	Hydroxide ion
PVC	Polyvinyl chloride
ΔP	Pressure gradient including gravitational force
Q	Volume flow rate
R	Tubular radius
$R\text{-}CO_2^-$	Negative carboxylate
SEC	Size exclusive chromatography
SFE	Supercritical fluid extraction
SO_4^{2-}	Sulfate ion
SPE	Solid-phase extraction
SPME	Solid-phase microextraction

SS	Suspended solids
STR	Standard Thai Rubber
TOC	Total organic carbon
μ	Fluid viscosity
μL	Microlitter
UV	Ultraviolet
V_r	Volume ratio

CHAPTER I

INTRODUCTION

1.1 Research rationale

Para rubber (Hevea Brasiliensis) is one of the leading economic crops of Thailand, which is widely planted in southern Thailand (Rubber Research Institute of Thailand, 1999). Thailand has been the number one producer of the natural rubber of the world since 1991 (Thailand Office of Industrial Economics, 2004). The export value as a raw material in 2006 was about 5.39 billion U.S. dollar with the growth rate up to 45.4%, compared with that of the previous year (Ministry of Commerce Thailand, 2007). There are over 900 of rubber-based factories in the country and a government's policy is expected to expand to other regions of Thailand in the near future according to continue huge demand of the rubber in the world's market. (Department of Industrial Works, 2007). These rubber-based factories produce various types of rubber products, *e.g.* Standard Thai Rubber (STR), ribbed smoked sheet, air dried sheet, skim rubber, concentrated latex and others. Among these, the concentrated latex, which is the upstream raw material of other industries, was selected for this research. Since this rubber industry consume a large volume of raw water through their manufacturing process including the cleaning of container, floor and equipments. This water will become the wastewater in the long run. The wastewater is contaminated with both organic and inorganic substances originating from the rubber and the chemical additives with very high loading (Chaisuksan *et al.*, 2005). Several environmental problems will be generated, if management is poor or inefficient. One of the frequently found problems is an obnoxious odor (Wittayakul, 2001). Regardless of toxicity, it causes a factory suffering from a complaint of the neighboring communities. In general, it is believed that sources of the unpleasant smelling are ammonia which is added as a rubber preservative agent and hydrogen sulfide derived from an anaerobic degradation of the high sulfate concentrated wastewater. Most research works merely focus on the reduction of these well-known malodorous substances (Rakkoed *et al.*, 1999; Wittayakul, 2001). However, Rucksapram (1996) found the correlation between hydrogen sulfide concentration and the level of wastewater odor is low and the smelling is possibly caused by other components in wastewater. Thus, it is interesting to identify those culprit compounds in order to solve the odorous problem properly. Another problem of concentrated latex industry is the effluent COD exceeding the industrial effluent standard. In agreement of our preliminary study, Rakkoed *et al.* (1999) presented that the discharge COD from 3 concentrated latex factories was in the range of 119-546 mg L^{-1}, compared to the industrial effluent standards of Thailand as for COD less than 120 mg L^{-1}. This indicates the need of some improvements in treatment system to make the effluent meet the standard regulation. Since the industrial treatment system relates to a biological treatment, the effluent is full of compounds recalcitrant to biodegradation. These compounds are worth to be identified in order to determine the proper improvement of treatment system.

This research was not only conducted to serve such needs, but it was also expanded the interest to other hazardous organic substances in wastewater. The study was divided into two major parts, the characterization the wastewater from the Para rubber industry and the treatment of the dominant species in the wastewater. The characterization was performed in order to identify the hazardous organic compounds in wastewater that obviously included the malodorous and non-biodegradable compounds. The study results also provided the basic information for further wastewater management. Moreover, this would offer the possible sources of each organics found in the wastewater and would be useful for the reduction of pollutants right at the sources. By using the information from the characterization, the industrial problems caused by the dominant species in the wastewater, including odor and high effluent COD, would be then solved by the proposed treatment technologies. The Fenton’s treatment was selected in this research, because it is fast degradation reaction and high oxidation potential, which can oxidation various kind of compounds (Lucas and Peres, 2006). Hence, this could solve both problems of the odor, and the COD exceeding the industrial effluent standard.

1.2 Objectives

The main objective is to identify hazardous organic substances in the wastewater from Para rubber (*Hevea brasiliensis)* industries located in the southern Thailand and treat found dominant species by Fenton's treatment.

There are four aspects of this research:

1. Characterization of the hazardous organic compounds, especially bad smelling and non-biological compound, in wastewater from the Para rubber industry.
2. Identification of the sources of the organic pollutants.
3. Optimization of the Fenton's operating conditions for the major hazardous organic compounds, which causes odor and COD problem, of the Para rubber wastewater treatment.
4. Study of the Fenton's reaction kinetics of the major hazardous organic compounds.

1.3 Hypotheses

The hypotheses of this research are based on:

1. The hazardous organic substances in the wastewater from Para rubber industry can be characterized by extracting according to polarity and then separating according to their molecular weight by using size exclusion chromatography and identifying them by gas chromatography coupled with mass spectrometry.
2. The major hazardous organic substances that cause odor and effluent COD problem can be treated by the Fenton's treatment.

1.3 Scopes of work

The work of this research included:

1. Wastewater samples collection from Para rubber industry located in the southern Thailand.

2. Characterization of hazardous organic substances dissolved in wastewater by any suitable physical, chemical or instrumental method.
3. Characterization of the hazardous organic compounds that have boiling point lower than 300 ^{O}C.
4. Use of the Fenton's process for the treatment of dominant species identified from the previous characterization study.

1.3 Advantages of this work

As it is expected, this research is contributed the following two aspects:

1. Providing the information of the wastewater characteristics that is useful for the further wastewater management.
2. Mitigation of the problem of the bad smelling and improvement of the effluent quality required by the environmental regulations by using the Fenton's method.

CHAPTER II

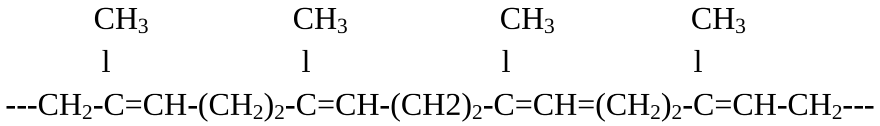
BACKGROUND AND LITERATURE REVIEWS

2.1 Natural Rubber

The natural rubber was first found by French C.F. Fresneaw at Brasil in 1747. It can be called in many names; for example, Hevea brasiliensis as the formal name, Sereingue in Protugese, Kautschuk in German, Cauchue in Spainese or Cahouchu in French. However, the most widely use is Para rubber tree, which comes from the name of the city where it is first exported to others part of the world. It was taken into Thailand in 1899 by Praya Rassadanupradit, the governor of Trang province (Ruengnarong, 1995). Since that, the Para rubber has become the important economic crops of Thailand. Thailand is the world largest exporter since 1991. (Thailand Office of Industrial Economics, 2004). One-third of the world's natural rubber is produced from Thailand. Out of 2.72 million ha of the peninsular area, 1.67 million ha are used for the rubber plantation, where most of them are cultivated in Suratthani (2660 km^2), Songkhla (2640 km^2), Nakornsrithammarat (2250 km^2) and Trang province (1695 km^2). This makes Southern Thailand is the single largest rubber plantation region in the world. (Krukanont and Prasertsan, 2004). The rubber latex can be used as the raw material in the manufacturing of more than 40,000 customer products, *e.g.* tire, glove, condom, belt, balloon, mattress, gasket and slipper (Cornish *et al.*, 2001).

The natural rubber latex is defined as a milky colloidal system of the hydrocarbon particle dispersed in the aqueous serum. Its density is in the range of 0.975-0.98 g cm^{-3} and pH is varied between 6.5 and 7.0 (Buakaew, 1988). The rubber latex can be divided into 2 main phases:

1) Rubber phase: It is a spherical shape of the hydrocarbon called *cis*-1,4 polyisoprene $(C_5H_8)_n$ (n=2,000-5,000 units per molecule). The molecular structure is as follows: (Ver haar, 1979)



$$---CH_2-\overset{CH_3}{\overset{|}{C}}=CH-(CH_2)_2-\overset{CH_3}{\overset{|}{C}}=CH-(CH2)_2-\overset{CH_3}{\overset{|}{C}}=CH=(CH_2)_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2---$$

The surface of the rubber particle is enveloped with phospholipids and proteins such that the phospholipid links between the inner hydrocarbon and outer protein layer (Kowuttikulrungsri, 1997). The protein layer plays an important role in preventing the combination of each rubber particle. The rubber still exists in the liquid form by the pushing between the negative carboxylate ($R-CO_2^-$) of the protein layer. Consequently, the rubber latex loses its liquid property due to the destruction of protein or/and the negative carboxylate, such as the dehydration in the protein layer. This causes the rubber particle is merged into a bigger particle or called the coagulum, and then it will separate from the serum. In addition to hydrocarbon (66%), protein (1%) and lipid (3%), the rubber particle contains the water (10%), magnesium, potassium and copper (0.05%) (Srisuwan, 1996).

2) Aqueous phase or serum: it consists of many compounds, *e.g.* carbohydrate and protein. Most of carbohydrate is L-methylinositol. Other carbohydrates are sugars, for example, glucose, sucrose, fructose, and galactose. When oxidized, they become volatile fatty acids, *e.g.* formic acid, acetic acid and propanoic acid. For Protein and amino acids, most of them are α-glubolin and hevelin. Moreover, the serum contains methylamine, organic acid, phosphate, carbonate, potassium, magnesium, iron, copper, cyanide, thiols, etc. (Kajornchaikul, 1982).

Furthermore, the non-rubber solids, which are lutoids and Frey-Wyssling particles, also present in the natural latex (Sethuraj and Matthew, 1992). These intracellular vesicles and organites play an important role in latex coagulation apart from their other biochemical functions such as pH control (Gazeley *et al*., 1988).

2.2 Production process of the Para rubber

Since this research related to the concentrated latex, skim crepe and rubber block industry, only 3 types of industry were mentioned.

2.2.1 Concentrated latex

The field latex contains about 25 –45% of dry rubber content. It would not be suitable if it is transferred to the factory in a long distance. Moreover, some substances in the latex might adversely affect to the quality of the rubber product. Therefore, the concentrated latex is essential to a whole rubber industry. In general, the fresh latex will be concentrated to approximately 60% dry rubber content. There are 4 methods to produce the concentrated latex, *i.e.* the electrodecantation, evaporation, creaming, and centrifugation (Buakaew, 1988).

- Electrodecantation: As mentioned previously, the rubber particle is surrounded by carboxylate anions ($R\text{-}CO_2^-$). This implies that the rubber particle can be separated from the serum by applying the electricity to the latex. It moves to the anode and then floats to the latex surface with its density lower than the serum. However, this method is not commercially practical, because it is complicated and expensive.
- Evaporation: A stabilizer, such as potassium soap, is added into the fresh latex before it is taken to a rotating container. The part of water in the latex is evaporated by heating the container. The rubber concentration will be increased to 60%. This method provides the very good stability of the concentrated latex. It is proper to transfer the latex in a long distance, and to the rubber product needed the high stability, *e.g.* latex-cement.
- Creaming: Because the density of the rubber particle is lower than the liquid serum, it trends to move to the latex surface. According to the Stokes' law, the rate of the movement depends on the size of the particle. The bigger particle, the higher motion rate. The particle size can be increased by the addition of creaming agents, *e.g.* sodium aliginate, locust bean gum, gum Karaya, gum tragacanth. These agents will coat on the rubber particle and make it float to the latex surface before it will be separated from the serum. However, this method is not popular, because of its complication and time consuming.
- Centrifugation: Another way to increase in the particle movement is the centrifugation. It increases the gravitation force about 2,000-3,000 times. There are many types of equipment, but the most popular is de Laval type.

Fig. 2.1 shows the centrifugal equipment Alfa-Laval (Model LRH 410). The latex is fed into the top of the device (1) and then adjusted the feeding volume by the distributor (2) before sent to inside. By the centrifugal force, the latex is moved through the separator disc (3) where two fractions of the latex are separated from each other, *i.e.* the upper cream phase (5) and the lower skim phase (6). The cream phase is abundant with the rubber content, so it is sold as the concentrated latex. Although the skim phase is full of the serum, it has still contained the residual rubber as much as 10% (Rippel *et al.*, 2003). It can be value-added by passing to the coagulation process. After the coagulation by the acid addition, the skim crepe will be produced for sale as the other form of the rubber raw material.

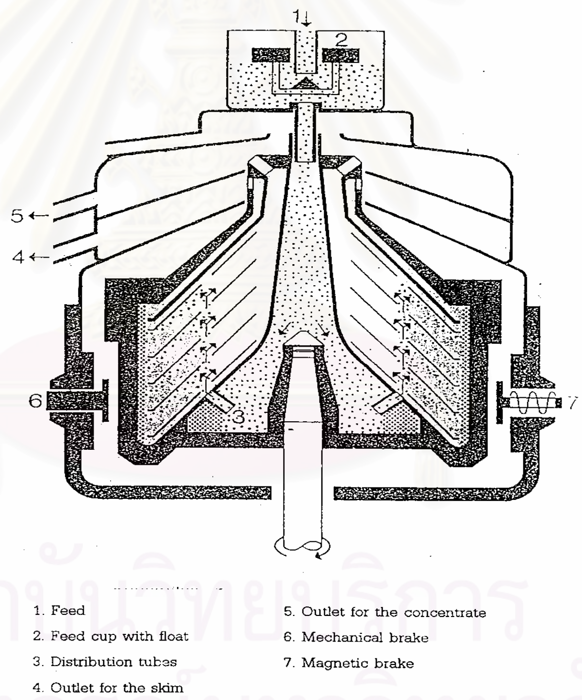


Figure 2.1 Longitudinal section of the centrifugal equipment (Kaew, 1997)

The last method is the most important, because it is only one process used in Thailand (Kajornchaikul, 1988). Like many other biotic liquids, it is apt to deteriorate rapidly, if left without preserved. Several factors have been proposed to explain the spontaneous destabilization (Blackley, 1997).

- The development of acidic environment due to bacterial activity. The isoelectric point of the natural rubber latex is around 3.9 to 4.6, depending on the type of proteins found on the surface of the latex particle. Therefore, the coagulation can be taken place when the pH falls below 5.

- The interaction of absorbed volatile fatty acid anions with multivalent cations. These anions (formate, acetate, and propionate) are produced by bacterial oxidation of the carbohydrates in the serum.
- The aggregation by cationic protein and attack by enzymes from the lutoid serum. The lutoid serum can release a host of inorganic cation (Na^+, K^+, Ca^+, Mg^+) as well as cationic proteins that can destabilize the rubber latex particles. The serum also contains enzymes (protease and phospholipase) that can attack the protein-phospholipid complex, which forms the protective envelope of the rubber particle.

It can be noticed that the degradation of bacteria is important to the stability of the rubber latex. The bacteria can be contaminated from the bark of tree, the latex container, or the atmosphere. In general, the ammonia is added into the freshly trapped latex as a preservative against bacterial attack. Moreover, it also provides the long-term stability through the hydrolysis of the phospholipids to the fatty acid soaps. In fact, the added ammonia might defect to some final rubber products, so the preservatives can be used in forms of the mixture between the ammonia and other chemicals, such as diamonium hydrogen phosphate, zinc oxide and tetramethyl tiuram disulphide. Furthermore, some chemicals may be added to the concentrated latex after centrifugation to prevent the coagulation and to build up the required stability, *e.g.* lauric acid and sodium sulfide.

2.2.2 Skim rubber

The skim rubber is the by-product from the production of the concentrated latex. After the centrifugation, the low rubber fraction is separated and sent through pipeline to the skim rubber process. The coagulation of the skim latex can be either spontaneous or through the acidification by sulfuric acid (H_2SO_4). It is important that the ammonia content must be kept as low as possible. At high ammonia content, the spontaneous coagulation would take too long time and the acidic coagulation would require a large amount of the acid, which is uneconomical. This is because the high number of ammonia leads to the high pH of the latex. The method used to mix the rubber with the acid depends on the factory. After the acid addition, the rubber coagulum endures several steps to eradicate the water inside. Then, it may be either pressed to produce the skim block or creep through a pair of driven rolls to create the skim crepe before is sold to the customer.

2.2.3 Rubber block

The rubber blocks can be divided into many types. The Rubber Research of Thailand (1999) has specified 6 different grades of STR rubber block, which are STR5L, STR5CV60, STR10, STR10CV, STR20 and STR20CV. The STR5L and STR5CV60 are made from the latex coagulate, while others are made from the non-smoked sheet. Each type is different in the composition and property, *e.g.* the dirt, ash, nitrogen, color and initial plasticity. However, the key parameter is the dirt content to ensure that only rubber of the guaranteed cleanliness is within a given consignment of STR. The production process of rubber block starts with the filter of the impurity from the fresh latex. Different chemical composition is added to the latex depending to types of the final product. The latex is then poured on a series of the long mold and the formic acid is added to coagulate the rubber particle. After the chemical reaction, the latex will change its status from the liquid to the solid in approximately 12 hours and the thick sheet rubber is obtained. Next, it will be transformed to thin sheet rubber by the creeper machine before cut to the small pieces of 2 -3 mm. by the shredding machine. Then, the small pieces of the rubber will be dried in the 110 ^{O}C oven to form the rubber blocks. Each block is weighed and set to the desired mass. After that, the finished rubber block or STR is enveloped by the plastic film. Finally, the package is reinforced by a wood container to protect the deformation of the rubber during a transport and it is easy to handle as well (Thai Hua Public Co., Ltd., 2007).

2.3 Characteristic of wastewater from Para industry

The rubber industry is one type of industries consuming thousands of tons of the raw water. The principal water usages are for the production process, floor washing, equipment cleaning and domestic purposes. According to Leong *et al.* (2003), the water consumption of the 40 ton/d STR20L factory comprises 149 m^3/d of the office and domestic purpose, 126 m^3/d of cleaning, 2525 m^3/d of the production process, 484 m^3/d of the wet scrubber and 63 m^3/ d of the backwash. All of them become the wastewater at the long run. The wastewater is contaminated with the different kind of impurities including the rubber fragments and chemicals. This causes the wastewater contains with the high organic loading. Kaewyod (1997) investigated the wastewater from nine concentrated latex plants and found the BOD_5 of the concentrated latex wastewater is varied in the range of 1,825- 3,766 mg L^{-1}. The SS is 1,082- 3,130 mg L^{-1} and pH is 8.56- 9.40. In addition, the skim crepe wastewater was also investigated and found that the BOD_5, SS and pH are between 6,533- 14,566 mg L^{-1}, 456- 933 mg L^{-1} and 1.87- 6.87, respectively. The STR5L possesses the 3,675-4,316 mg L^{-1} BOD_5, the 449- 975 mg L^{-1} SS and the 4.16- 5.47 pH. In the same year as Kaewyod, Inthamanee (1997) found that the COD of the skim crepe wastewater is around 25,000- 35,000 mg L^{-1}, while Srisuwan (1997) found the BOD_5 of the integrated wastewater is about 12,000- 18,000 mg L^{-1} and pH is 3-5. In addition to the high organic loading, the latex industry generates the high sulfate wastewater of 350-400 mg L^{-1} (Rucksapram, 1996). The TKN is in the range of 455- 1,686 mg L^{-1}, which comprises the org-N of 101- 738 mg L^{-1} and the NH_3-N of 354- 948 mg L^{-1} (Rakkoed *et al.*, 1999).

Agreed with the 9 plant studies (Kaewyod, 1997), Rakkoed *et al.* (1999) found that the wastewater treatment system of 3 latex factories are the pond system, such as anaerobic, facultative and aerobic ponds as well as aerated lagoon. They generate the treated effluent with the characteristics: pH = 7.93- 8.99, COD = 119- 546 mg L^{-1}, BOD_5 = 26- 78 mg L^{-1}, SS = 80 -316 mg L^{-1}, TKN = 17-324 mg L^{-1}, org-N = 7- 61 and NH_3-N = 5- 263 mg L^{-1}. As required by the Thailand industrial effluent standard, the BOD_5 and COD must be less than 20 mg L^{-1} and 120 mg L^{-1}, respectively. Furthermore, the SS and TKN concentrations have to be less than 50 and 100 mg L^{-1}, respectively (Pollution Control Department, 2006). Compared with these standards, it can be seen that the effluent from the concentrated latex factories does not meet the effluent standard criteria. Thus, the improvement in the treatment performance should be further studied.

2.4 Wastewater characterization

As the discharge standard become increasingly more stringently throughout the world, treatment processes become more complex and often are not limited to a single-stage treatment, but consists of a chain of various biological, chemical and physical processes. Generally, the water quality is indicated in terms of global parameters such as total oxygen demand (TOD), chemical oxygen demand (COD), biological oxygen demand (BOD) and total organic carbon (TOC). Those non-specific parameters provide only limited information on the nature of the organic substances in the wastewater. Consequently, they are not suitable to use to design the treatment system serving the stricter standard, especially the large variety organic wastewater (Panzer and Komanowsky, 1985). To get the best treatment system, the information about the wastewater should be obtained as mush as possible. One way to serve this need is the characterization of the wastewater. Indeed, the characterization is used to identify organic matter refractory to removal by biological processes, which will remain the core of wastewater treatment, to improve existing processes, optimize secondary and/or tertiary treatment process, and meet discharge criteria or reuse water standards. In the past, the characterization is performed by many researchers for various purposes. For example, Puig *et al.* (1996) characterized the river water in Spain and 46 compounds were identified. After that, they also sought the origin of those compounds by means of the characterization of water samples collecting from many sites along the river. The results was shown that majority of compounds come from the factory of rubber additives located 180 km upstream. Due to the stability of pollutants to biological treatment, the ozonation was subjected to factory effluent to help the factory solving this environmental problem. This is the good example to use the characterization to real situation, not only laboratory scale. Eight years later, another similar work was done. Dsikowitzky *et al.* (2004) identified organic pollutants in Germany river by using the GC/MS-screening analysis. Most of the detected compounds are contributed as the anthropogenic input. They are used as plasticizers, flame retardants, pharmaceutical drugs or fragrances. Like Puig's work, the input pathways of the detected compounds were traced back by sampling 5 input sources of organic matter. Several contaminants are ubiquitous in the river and also occurred in the sewage effluent from a municipal sewage treatment plant. In addition to the surface water, the characterization could be applied to the industrial case as well. Reemtsma and Jekel (1997) used GC/MS screening analysis to determine 12 substances classes in a high organic load tannery wastewater; fatty acids, short chain carboxylic acids, aliphatic dicarboxylic acids, cyclohexanes, aromatic carboxylic acids, aliphatic hydroxylated carboxylic acids, aromatic hydroxylated carboxylic acids, phenols, alcohols, indoles, ethoxylates and others. Based on the characterization study, the pilot-scale treatment system applied with the wastewater so order to investigate the treatment efficiency of each compound group on the anaerobic and aerobic treatment. Under anaerobic condition, aromatic compounds are poorly removed. Incompletely removed and reproduced substances are of equal importance in anaerobic treated tannery wastewater. New substances comprise up to 25% of anaerobic effluent. In contrast, aerobic processes are clearly directed towards mineralization and are effective against all substances classes. In addition to the widely use with the industrial wastewater (Jungclaus *et al.*, 1976; Jungclaus *et al.*, 1978; Castillo *et al.*, 2001), some researchers have extended the characterization study to the landfill leachate (Castillo and Barceló, 2001) and municipal wastewater (Paxéus, 1996; Görgün *et al.*, 1999; Grung *et al.*, 2007) as well. Besides the direct advantage of the characterization, which is to determine toxic pollutant in the wastewater, it could be applied for other purposes. For instance, Quesnel and Nakhla (2005) characterized the effluent obtained from granular activated carbon (GAC) and a conventional activated sludge (CAS) treatment. The organic characterization was used as a tool to compare the treatability of both processes. Although both systems can remove the dissolved organic carbon (DOC) similarly, the difference is shown in terms of the organic kind. While GAC is able to attain better effluent concentrations of toluene and methyl isobutyl ketone (MIBK), the CAS is much more efficient for acetone removal.

The procedure in the characterization study usually begins with the sample collection. A good sample must be representative of a whole wastewater so that the final result represents the entire system that it is intended to present (Hoenig, 2001).

As widely known, samples collected at a particular place and time are called a “grab or individual sample”. This type of sample represents conditions at the certain time it is collected. Therefore, a grab sample should not be used as a basis for a decision about the pollution abatement. If results for an entire system have to be reported, a series of smaller samples are collected in a single container and blended for analysis. The mixing process averages the variations in sample composition and minimizes analytical effort and expense. This type of samples is called “composite sample”. (Csuros, 1997). The sampling pattern can be whatever random, systematic, judgmental or continuous sampling (Kebbekus and Mitra, 1998) depending on the resources and data needed. After the sampling, the next step is the sample preparation. It is one of most important steps in the analytical science procedure. About 60-80% of the work activity and operating cost in the analysis is spent to prepare samples for the introduction into analytical system or instrument of detection. Frequently, it has been observed that the components of interest present in traces levels too low to be detected easily by the analytical instrument. Hence, it needs to pre-concentrate (Smith, 2003). In many cases, the analytes are present in either biological or environmental matrices that are too complex and often contain interfering elements, which can mask or disturb with analysis of the interest components such that direct analysis may not be possible. Therefore, sample preparation is without doubt a prerequisite step to the sample analysis (Msagati and Nindi, 2006). Sample preparation for environmental samples might either solid-phase microextraction (SPME), supercritical fluid extraction (SFE) or membrane-based extraction (MBE) (Kataoka, 2003). Among them, two extraction methods are currently popular for the environmental water samples in the research and commercial work, *i.e.* a liquid-liquid extraction (LLE) and solid-phase extraction (SPE) (Mitra, 2003).

2.4.1 Liquid-liquid extraction (LLE)

Liquid-liquid extraction is traditionally one of the most popular methods of extraction, particularly for organic compounds from aqueous matrices. Organic substances in solution or liquid samples can be extracted by direct partitioning with an immiscible solvent. LLE is based on the relative solubility of analytes in two immiscible phases and is governed by the equilibrium distribution coefficient. (Ridgway *et al., article in press*).

$$D = \frac{C_S}{C_W} \qquad (2.1)$$

Where D is the partition or distribution coefficient

C_S and C_W are the concentration in the solvent and aqueous phase, respectively (Kebbekus and Mitra, 1998)

Because the extraction efficiency is achieved by the differences in solubilising power (polarity) of the two immiscible liquid phases, various organic solvents can be used, including pentane, hexane, diethyl ether, ethyl acetate, chloroform and methylene chloride (Pedersen-Bjergaard *et al.*, 2000). To get the solvent polarity matched with the interested analyte, the mixture of various solvent might be sometimes applied (Mamidipally and Liu, 2004). Typically, LLE is carried out in a separating funnel and the two immiscible phases are mixed by shaking and then allowed to separate. To ensure the complete extraction of an analyte into the required phase, repeat extraction may be preferable (Ridgway *et al., article in press*). The successful LLE relies on a pre-concentration step to obtain high analyte concentrations in the final solution. Normally, the extract (organic phase) is then evaporated to dryness and the residue is reconstituted in the small volume to ensure a high analyte enrichment. For practical reasons, the volume of reconstitution is normally in the range 50- 500 µL. Thus, when the amount of sample is limited to, e.g. 1 mL, the maximum theoretical analyte enrichment factor is in the range 2- 20 (with 100% extraction efficiency) (Pedersen-Bjergaard *et al.*, 2000). Once in the blue moon, the mixing between the extract solvent and water sample might generate an emulsion. To avoid it, in some case, a salt may be added and centrifugation can be used if it is necessary (Ridgway *et al., article in press*).

Even through the modern tendency is to replace LLE by other techniques, its advantage of the low cost and simplicity, several researches have still used the LLE as shown in Table 2.1.

Table 2.1 Selected researches using LLE as the extraction method

Analytes	Sample Matrix	Extract Solvent	Analysis	Ref.
81 acidic drugs, *e.g.* paracetamol, salicylic acid, coumarin, chloramphenicol, barbitone, phenacetin, sulphanilamide	Blood	Ethyl acetate	GC-FID and HPLC-DAD	Lo *et al.* (1997)
Fulvic and humic acids	Landfill Leachate	Diethyl ether	GC-MS	Göbbels and Pűttmann (1997)
Trihalomethanes	Tap water and drinking water	Pentane	GC-ECD	Gibbons and Laha (1999)
Amphetamine, methamphetamine, ecstasy and derivatives (MDMA, MDA, MDE), methadole and 2-ethylidene-1,5-dimethyl-3,3-diphenylpyrrolodine (EDDP)	Urine	CH_2Cl_2 and $C_2H_4Cl_2$	CZE	Ramseier *et al.* (1999)
Trihalomethanes, haloacetonitriles, haloketones, chloral hydrate and chlorociprin	Drinking water	Methyl-*tert*-butyl ether (MTBE)	GC-ECD and GC-MS	Nikolaou *et al.* (2002)
Trihalomethanes and volatile chlorination by-products	Surface water	Methyl-*tert*-butyl ether (MTBE)	GC-ECD and GC-MS	Nikolaou *et al.* (2004)

Table 2.1 Selected researches using LLE as the extraction method (cont.)

Analytes	Sample Matrix	Extract Solvent	Analysis	Ref.
Tramodal derivatives	Plasma	Hexane/ethyl acetate (80:20)	CZE	Rudaz *et al.* (2000)
Odoriferous terpenic substances	Wine	12% ethanol in water	CZE	López and Gómez (2000)
17 pesticides, *e.g.* Dichlorvos, Fenobcarb, Simazine, Diazinon-oxon, and Iprobenfos	River water	DCM	GC-MS	Hada *et al.* (2000)
21 polyphenolic compounds	Olive oil wastewater	NaCl added and extracted by ethyl acetate	GC-MS	Zafra *et al.* (2006)
Chlorinated derivatives of estrones, *i.e.* 2-chloroestrone, 4-chloroestrone and 2,4-dichloroestrone	Effluent from municipal sewage treatment plant	NaCl added and extracted by DCM	GC-MS	Nakamura *et al.* (2007)
Reactive Blue 19 Dye	Textile dyeing wastewater	DCM extracted under the acidic and basic condition	GC-MS	Rajkumar *et al.* (2007)
PAHs, benzenes, phenolics, N-, S- and O-heterocyclic compounds	Groundwater	DCM	GC-MS	Hartnik *et al.* (2007)

2.4.2 Solid phase extraction (SPE)

Solid phase extraction (SPE) is today the most popular sample preparation method (Hennion, 1999). It is a cost-effective and recognized alternative to LLE for sample preparation, purification, concentration and/or solvent exchange of solutes from solution (Wells and Yu, 2000). It is designed to overcome many drawbacks of the traditional extraction by using immiscible liquids. Unlike LLE, the SPE does not require large volume of (toxic) organic solvents, analysis times can be decreased significantly (Marcé and Borrull, 2000), a sample loss from the solvent evaporation is minimized, there are no problems with miscibility of solvents (Boyce, 2006) and no emulsion formation that diminishes the efficiency for extracting some compounds (Ruiz-Gutiérrez and Pérez-Camino, 2000). Another advantage of SPE over LLE is that it can extract some polar compounds, which cannot be extracted with good recoveries by LLE whatever the organic solvent selected (Hennion, 2000). Moreover, the analyte prepared by SPE is high stable allowing long-time storage (Alpendurada, 2000). It can be also used in both off-line and online mode (Bovanová and Brandšteterová, 2000). If automated method are used, it required very small volume of sample (50 -100 µL) (Huck and Bonn, 2000). With all advantages of SPE, it leads to the widespread adoption in many official methods, including EPA methods for analysis of some organic compounds in drinking water and wastewater (Hennion, 1999; Carson, 2000).

The principle of SPE is similar to that of LLE involving a partitioning of compounds between two phases. In SPE, when a liquid sample is passed over an adsorbent, analytes in the sample are partitioned between a solid adsorbent and a liquid sample—rather than between two immiscible liquids as in LLE—and these analytes must have a greater affinity for the solid phase than for the sample matrix (called retention or adsorption step). Compounds retained on the solid phase can be removed at a later step by eluting with a solvent with a greater affinity for the analytes (called elution or desorption step). High concentration factors can be achieved by loading large sample volumes to column and eluting the analyte in a very small solvent volume (Cichna-Markl, 2006). In modern SPE, the adsorbent is packed between two fritted disks in a polypropylene cartridge and liquid phases are passed though the cartridge either by suction or by positive pressure (gravity, gas pressure from syringe or by centrifugation). (Huck and Bonn, 2000). The experimental procedure consists of the following steps: (Poole *et al.*, 2000)

a) Activation of sorbent by passing though an appropriate solvent. This improves the reproducibility of analyte retention and reduces the carry through of sorbent impurities at elution stage (Mayer and Poole, 1994; Thurman and Mills, 1998; Fritz, 1999; Dean, 1998; Simpson, 2000).

b) Replace the activation solvent with the same solvent. De-ionized water may be used, if the sample is an aqueous sample.

c) Application of sample. The analyte will be retained by the sorbent (sorption and retention step). The flow rate of sample is an important parameter to the retention of analyte on the sorbent. This is due to the mass transfer resistance affects to the chromatographic performance of the cartridge. It does not affect the recoveries of the analytes, but also controls the analysis time (Cai *et al.*, 2003).Thus, it should be balanced between the minimal time and the amount of adsoption.

d) Removal of interfering compounds by a weak solvent. Usually, 1-2 mL. De-ionized water is used, which is assumed to be adequate to remove interferences from the sorbent column (Chen *et al.*, 1992; Chen *et al.*,1992; Zweipfenning *et al.*,1994).

e) Dry the solid sorbent by applying the vacuum and/or by centrifugation of sorbent column. Further drying can be carried out by applying a small volume (*e.g.* 50 µL) methanol or larger volume, typically 1 mL hexane followed by vacuum for about 2 min. The use of hexane has the advantage that a dry column is easily obtained, but there is a risk of partially eluting hydrophobic substances (Franke and Zeeuw, 1998). The purpose of drying step is to reduce the volume of water retained by eluting solvent. Excess water may interfere in further concentration of the elution.

f) Elution of the analytes by the small volume of suitable solvent. The eluting solvent should be strong enough to displace all analytes from the sorbent. The solvent polarity determines the solvent strength or ability to elute the analytes from the sorbent in a smaller volume than a weaker solvent

(Dean, 1998). Moreover, the flow rate of eluting solvent has to be fastest as much as possible that still yields the good sample recoveries. This typically ensures enough residence time for the eluting solvent to sufficiently interact with the sorbent.

Another important parameter to be taken into account in SPE is the selectivity of the stationary phase. To date, typical SPE materials are based on silica with functional C_{18}, C_8, CN and other groups bonded. Other materials as carbon black or poly styrene-divinylbenzene (PS-DVB) copolymers are frequently used, but all these stationary phases are generally non-selective (León-Gonzalez and Pérez-Arribas, 2000). More selective sorbents involving antigent-antibody interactions have recently produced. Antibodies produced against a target compound are immobilized on a support to form a so-called immunosorbent. The other selective sorbent is molecular imprinted polymer (MIPs) that consists in the preparation of polymers with specific recognition sites for certain molecule (Pichon, 2000). However, several studies have pointed out the specific problem with the use of these two selective sorbents, i.e. not stable at high temperature and in some pH range for immunosorbent and difficult to desorb for MIPs (Hogenboom *et al.*, 1997). The SPE sorbent can be classified into non-polar phases, polar phases, and iso-exchange phases (Lopez-Avila, 1999).The non-polar sorbents are those that contain ethyl, octyl or octadecyl functional groups bonded to the surface of silica to alter their retentive properties. Polar sorbents are unmodified silica or silica with cyano, amino and diol bonded groups. The ion-exchange phases have either cationic or anionic functional groups. Modified silica with C_{18} reversed-phase sorbent is one of the most widely used packing materials for SPE. The mechanism of retention is based on hydrophobic interactions between the solutes and the stationary phase (Vander Waals forces) and on secondary interactions such as hydrogen bonding and dipole-dipole forces (hydrophilic or polar interaction) (Ruiz-Gutiérrez and Pérez-Camino, 2000). Nevertheless, the main drawback of such sorbents is their narrow pH stability range. Consequently, when SPE has to be carried out in extremely acidic or basic media, reversed-phase polymeric sorbents (generally based on PS-DVB) are used. One of them is Oasis HLB. It is a macroporous copolymer consisting of two monomer components, the lipohilic divinylbenzene and hydrophilic *n*-vinylpyrrolidone. Thus, it is the universal extraction sorbent that can be used for the determination of polar and non-polar organic compounds from aqueous solution. Acidic, neutral and basic components can also be isolated, because of high pH-stability (pH= 1-14) and the high compatibility to organic solvents (Huck and Bonn, 2000). The retention of some analytes measured on a column packed with this polymer was higher than that obtained on C_{18} silica (Bouvier *et al.*, 1998).

Because of many advantages, the SPE was widely used by researchers in different liquid matrix. Some of them were shown in Table 2.2.

Table 2.2 Selected researches using SPE as the extraction method

Analytes	Sample Matrix	SPE Phase	Analysis	Ref.
Endocrine disruptor (4-*tert*-octylphenol, estrone, bisphenol and 17β-estradiol)	Effluent from municipal sewage treatment plant	Oasis HLB	GC-MS and GC-MS-MS	Hernando *et al.* (2004)
Pharmaceutical compounds (a sulfonamides, a sulfonamide synergist, a tetracycline, a fluoroquinolone and a β-lactame)	Pharmaceutical industry wastewater	Oasis HLB	HPLC-DAD	Babić *et al.* (2006)
Alkylphenols and bisphenol A	Mineral drinking water	Oasis HLB	LC-ESI-MS/MS	Shao *et al.* (2005)
5 macrolide antibiotics (roxithromycin, erythromycin, kitasamycin, azithromycin and clarithromycin)	River water	Oasis HLB	LC-MS	Abuin *et al.* (2006)

Table 2.2 Selected researches using SPE as the extraction method (cont.)

Analytes	Sample Matrix	SPE Phase	Analysis	Ref.
Bisphenol A	Seawater and river water	Oasis HLB	HPLC-fluorescence	Kang and Kondo (2005)
16 pesticides, *e.g.* aldicarb, atrazine, desethylatrazine, carbofuran and iprodione.	Groundwater	Oasis HLB, Isolute SPEC18 (EC), Envi-Carb, Lichrolut EN, and Strata X,	HPLC-DAD	Archivio *et al.* (2007)
Haloacetic acids (mono-chloroacetic acid, monobromoacetic acid, dichloroacetic acid, dibromoacetic acid, trichloroacetic acid.	Tap water	Oasis HLB, LC-SAX, LiChrolutEN and Envi-Carb	CZE	Martínez *et al.* (1998)
2 pesticides (isoproturon, diuron)	Runoff	Styrene divinylbezene co-polymer	HPLC-UV	Dur *et al.* (1998)
29 organophosphorous pesticides, *e.g.* vamidothion and dimethoate	Blood and serum	Oasis HLB	GC-MS	Lacassie *et al.* (2001)
Metabolite (Patulin)	Apple juice	Oasis HLB and PVPP-C18	LC-UV	Gökmen *et al.* (2005)

2.4.3 Size exclusive chromatography (SEC)

In general, the organic compounds in water samples are characterized/ identified by using mass spectrometry, as reported by researches (Alonso and Barceló, 1999; Crescenzi *et al.*, 2001; Grung *et al.*, 2007). Among spectrometric instruments, GC-MS is most popular (Gracia *et al.*, 2000; Heemst *et al.*, 2000; Garcia, *et al.*, 2001; Dsikowitzky *et al.* 2004; Chaler *et al.*, 2004; Schrank *et al.*, 2005; Schwarzbauer and Heim, 2005; Filipy, *et al.*, 2006; Fernandez *et al.* 2007), because it is more common and less expensive (Sigmaaldrich, 2007), *i.e.* its price is a half of LC-MS (Miljøstyrelsen, 2007). Although GC-MS analysis covers mainly a low molecular weight portions, they might be of particular environmental relevance, *i.e.* the greater biological activity is normally ascribed to low molecular weight compounds (Lundgren, 1992; Klinkow *et al.*, 1998). However, the determination of organic substances by GC-MS or LC-MS alone can usually qualify and quantify less than 10% dissolved organic matter whereas the bulk of organic matter remain still insufficiently characterized (Oleksy-Frenzel and Jekel, 1996). Luckily, in combination with fractionation of organic compounds according to molecular weight (Gloor *et al.*, 1981), polarity and adsorption ability (Schneider *et al.*, 1984), enhanced information can be obtained. The fractionation can be done by several methods such as resin (Imai *et al.*, 2002) and multistage ultrafiltration (Müller and Frimmel, 2002). Size Exclusive Chromatography (SEC) provides the advantage over others in the aspect of automated and not complicated procedure. It can be also employed with broad compositional heterogeneity without the need of extensive sample preparation (Oleksy-Frenzel and Jekel, 1996). Therefore, it is proper to use in this research.

The SEC is the easiest of the liquid chromatographic method to understand, use and the most predictable (Snyder and Kirkland, 1979). It can be subdivided into gel filtration chromatography and gel permeation chromatography. The former uses aqueous solvents and hydrophilic packing, while the latter is based upon non-polar organic solvents and hydrophobic packing. The methods are complementary in the sense that the one is applied to water-soluble samples and the other to substances soluble in less polar organic solvents. The SEC column is packing with small silica or polymer particles containing a network of uniform pores into which solute and solvent molecules can diffuse. While in pores, molecules are effectively trapped and removed from the flow of mobile phase. The average residence time in pores depends on the effective size of analyte molecule. Molecules that are larger than the average pore size of packing are excluded and thus suffer essentially no retention; such species are the first to be eluted. Molecules that have diameters smaller than the pores can penetrate throughout the pore maze and are thus entrapped for the greatest time; these are last to be eluted. Between this two extremes are intermediate-size molecules whose average penetration into the pores of the packing depends upon the diameters. Within these groups, the fractionation occurs, which is directly related to molecular size and to some extent molecular shape. Note that size-exclusion separation differs from other chromatographic procedures, *i.e.* no chemical and physical interaction between analyte and the stationary phase. There are two types of column packing, which are silica and polymer-based. The polymer-based column is selected in this study, because it provided some advantages over silica-based. They are no retention by adsorption and no catalytic degradation of solute molecules. These two phenomena can impair column efficiency (Skoog and Leary, 1991).

As mentioned previously, the SEC can be applied to water sample in order to fractionate the organic content leading to achieve a more detailed characterization (Abbt-Braun *et al.*, 1991). Pfeifer *et al.* (2001) combined 2 types of mass spectrometry, atmospheric pressure chemical ionisation (APCI) and electrospray ionization (ESI) mass spectrometry, with SEC to characterize humic substances. Without the SEC, the mass spectra of humic substances show a high degree of complexity. The results present the SEC simplifies interpretation. By this means, the complex behavior of humic substances can be understands; for example, the self association of humic substances can be broken by adding an organic acid. Another major application of SEC is to the rapid determination of molecular weight or molecular-weight distribution of large polymer or natural product. Here, the elution volumes of the sample are compared with elution volume for a series of standard compounds that possess the same chemical characteristics (Skoog and Leary, 1991). Lots of researchers employed the SEC to serve this purpose. For instance, Lingbo *et al.* (2005) investigated the refinery effluent after concentrated by portable reverse osmosis system. The SEC was utilized to determine the molecular weight of humic substances (HS) and fulvic substances (FS). Refinery effluent-derived HS display lower molecular weight than the natural HS. The number-average molecular weight (M_n) and the weight-average molecular weight (M_w) of humic acid are 1069 and 2934, and those of fulvic acid are 679 and 1212, respectively. Another example of molecular weight determination belongs to Drewes *et al.* (2003). In this study, the quality of potable water reuse after treated by microfiltration, followed by reversed osmosis and soil-aquifer, was investigated by the SEC. It was found that approximated 40-50 percent of remaining TOC in membrane permeate consists of low molecular weight acids and neutrals representing a molecular weight range of around 500 Da or less. However, the character of bulk organics presenting in the final effluent resembles the character of natural organic matter presenting in drinking water. In addition to the drinking water, the quality of the effluent from the municipal treatment plants was also determined by SEC. The effluents from 3 plants in Japan were collected and the molecular size distribution was determined by Imai *et al.* (2002). It was found that the size range is narrow and weight-average molecular weight is quite low ranging from 380 to 830 g mol^{-1}. That is the end-of-pipe determination. Another example study is related to the application of SEC to all treatment stages. Marquet *et al.* (1999) used the SEC to investigate the change of dissolved fraction of wastewater through the treatment process. They comprise a series of trickling filter, settlement and microfiltration, respectively. According to the SEC results, most substances in wastewater could be consumed by the biomass in the trickling filter, especially ammonium chloride, which is completely disappeared in the effluent. However, there are two new peaks or substances generated after trickling filter treatment. They are suspected to be a nitrate compounds since the analysis is undergone at 220 nm, where is used for nitrate determination by APA-AWWA-WEF standard method. Thus, this hypothesis is confirmed by the analysis of standard solution of potassium and sodium nitrate For the microfiltration, the SEC showed the permeate effluent provides the similar chromatogram as the unfiltered. This is exceptional for the high molecular weigh substances. It can be eliminated by the membrane and increase in the concentrate side. According to the experimental results, authors concluded that the SEC is efficient tool to assess the performance of the wastewater treatment processes. Other applications for SEC are related to a fouling of membrane treatment. It was used to determine molecular weight distribution of organic fraction causing the membrane fouling (Jarusutthirak *et al.*, 2002; Shon *et al.*, 2006). Fabris *et al.* (2007) proposed a series of three pre-treatment methods, *i.e.* commercial adsorbent (MIEX®), powdered activated carbon and coagulation, to reduce the microfiltration membrane fouling. According to SEC results, it indicated that the treatments can reduce the majority of dissolved organic carbon in all molecular weight ranges, including colloidal (very high molecular weight) material. This successfully prevents short-term fouling of microfiltration membrane.

2.5 Fenton's Treatment

Advanced oxidation processes (AOPs) have been developed and studied over the past 30 years. It has been viewed with great interest as a promising method for the removal organic contaminants from water. The number of papers had significantly increased decade after decade (Suty *et al.*, 2003). AOPs rely on the formation of reactive and short-lived oxygen containing intermediates such as hydroxyl radical (•OH) that can be used in the wastewater treatment to degrade organic pollutants resistant to biological and classical physico-chemical process (Andreozzi *et al.*, 1999; Esplugas *et al.*, 2002). The ultimate aim of the oxidation of pollutants is to "mineralize", that is to convert the constituents of an organic pollutant into simple, relatively harmless molecules, *i.e.* CO_2 and H_2O (Martins *et al.*, 2005). The most widely AOPs' study included: heterogeneous photocatalytic oxidation (Pérez *et al.*, 1999; Dhananjay *et al.*, 2003; Grieken *et al.*, 2005; Bizani *et al.*, 2006), treatment with ozone (often combined with H_2O_2, UVA or both) (Muller *et al.*, 1998; Klare *et al.*, 1999; Balcioğlu and Őtker, 2003; Oguz and Keskinler, 2007), H_2O_2/UV systems (Schrank *et al.*, 2007), Fenton (Bandala *et al.*, 2007; Sun *et al.*, *article in press*; Pirkanniemi *et al.*, *article in press*; Siedlecka *et al.*, *article in press*) and photo-Fenton reaction (Bautitz and Nogueira, 2007; Peternel *et al.*, *article in press*; Kajitvichyanukul *et al.*, *article in press*; Ravichandran *et al.*, *article in press*). However, the high electrical energy demand is still the common problem for AOPs (Bauer and Fallmann, 1997). In contrast, one of AOPs, Fenton's oxidation provides the advantage over other AOPs. It does not energy input to activate its reagent

(Lücking *et al.*, 1998). This is proved it is economical methods (Al-tawabini, 2003). The main advantage of Fenton's reagent is its simplicity. The chemicals are readily available at moderate cost and there is no need for special equipment (Chung and Stevens, 1993). It can treat various classes of organic compounds, as listed by Neyens and Baeyens (2003), and Gogate and Pandit (2004). Furthermore, it commonly requires a relatively short reaction time compared with other AOPs (Zazo *et al.*, 2005). The Fenton's reagent has not only oxidation function, but also coagulation by formation of ferric-hydroxo complex (Kuo, 1992; Kang and Chang, 1997). The coagulation step acts as a polishing step, and removes the remaining after Fenton's oxidation (Tekin *et al.*, 2006). The other advantage of Fenton's oxidation is an improvement in the biodegradability of wastewater, as reported by researchers (Chamarro *et al.*, 2001; Morais and Zamora, 2005).

Fenton's reagent was discovered in 1894 by H.J.H. Fenton., but it application as an oxidizing process for destroying toxic organics was not applied until the late 1960s (Huang *et al.*, 1993). Fenton's reagent is a mixture of H_2O_2 and ferrous ion, which generates hydroxyl radicals according to the reaction (Yoon *et al.*, 2001; Lu *et al.*, 2001);

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^- \qquad (2.2)$$

The ferrous iron (Fe^{2+}) initiates and catalyses the decomposition of H_2O_2, resulting in the generation of hydroxyl radicals. The generation of the radicals involves a complex reaction sequence in an aqueous solution (Walling and Goosen, 1973);

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + Fe - OOH^{2+} + H^+ \qquad (2.3)$$

$$Fe - OOH^{2+} \longrightarrow HO_2 \bullet + Fe^{2+} \qquad (2.4)$$

The reaction of hydrogen peroxide with ferric ions is referred to as a Fenton-like reaction (De Laat and Gallard, 1999), which can be used to treat the wastewater instead of conventional Fenton's oxidation in order to achieve in the reduction of the chemical cost (Wang, *article in press*). The complicated reaction sequences in Fenton's system are summarized in Table 2.3.

Table 2.3 Reaction and rate constant in Fenton's system (Chen and Pignatello, 1997; Crittenden *et al.*, 1999; Lunar *et al.*, 2000; Gallard and De Laat, 2000; Grymonpre *et al.*, 2001; Kang and Lee, 2002; Grymonpre *et al.*, 2003; Bergendahl and Thies, 2004; Burbano *et al.*, 2005)

	Reactions	**k (mol^{-1} dm^{3} s$^{-1)}$)**
1.	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^-$	63-76
2.	$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2\bullet$	0.001-0.02
3.	$Fe^{2+} + \bullet OH \rightarrow Fe^{3+} + OH^-$	(3.0-4.3)x10^8
4.	$Fe^{3+} + HO_2\bullet \rightarrow Fe^{2+} + O_2 + H^+$	(0.1-3.1)x10^5
5.	$Fe^{2+} + HO_2\bullet \rightarrow Fe^{3+} + HO_2^-$	1.2 x 10^6
6.	$Fe^{3+} + O_2\bullet^- \rightarrow Fe^{2+} + O_2$	(0.5-1.5)x10^8
7.	$Fe^{2+} + O_2\bullet^- + 2H^+ \rightarrow Fe^{3+} + H_2O_2$	1.0x10^7
8.	$\bullet OH + H_2O_2 \rightarrow HO_2\bullet + H_2O$	(1.2-4.5)x10^7
9.	$2\bullet OH \rightarrow H_2O_2$	(4.2-5.3)x10^9
10.	$HO_2\bullet + \bullet OH \rightarrow H_2O + O_2$	6.6 x 10^{11}
11.	$2HO_2\bullet \rightarrow H_2O_2 + O_2$	8.3x10^5
12.	$O_2\bullet^- + HO_2\bullet \rightarrow HO_2^- + O_2$	9.7x10^7
13.	$O_2\bullet^- + \bullet OH \rightarrow HO^- + O_2$	1.0x10^{10}
14.	$HO_2\bullet \rightarrow O_2\bullet^- + H^+$	(1.6-7.9)x10^5 s^{-1}
15.	$O_2\bullet^- + H^+ \rightarrow HO_2\bullet$	1.0x10^{10}
16.	$\bullet OH + H_2O_2 \rightarrow HO_2\bullet^- + H_2O$	2.7x10^7
17.	$\bullet OH + HO_2^- \rightarrow HO_2\bullet + OH^-$	7.5x10^9
18.	$HO_2\bullet + H_2O_2 \rightarrow H_2O + \bullet OH + O_2$	3.0
19.	$O_2\bullet^- + H_2O_2 \rightarrow OH^- + \bullet OH + O_2$	0.13

Although there are a large number reactions occurring in the Fenton's system, hydroxyl radical are mainly responsible for the degradation of pollutant. This is attributed to the high rate of production and high oxidation potential. It is powerful oxidation agent that has an oxidation potential only lower than fluorine and higher than ozone, as shown in Table 2.4 (Parsons, 2004).

Table 2.4 Oxidation potential of common species

Species	Oxidation Potential
Fluorine	3.03
Hydroxyl radical	2.80
Ozone	2.07
Hydrogen peroxide	1.78
Perhydroxyl radical	1.70
Permanganate	1.68
Hypobromous acid	1.59
Chlorine dioxide	1.57
Hypochlorous acid	1.49
Chlorine	1.36

Thus, it can oxidize organic and inorganic pollutants by different type of reaction, electron transfer, electric addition, and hydrogen abstraction, as illustrated in Eq. (2.5) to (2.7) (Legrini *et al.*, 1993; Hoigné, 1998).

Electron transfer:

$$\bullet OH + M^{n} \longrightarrow M^{n+1} + OH^{-}{}_{aq} \qquad (2.5)$$

Electrophilic addition

$$\bullet OH + R_2C = CR_2 \longrightarrow \bullet CR_2 - C(OH)R_2 \qquad (2.6)$$

Hydrogen abstraction

$$\bullet OH + R - H \longrightarrow \bullet R + H_2O \qquad (2.7)$$

The rate of oxidation depends on radical concentration and pollutant concentration. Many factors can affect the radical concentration, such as pH, temperature, the Fe^{2+} and H_2O_2 concentration, the type of pollutant (Kurt *et al.*, 2006).

According to Eq. (2.2), it indicates that Fenton’s reactionis strongly dependent on the solution pH. The pH value has to be in the acidic range to generate the maximum amount of hydroxyl radicals to oxidize organic compounds (Tekin *et al.*, 2006). It is efficient only in the pH range of 2- 4 and is usually most efficient at around pH 2.8 (Pignatello, 1992; Tang and Tassos, 1997; Kang and Chang, 1997; Kochany and Lugowski, 1998; Kavitha and Palanivelu, 2005). Hence, the process is inefficient in the pH range of most natural water (pH 5-9). This is particularly due to the tendency for ferric oxyhydroxide precipitation (which has a low catalytic activity) to occur at pH>3-4 (depending on the iron concentration) (Kuo, 1992; Parsons, 2004). In a study of Chou *et al.* (2001) in which iron oxyhydroxide and Fenton’s reagent were used in a fluidized-bed reactor (FBR), the pH was found to strongly affect the efficiencies of mineralization and Fe^{3+} precipitation rates. When treating benzoic acid, they found that the degradation efficiency decreased with increasing pH, while the removal efficiency of total iron increased with pH in the pH range of 2.8- 4.5. Other researcher concentrated on pH effect is Liu *et al.* (2007). The degradation and decolorization of 3 dyes (Everdirect supra turquoise blue FBL, Isolan orange S-RL, Indanthrene red FBB) by Fenton was investigated. Effect of initial pH was determined in a range of 1-6 and the optimum pH was found at pH 3 for all three different dye wastewater. At very low pH, the removal efficiency is quite limited due to the hydroxyl free radical scavenging effect of H^+ ion.

The reaction rate trends to increase with increasing H_2O_2 However, the ferrous ion and H_2O_2 not only react to form hydroxyl radicals, but they are also scavengers of hydroxyl radical. The ratio of Fe^{2+} to H_2O_2 can affect the rates of hydroxyl radical production and consumption. Hence, it is important to use the optimum Fe^{2+}: H_2O_2 ratio. Even though the Fenton’s reaction has been widely studied, there is no agreement on the ratio $[H_2O_2]/ [Fe^{2+}]$ that gives the best results (Schrank *et al.*, 2005). Therefore, many researches, who studied with the Fenton’s treatment, can not neglect to determine the ratio by themselves. For example, Chamarro *et al.* (2001) used the Fenton reagent to degrade different organic compound, *i.e.* formic acid, phenol, 4-

chlorophenol, 2,4-dichlorophenol and nitrobenzene, in aqueous solution. A stoichiometric coefficient for the Fenton reaction was found to be 0.5 mol of organic compound/ mol of hydrogen peroxide, except for the formic acid where a value of approximately 1 was obtained (due to the direct formation of carbon dioxide). The 2,4-dichlorophenol was also studied by Wang and Lemley (2001). The optimum Fe^{2+}: H_2O_2 ratio was 1: 10. This is closed to the theoretical optimum ratio predicted before that by Tang and Huang (1996). For the real wastewater, the optimization is generally expressed in the terms of COD or TOC reduction. For instances, Guedes *et al.* (2003) applied Fenton's reagent as the pre-treatment for corking cooking wastewater. The optimum Fe^{2+}: H_2O_2 ratio is 1.5 (by weight) and pH 3. Under such condition, TOC and COD is reduced about 66.4% and 87.3%, respectively. The biodegradability index is increased from 0.27 to 0.63 as well. The other example belongs to Zhang *et al.* (2005). In this study, landfill leachate is treated by Fenton's oxidation. The optimum condition was determined in the terms of % COD removal. The optimal pH is 2.5 and the favorable H_2O_2 to Fe^{2+} molar ratio was 1.5 for every initial COD strength.

Another parameter affecting to the performance of Fenton's oxidation process, especially batch mode, is the initial concentration of pollutant. There are several literatures focusing on this parameter. For instance, Modirshahla *et al.* (2007) reported the effect of AY23 dye concentration on the decolorization efficiency by Fenton's treatment. By keeping other conditions constant, it was observed that the decolorization decreases with increasing the initial concentration of dye. The presumed reason is that when the initial concentration of the dye is increased, the hydroxyl radical concentrations remain constant for all dye molecules and hence the removal rate decreases. This phenomenon is in agreement with the Sun *et al.* (2007)'s study dealing with another type of dye, Amido black 10B. In addition to the pollutant concentration, its structure is also important to the degradation efficiency. The degradation of alicyclic compounds is given little attention since most of the water pollutants with a low biodegradability have an aromatic structure. Ruppert and Bauer (1993) studied the influence of the structure of several organic pollutants on the way they are mineralized by •OH. In alicyclic compounds, the attack of the electrophilic hydroxyl radicals can not occur at conjugated C=C bonds in contrast with aromatic compounds where ring opening and further degradation take place. Although a parameter temperature is attended by many researchers (Lin *et al.*, 1999; Pérez *et al.*, 2002; Ramirez *et al.*, 2005; Zhang *et al.*, 2006; Deng and Englehardt; 2006), the wastewater heating has always been assumed to be economically inconvenient (Basu and Wei, 1998). Because the wastewater from the concentrated latex industry is not the heated wastewater, the temperature effect will be not mentioned in this study.

CHAPTER III

METHODOLOGY

3.1 Materials, instrumentation and methods

3.1.1 Materials

All chemicals used in this work were analytical reagent grade. Solutions were prepared using 18.2 MΩ deionized water treated by a Millipore-Q system (Millipore Simplicity, France).

In characterization part, Helium (He) gas with purity of 99.999% was purchased from Thai Industrial Gases Public Co., Ltd for GC-MS analysis. Dichloromethane as mobile phase for Size Exclusive Chromatography (SEC) and the extracted solvent was obtained from Merck, Darmstadt, Germany. For other extracted solvents, hexane and methanol were also purchased from Merck, Darmstadt, Germany, while ethyl acetate was bought from Labscan Asia, Bangkok, Thailand. Standard 3-methylindole and diisobutyl phthalate were purchased from Merck. OASIS® HLB Extraction cartridge (Waters, Milford, Ireland) was used as the solid phase extraction. This adsorbent composes of both hydrophilic and hydrophobic (lipophilic) part, so it could be used to extract any polar or non-polar compounds.

The Fenton's treatment, iron (II) sulfate heptahydrate and 35% hydrogen peroxide (Merck, Darmstadt, Germany) were used as Fenton's reagent. Due to unstable property, the high concentration of H_2O_2 in the original bottle was determined by a potassium permanganate ($KMnO_4$) standard method (Mendham *et. al.*, 2000). Such $KMnO_4$ was from Mallinckrodt (St. Lious, Missouri, USA). The concentration of residual ferrous was measured by phenanthroline method (APHA, 1989). Chemicals used in this methods consist of 1,10-phenanthroline (Merck, Darmstadt, Germany), ammonium acetate (Ajax Finechem, Auckland, New Zealand) and 37% HCl (Labscans Asia, Bangkok, Thailand). pH was controlled by a pH controller (HOTEC, Taiwan) connected with two feeding pumps (Nikkiso Liko

Chemipon B, Japan). The desired pH was controlled by using 0.1 N NaOH and 0.1 N H_2SO_4 and the pH variation was within 0.2 units. Therefore there’s no need of any pH buffer solution in the experiments. Both acid and base were from Labscan Asia, Bangkok, Thailand. All glassware was soaked in 10% nitric acid solution (J. T. Baker, Phillipsburg, New Jersy, U.S.A.) for one night to remove metal.

3.1.2. Instruments

Solid Phase Extraction was carried out on12-Port Visiprep vaccuum manifold (Supelco, U.S.A.) equipped with a vacuum pump (Gast Manufacturing Inc., Michigan, U.S.A.) while the fractionation was performed on the size exclusive chromatography (SEC) that composed of a Waters 515 pump, a 19 mm x 300 mm styrene divinylbenzene column (Waters Envirogel^{TM}) contained 100 Ǻ pore size material with a nominal particle size of 15 µm, Water 717 plus autosampler and Waters 2487 Dual λ Absorbance Detector. The SEC was connected with a fraction collector (Water Fraction Collector II). The SPE manifold, SEC and fraction collector was shown in Fig. 3.1, 3.2 and 3.3, respectively. The organics in extractant were identified by the Gas Chromatography (HP Model 6890) with capillary column, 30 m x 250 µm x 0.25 µm HP-5(5% phenyl methyl siloxane) interfaced with mass selective detector (HP Model 5973). The optimum GC conditions were column temperature programmed at 60 ^{O}C to 300^{O}C at 20^{O}C/min with a final hold time of 10 min; carrier gas, helium 99.999% at 30 cm/s linear velocity; and injector temperature 250^{O}C. The MS optimum conditions were as follows: ionization energy, 70 eV; scan mode, full scan, 50-550 amu, 1.68 san s^{-1} and transfer-line temperature, 250^{O}C.

Figure 3.1 SPE Manifold Connected with the Pump

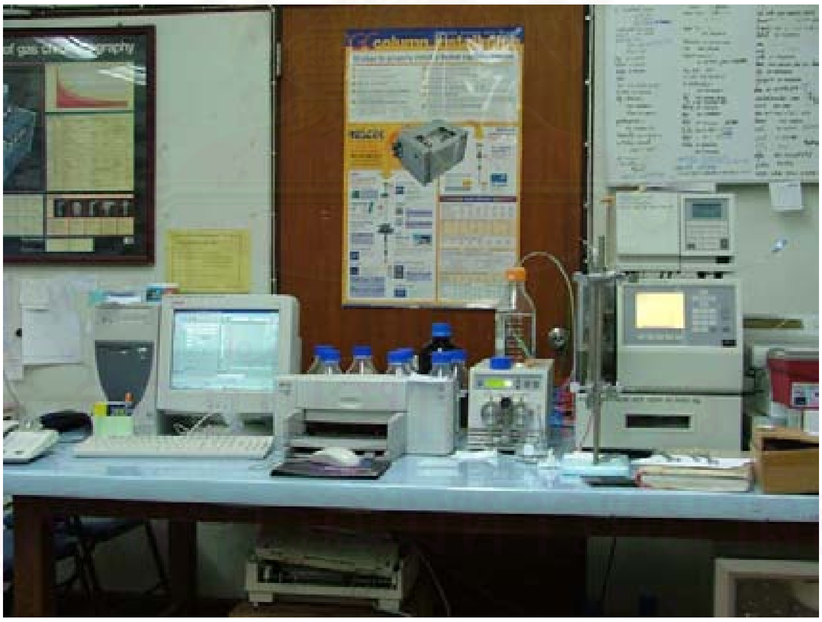


Figure 3.2 Size Exclusion Chromatography

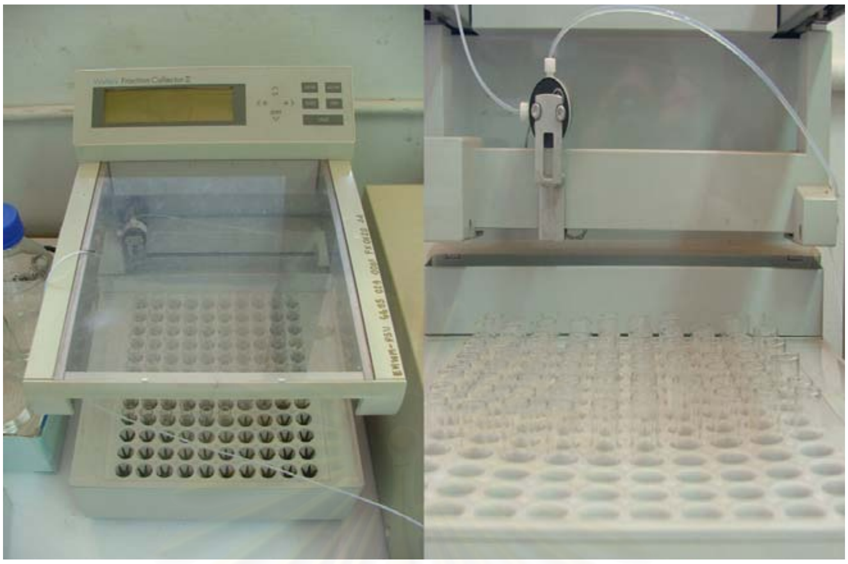


Figure 3.3 Fraction Collector

For the treatment part, the above mentioned GC-MS was employed to analyze 3-methylindole (3MI) in synthetic wastewater. The GC column temperature was 60 ^{O}C (and 2 min. holding time) to 270^{O}C at ramp rate 5^{O}C/min. without a final holding time (Williams *et al.*, 1995). In addition, it was used for all real wastewater samples under condition such as: GC column temperature set at 80 ^{O}C to 300^{O}C at ramp rate 20^{O}C/min. with 10 min. holding time. For Diisobutyl phthalate (DIBP) in the synthetic wastewater, it was analyzed by a Dionex liquid chromatograph, which is equipped with PDA-100 photodiode array detector, Acclaim®120 C18 column (5 m, 250 x 4.6 mm ID), TCC-100 column thermostat maintained at 30^{O}C, ASI-100 automated sample injector, and P680 HPLC pump. In this research, the needs of absorbance value were supported by HP 8452A Dioade Array and Specord S100 spectrophotometer.

3.2 Experimental procedure

The experiments were divided into two major sections:

3.2.1. Wastewater characterization study

Sample Collection and Preservation

From the study of Kaewyod (1997), there are a few differences in the production and treatment process among 9 Para rubber plants in Songkhla provinces, one plant was selected as a representative in this study. Wastewater was collected from Thai Hua Rubber (Public) Co., Ltd. located in Tha Chang District, Bangklam, Songkhla.

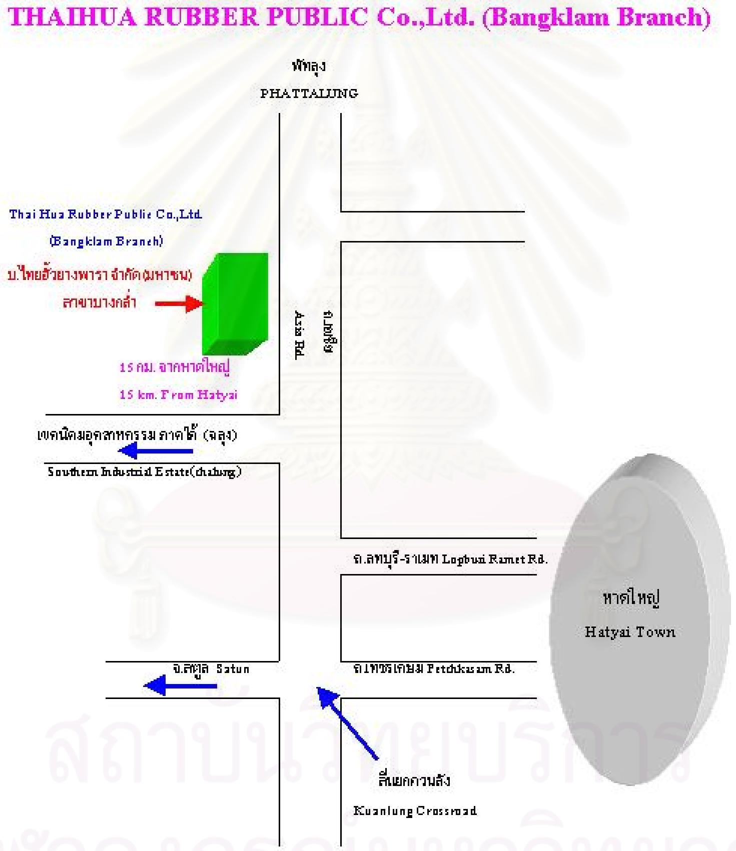


Fig.3.4 Sampling site location

This factory produces 3000 tons of natural latex rubber per month and 800 tons of Standard Thai Rubber (STR5L) per month and 150 tons of skim rubber per month. The wastewater is generated approximately 200 – 500 cubic meters per day. The treatment system, which is responsible for this large volume wastewater, is shown in Fig. 3.5

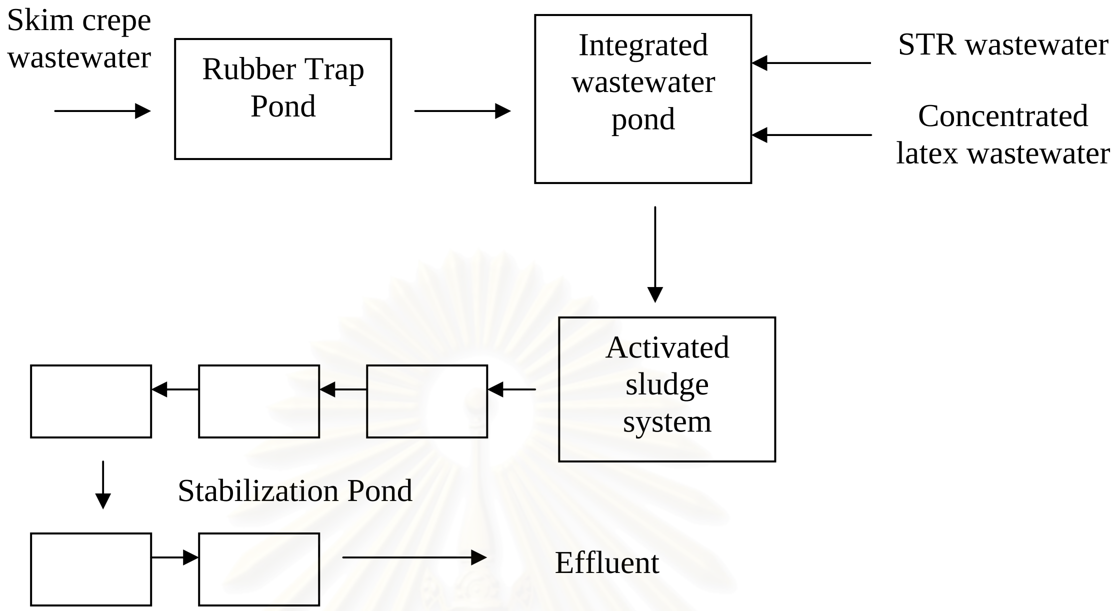


Fig.3.5 Industrial Wastewater Treatment Diagram

The wastewater is discharged to the treatment system in two lines. First stream from skim crepe production reaches the system at the rubber trap pond, while the second from concentrated latex and rubber block production is joined into the integrated wastewater pond. Although there is anaerobic digestion in the rubber trap pond, some people considers it as one of the production units. This is due to the rubber fragment coagulated in the bottom of the pond and taken out for sale. After the integrated wastewater pond, the wastewater stream is delivered to the activated sludge unit with three aeration ponds and one clarifier. Finally, the water is passed to five stabilization ponds before discharge into the environment.

The sample was collected at the integrated wastewater pond representing the raw wastewater sample, and the sample collected at the last stabilization pond as the treated wastewater sample. The temperature, pH, color, odor and dissolved oxygen were measured at the site. The collected samples were contained in PE bottles and sealed with Para-film to prevent the oxidation, stored and transferred to the laboratory with the temperature controlled at <4 ^{O}C. All the samples were refrigerated and kept in the dark to prevent the further reaction in the laboratory. Before analysis, all samples were filtered through a 1.2 μm glass filter paper (Whatman GF/C) to remove the suspended solids from the wastewater. The general properties, BOD_5 and COD, were determined by the EPA Standard method (APHA, 1989).

Characterization of organic compounds in wastewater

a) Comparison between 2 extraction methods, *i.e.* liquid-liquid extraction (LLE) and solid phase extraction.

- Liquid-liquid extraction: 100 mL of wastewater was extracted by various extract solvent based on the polarity. Hexane with polarity index, 0.1 was the representative of non-polar solvent, while the other one was ethyl acetate with polarity index of 4.4 (Snyder and Kirkland, 1979). The high polar solvent can not be used, because it could completely dissolve in the wastewater. Samples were extracted by using a 250 ml. separatory funnel, then the solvent layer was transferred and centrifuged for at least 20 min. to separate the suspended rubber particle out. Then the extractant (filtrate) was evaporated at boiling point of each solvent to reduce the volume down to 1 ml. The final concentrated extractant was analyzed by Size Exclusive Chromatography (SEC) and followed by gas chromatography coupled with mass spectrometry (GC-MS).

Parameters affected to the extraction efficiency are shown in Table 3-1

Table 3.1 Factors affecting to LLE

Factor	Independent variable	Dependent variable	Controlled Variable
Type of the extract solvent	-Hexane -Hexane: Dichlomethane1:1 (v/v) -Dichloromethane -Dichloromethane: Ethyl Acetate 1:1 (v/v) -Ethyl Acetate -Ethyl Acetate: Methanol 1:1 (v/v)	The amount of the extraction in the form of Peak Area (response)	- An volume of solvent used = 20 ml. - A number of extraction = 1 times - The shaking time = 2 min
The volume of extract solvent	- 20 -100 ml	The amount of the extraction in the form of Peak Area (response)	-Type of elution solvent = Best Solvent. - A number of extraction = 1 - The shaking time = 2 min
The number of successive extraction	- 1 - X times X depends on the volume of solvent and type of the solvent	The amount of the extraction in the form of Peak Area (response)	- Type of elution solvent = Best Solvent - An volume of solvent used = Optimum - The shaking time = 2 min
The shaking time	- 1- 15 minutes	The amount of the extraction in the form of Peak Area (response)	- Type of elution solvent = Best Solvent - An volume of solvent used = Optimum - The number of extraction = Optimum

- Solid phase extraction: All wastewater samples were filtered by 0.7 µm glass fiber paper (Whatman GF/F) to protect the damage of SPE cartridge by suspended solid. The experiment procedure was adjusted from the generic method described in the instruction manual. First step, conditioning step, the HLB cartridge was conditioned by 5 mL methanol and followed by 5 mL of the de-ionized water at the same pH as the wastewater in order to equilibrate the adsorbent. Then 50 mL of filtered wastewater sample was applied to the top of the cartridge and drawn through the packing adsorbent bed by vacuum pump. The sample loading flow rate was varied by adjusting the vacuum pressure. Then, the cartridge was dried at vacuum pressure of 5 in.Hg. for 15 min. to eliminate the remaining wastewater**.** In the elution step, various elution solvent at different flow rates and volume were investigated for completely elution and collected in the tube. Finally, the collected solvent was evaporated at 50^{O}C to reduce the volume down to 1 mL before analysis by SEC and GC-MS. The experimental variables were summarized in Table 3.2 and the two extraction methods were optimized and compared to each other.

Table 3.2 Factor affecting on SPE

Factor	Independent variable	Dependent variable	Controlled Variable
Type of elution solvent	- Hexane - Hexane: Dichloromethane (1:1, v:v) - Dichloromethane - Dichloromethane: Ethyl Acetate (1:1, v:v) - Ethyl Acetate - Ethyl Acetate: Methanol (1:1, v:v)	The amount of the extraction in the form of Peak Area	-Elution amount =5 ml. -Sample vacuum pressure = 5 in.Hg.
Elution Volume	1 - 15 ml.	The amount of the extraction in the form of Peak Area	- Type of elution solvent = the best solvent - Sample vacuum pressure = 5 in.Hg.
Sample flow rate, or sample vacuum pressure	1 – 15 in.Hg.	The amount of the extraction in the form of Peak Area	- Type of elution solvent = the best solvent - Elution amount = Optimum

b) Fractionation and Organic Compounds Identification: Different solvents with different polarities were applied to the best extraction method. The extractants were fractionated according to molecular size by SEC and then each fraction was analyzed by GC-MS to identify the organic substances.

c) Monitoring: To confirm the results/data, the raw and treated wastewater was monitored every 2 weeks for 6 months.

d) Potential source Identification: The sources of a dominant species were identified to provide the useful information for the future management.

3.2.2 Fenton’s treatment

From the preliminary study, Two major hazardous compounds were found in wastewater, *i.e.* 3-methylindole (or called skatole, 3MI) and 1,2-benzenedicarboxylic acid, bis(2-methylpropyl) ester (or called diisobutyl phthalate, DIBP). The first species is malodorous compound (Hwang *et. al.*, 1994). This culprit may cause the Para rubber plant to face frequently with the odor claim from the neighboring communities, apart from ammonia and hydrogen sulfide. Consequently, there was obligatory necessity to treat this compound in the short time. For more information on toxicity of 3MI. see Chapter 4. As for the second dominant compound, it was difficult to biologically degrade according to the literature survey (Zhao *et. al.,* 2004), which corresponds to the preliminary study. For the above reasons, the advanced oxidation technology, *i.e.* Fenton’s oxidation, was selected in this research. Another reason of choosing this Fenton process in this research is that it could be performed better under the acidic condition and the pH of the raw wastewater was found in acidic zone, around 4-5. The overview of the experiment is summarized in Fig. 3.6.

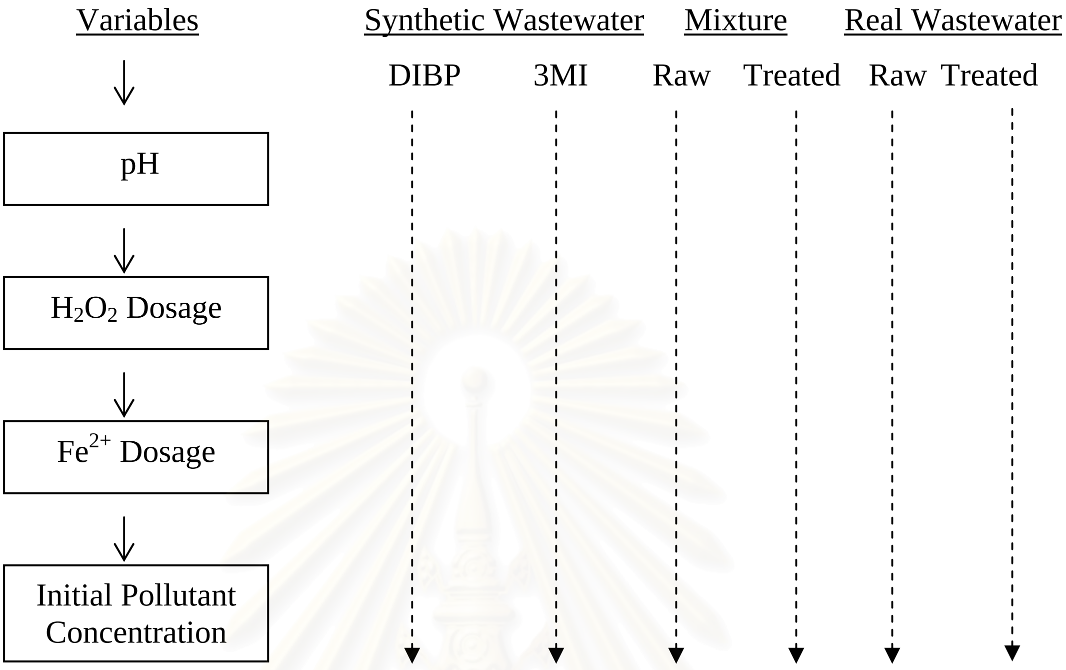


Fig. 3.6 Schematic Diagram of Experimental Procedure

The wastewater was synthesized with single DIBP. The effect of 4 variables such as pH, [H_2O_2], [Fe^{2+}] and [initial DIBP concentration] was investigated. Optimum operating conditions were applied to the industrial raw and treated wastewater and comparisons were made among different types of wastewater samples in terms of process performance.

The synthetic wastewater

a) The wastewater was synthesized by dissolving DIBP in de-ionized water and was left overnight to reach the state of equilibrium. The initial DIBP concentration was fixed at 14 mg L^{-1} in all experiments, unless mentioned elsewhere.

b) Due to unstable property, the high concentration of H_2O_2 stock solution was daily determined by a potassium permanganate standard method (Mendham *et. al.*, 2000).

c) To prevent the change in iron form, ferrous solution was prepared in acid condition before transferring into the reactor.

d) The batch mode experiment was carried out in 1 L beaker with stirrer. The solution pH was controlled by 0.1 N NaOH and 0.1 N H_2SO_4, and its variation was within 0.2 units. Therefore there's no need of any pH buffer solution in the experiment.

e) A samples volume of 5 mL was taken at different reaction time intervals and the reaction was quenched immediately by adding 100 µL of 10% Na_2SO_3 into the taken sample. Then, 2 mL sample was extracted by 2 mL hexane and directly injected into HPLC to determine the remained DIBP concentration.

f) Another sample of 2 mL was collected at the same time and filtered with the 0.45 µm cellulose acetate membrane to separate the iron sludge out. The supernatant was taken into 50 mL volumetric flask containing the phenantroline solution to measure the residual ferrous concentration. See the standard phenanthroline method in Appendix A.

g) Repeat Step b) – f) using another synthetic 3MI wastewater with the initial concentration fixed at 100 mg L^{-1} in all experiments, unless mentioned elsewhere. Unlike DIBP, the analytical instrument for 3MI was GC-MS. However, the extraction method was still the same, *i.e.* LLE by hexane.

h) The concentration range of variables were shown in Table 3.3

Table 3.3 Parameter affecting on Fenton's oxidation of the DIBP and 3MI synthetic wastewater

Parameter	DIBP	3MI
$[H_2O_2]$/[Pollutant]	0 - 20	0 - 2
$[Fe^{2+}]$/[Pollutant]	0 - 15	0 - 3
pH	1 - 6	1 - 6
[Pollutant] (mg L^{-1})	2 - 14	50 - 500

i) The experimental results provided information on the reaction order and kinetic equation.

The mixture of 3MI and DIBP

The mixture of 3MI and DIBP was also investigated in both the raw and treated wastewater. In the raw wastewater study, the 3MI and DIBP were prepared at same concentration found in the raw wastewater. Because 3MI was the dominant species in raw wastewater, the raw mixture was treated with the optimum condition of 3MI. Like 3MI, DIBP was the dominant species in the treated wastewater, so the synthetic mixture considered as the treated wastewater was treated by the optimum condition with respect to DIBP. The results of synthetic mixture were compared with those obtained from synthetic wastewater with single component.

The industrial wastewater

From the preliminary study, the first dominant species in raw wastewater was 3MI, while it was DIBP in treated wastewater. Consequently, the optimum conditions obtained from the 3MI synthetic study were applied to the raw wastewater and those from the DIBP synthetic study were employed for the treated wastewater. The results between the artificial and genuine wastewater were compared to each other. From the experiment, the difference was so high (See Chapter 4). The operating condition was optimized again.

For the raw wastewater, the initial 3MI concentration was adjusted to 19 mg L^{-1} in all experiment, if not mentioned elsewhere. This concentration was the average value found from the monitoring of 6 months. For the treated wastewater, the average DIBP concentration of 0.5 mg L^{-1} was also set in all experiments. The experiment was operated in the same way with the synthetic wastewater, except the extraction method. Since the rubber particle could dissolve well in organic solvent, LLE was not appropiate for the real wastewater sample. SPE was employed instead of LLE. 4 mL of sample was loaded to the cartridge and extracted under the conditions obtained from the characterization study. In the treated wastewater study, the sample loaded was increased up to 10 mL dues to the low concentration of organic compound. In addition, the sample preparation step was also extended for treated wastewater. The extracted sample was necessary to naturally dry and adjust the solvent volume to 60 µL. These improved DIBP concentrate enough for analysis. The GC-MS was used to analyze both raw and treated wastewater. The range of variables was shown in Table 3.4

Table 3.4 Parameter affecting on Fenton's oxidation of the real wastewater

Parameter	Raw wastewater	Treated wastewater
$[H_2O_2]$/[Pollutant]	0 - 100	0 – 20000 (or 0 – 1234 mg L^{-1})
$[Fe^{2+}]$/[Pollutant]	0 - 20	0 – 1000 (or 0 -100 mg L^{-1})
pH	1 - 5	1 - 5
[Pollutant] (mg L^{-1})	4.75 – 27.50	0.1 – 0.5

3.3 Quality assurance and quality control

The precision was determined by making replicate measurement for every part of this research (at least 3 replications). The contamination can occur in the laboratory at any stage of sample preparation and analysis. Therefore it was assessed by blank measurement composed of reagent blank and method blank. The reagent blanks are reagents used during the analytical process, including solvents used for extraction or dissolution). These are analyzed in isolation in order to see whatever they contribute to the signal of analytical instrument. The measured signal arising from the analytical can then be corrected accordingly (Eurachem, 1998). Reagent blanks were prepared and analyzed prior to the sample preparation steps. Method blank is performed by carried through all the steps of sample preparation and analysis as if they were an actual sample. It is used to evaluate the laboratory contamination for the targeted analytes and corrected systematic errors due to impurities that could arise from the reagents, the glassware, or the laboratory environment (Harvey, 2000).

CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Wastewater background

4.1.1 Wastewater characteristic

Possessing turbid creamy property, the raw wastewater with very high suspended solid was collected every two weeks for six months. The wastewater characteristics are presented in Table 4-1.

Table 4.1 Physical and chemical characteristics of wastewater

Sources	BOD_5 (mg L^{-1})		COD (mg L^{-1})		SS		pH
	Range	Average	Range	Average	Range	Average	Range
Influent	3,400-6,700	5,517	10,700-27,600	11,349	1,000-3,500	1,519	4.9 – 5.0
Effluent	30-190	108	100-380	223	130-370	165	8.19-8.57

The pH of the raw wastewater was in acidic zone and varied in the narrow range of 4.9 – 5.0. It was obligatory to control the pH to fall in this range, because the rubber particle could best coagulate and separate from the liquid at pH = 4.6 – 4.9. At this pH range, it could reduce the suspended solid and recover the residual rubber in wastewater (Kajornchaikul, 1989). Regarding suspended solid, most of them were come from the concentrated latex process. The release of skim crepe process was a minor source of suspended solid because of acid addition to coagulate the rubber particle in this process. Unlike the suspended solid, sources of BOD_5 and COD were mainly from the skim crepe production. This was because of the high organic constituents in the serum.

Regarding the treated wastewater, it was quite acceptable in terms of neutral pH, but, frequently, the other parameters did not meet the standard value required by the regulation. For example, according to the announcement of Ministry of Industry (B.E.1996), BOD_5 in the discharged water has to be less than 20 mg L^{-1}, COD 120 mg L^{-1} and SS 50 mg L^{-1} (Department of industrial works, 2007). In view of the rubber industry, the Songkhla Provincial Industry Office determined that BOD_5 for all rubber industries in Songkhla Province has to be no more than 60 mg L^{-1}, while SS was less than 150 mg L^{-1} (Kaewyod, 1997). Obviously, the averages of all parameters, except the pH, exceeded the standard value. This led to the need of improving the treatment efficiency by the proposed method in this research.

4.1.2 Source of wastewater

Approximately, 90% of the raw water for the rubber industry was supplied from the ground water. The other 10% was obtained by the rain water reserved in the large pond. After production, those waters become the wastewater in the long run. The average 281 m^3 day^{-1} wastewater was generated from many sources, especially the washing container step. As report by Kaewyod (1997), the sources of the wastewater could be roughly illustrated in Fig.4-1 and Fig. 4-2.

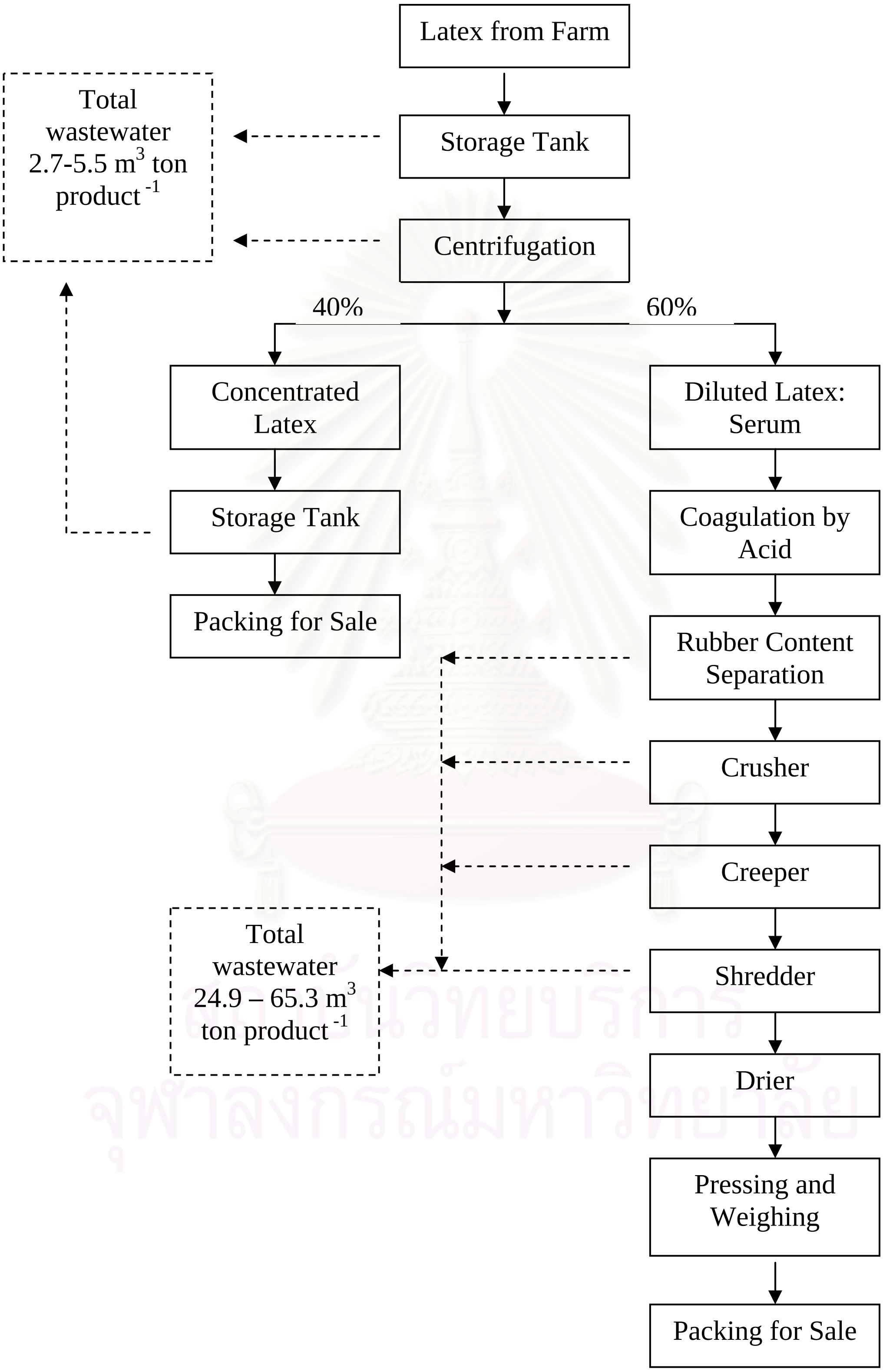


Figure 4.1 Sources of wastewater generated from the concentrated latex and the skim crepe production (Kaewyod, 1997)

As shown in Fig.4-1, the concentrated latex process resulted in the wastewater generation around 2.7 – 5.5 m^3 ton production $^{-1}$. The major sources of wastewater could be divided into three different categories. The first one was from the cleaning of the tank that stored the farmed latex. The second was from the cleaning of the centrifugal machine, and the last one was the cleaning of the concentrated latex container. For skim crepe production, the wastewater would be given off from the separation of rubber residual fraction and cleaning its storage pond. In addition, it might be released from the crushing of the rubber after the coagulation with the acid, in addition to the washing of the rubbers. Integrating the two sources of wastewater, total wastewater discharged from the skim crepe process was in the range of 24.9 – 65.3 m^3 ton production $^{-1}$. From the preliminary investigation, the skim crepe process generated larger amount of wastewater than the concentrated latex production. Even though, it has to be reminded that the skim crepe itself was the waste remained from the production of the concentrated latex. It was the value added to the waste. Generally, the skim crepe process released the wastewater at the end of the working hour. It was not continuous discharge, unlike the concentrated latex process. Thus, it adversely affected to the working of bacteria in the biological treatment. That‘s another reason why the proposed method was chosen in the last section of this research.

For the rubber block, the wastewater was generated around 5.8 – 37.0 m^3 ton production^{-1}. Although the number of this wastewater seems to be more than those obtained from the concentrated latex process, the number of contaminants was lower than the wastewater from the concentrated latex. This was caused by the water dilution of the latex before coagulation, followed by the washing of the rubber. Most of the rubber block wastewater was released from the coagulation tray after separating out the rubber content. The wastewaters consisted of the serum, acid, and water added in the coagulation step. Other sources included the crushing and cleanings of the trays, storage tanks, and machines.

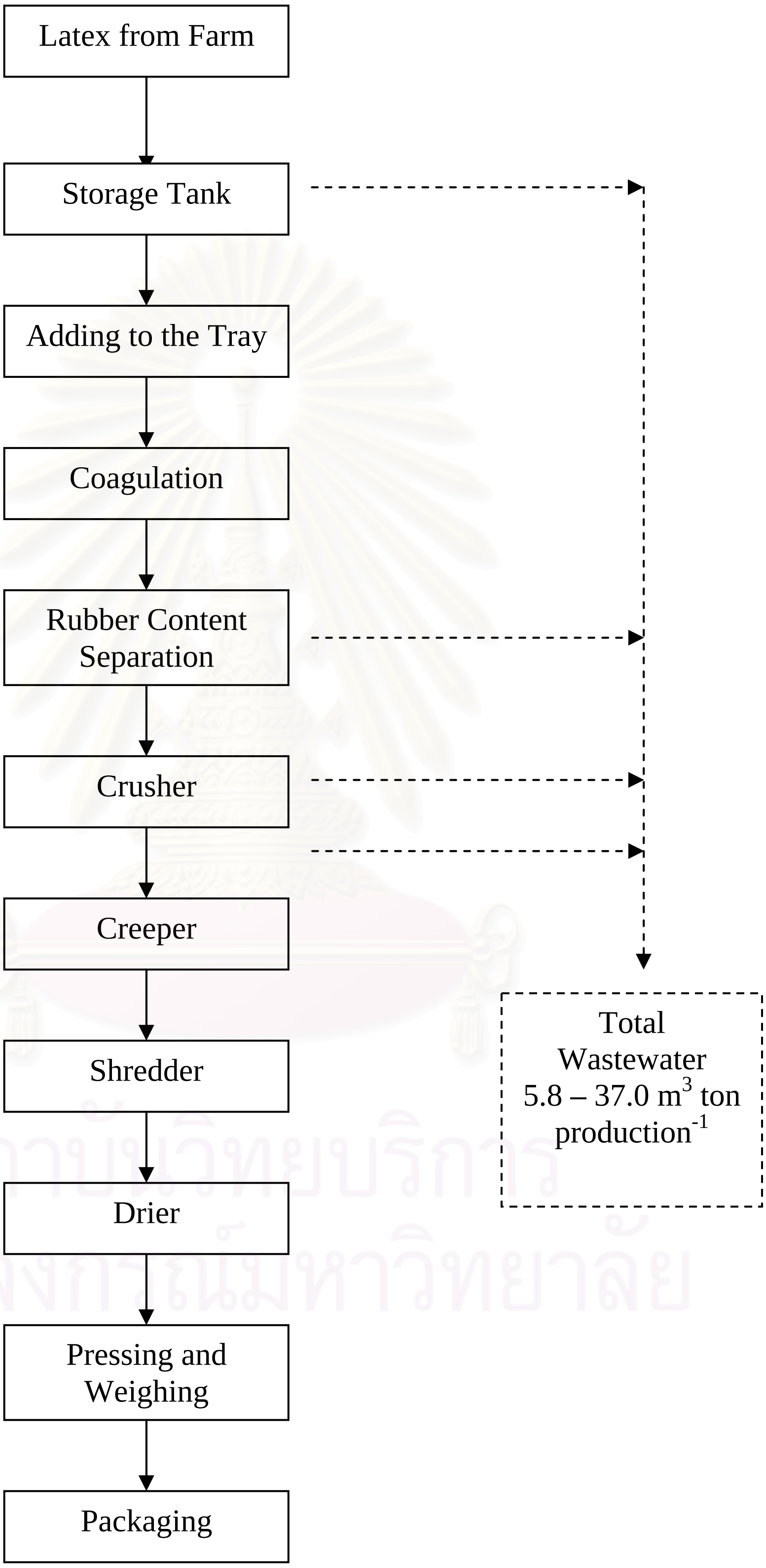


Figure 4.2 Sources of wastewater generated from the rubber block STR5L (Kaewyod, 1997)

4.2 Wastewater characterization

To obtain the organic compounds in the wastewater as much as possible, the extraction would be requisite to be optimized. In this research, the conventional extraction method, the liquid-liquid extraction, and the solid phase extraction were optimized and the consequent results were compared to each other.

4.2.1 Liquid – liquid extraction (LLE)

Simple, inexpensive, reliable, and efficient, LLE or called as solvent extraction was used the most for organic matter (Batterhan and Parry, 1996 and Komjarova and Blust, 2006). This method could be used to determine organic pollutants in water, and it allows extraction of organic compounds from both particulate and dissolved fractions. (Lacorte *et al.*, 2003) This method could be used for separation of all compounds, which are low, medium and high volatility (Mamede and Pastore, 2006). Hence this method was selected in this study, according to its advantages. There were several factors that could influence LLE efficiency. Of these factors, four variables were studied for the optimization of LLE method, including the type of the organic solvent, the volume of the solvent, the number of the extraction and the shaking time.

4.2.1.1 Type of organic solvents

Because LLE was based on the partition of organic compounds between the aqueous sample phase and an immiscible organic solvent (Christian, 1994), the solvent polarity is an important factor affecting LLE. In this study, n-hexane (polarity index = 0.1), dichloromethane (polarity index = 3.4), and ethyl acetate (polarity index = 4.4) were used (Snyder and Kirkland, 1979). The extractants from various solvents were analyzed by SEC under the optimum conditions. The solvent providing the highest response was selected as the best extraction solvent for the next experimental step. Since there were many peaks of organic fractions, the highest peak was concerned. The reason was based on the risk assessment. The risk depends on exposure and toxicity, as presented in Eq. (4.1): (U.S. Deapartment of Energy, 2006)

$$Risk = Exposure \ x \ Toxicity \qquad (4.1)$$

In addition to the type of pollutant, the toxicity depends on the dose as well. Because of this, the optimization was based on the highest peak, representing the highest dose or dominant species group.

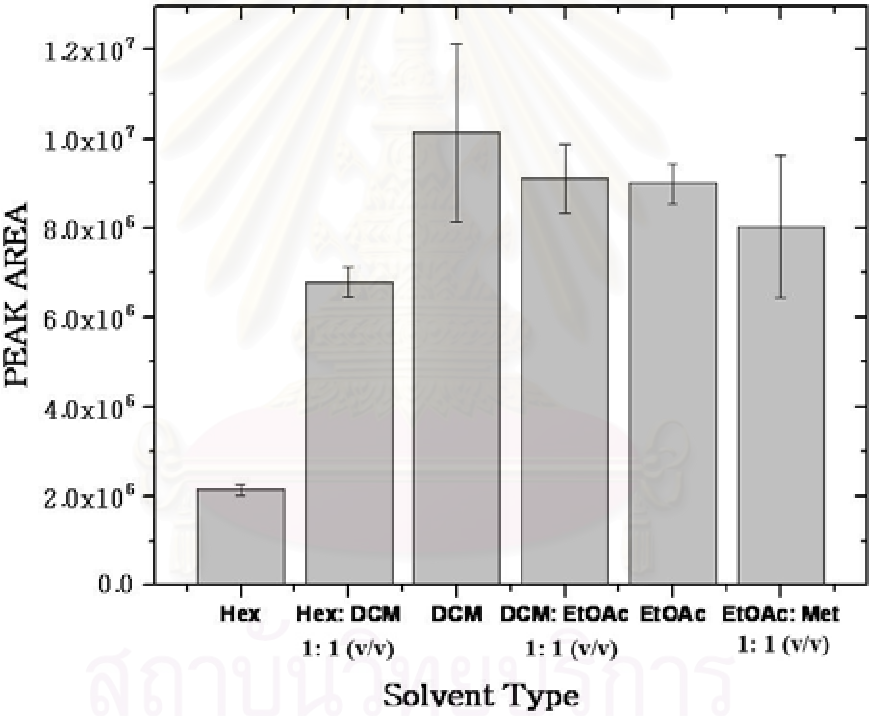


Figure 4.3 Effect of the organic type on LLE based on 20 mL solvent and 100 mL wastewater

Even though the identical chromatogram profiles of contaminated organic compounds were obtained from all solvents, it gave the difference in the number of the peak area. As shown in Fig. 4.3, the dichloromethane provided the highest peak area. However, it created the problem of repeatability because of its high volatility. The repeatability/precision problem appeared again when the polarity was increased by using the mixture of the ethyl acetate and methanol with volume ratio of 1:1 (v/v).

Even though, unlike dichloromethane, the problem was due to the increased polarity, large quantification error may be resulted from the evaporation stage (Serrano and Gallego, 2006). Comparing the use of dichloromethane:ethyl acetate 1:1 (v/v) with the pure ethyl acetate, both of them led to insignificantly difference. To simplify sample preparation, the pure ethyl acetate was selected as the suitable solvent for LLE.

4.2.1.2 <u>Volume of the extract solvent</u>

Since LLE possessed the partition mechanism, the separation efficiency mainly depends on the interfacial area generated through mixing the two phases, *i.e.* the higher the interfacial area, the higher was the separation efficiency (López-Montilla *et al.*, 2005). One way to improve the interfacial area is the increase in the volume of the extract solvent. The effect of the extract solvent on the extraction efficiency was shown in Fig.4.4

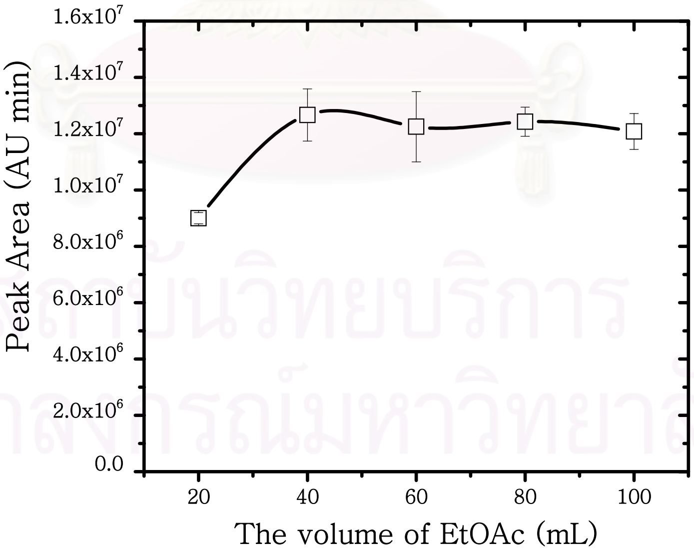


Figure 4.4 Effect of the solvent volume on LLE based on 100 mL wastewater

As presented in Fig. 4.4, when the volume of ethyl acetate increased from 20 mL to 40 mL, the peak area was increased by about 40%. This was attributed to the increase in the interfacial surface area. The increased extraction efficiency from the increasing solvent volume could be also confirmed by Eq.(4.2): (Kebbekus *et al.*, 1998)

$$E = \frac{1}{1+V_r/D} \qquad (4.2)$$

Where E = Extraction efficiency.

V_r = Volume ratio of the wastewater and organic solvent.

D = Partition coefficient between the concentration of the pollutant in the solvent and the concentration of the pollutant in the wastewater.

However, the increasing amount of the solvent volume more than 40 mL did not promote any further extraction efficiencies. In turn, it caused the problem of the evaporation and it also decelerated the separation rate of colloidal droplet (Treybal, 1980). Thus, the optimum solvent volume was fixed at 40 mL ethyl acetate for further experiments.

4.2.1.3 Number of successive extractions

In general, a single extraction did not provide sufficiently high extraction efficiency. Better efficiency could be obtained by carrying out several successive extractions using smaller volumes of the solvent (Kebbekus *et al.*, 1998; López-Montilla *et al.*, 2005). For this reason, analytical LLE was frequently carried out by using repeated extraction of the wastewater, each time using the same volume of solvent. In this study, the number of successive extractions varied within the range of 1-4. It could be not divided more than 4, because of limitation from the ethyl acetate solubility.

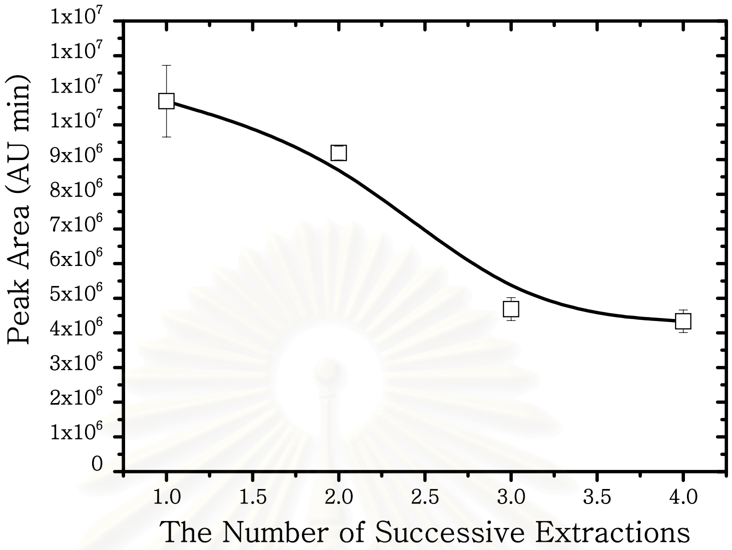


Figure 4.5 Effect of number of successive extractions on LLE based on 100 mL wastewater and 40 mL ethyl acetate

In contrast with the general case, as shown in Fig. 4.5 the increase in the number of extractions led to the decreased of the extraction efficiency. It was possible that the small rubber particles remaining in wastewater could adsorb the ethyl acetate. The higher number of successive extractions, the less solvent volume per one times extraction. This increased the contacting between the rubber particles and the extract solvent. The solvent adsorption by rubber particles was increased first and then decreased in terms of the solvent volume. This caused the extraction efficiency decreasing. Therefore, the best number of the extractions was only one time extraction in this case.

4.2.1.4 Shaking time

As mentioned above, the extraction efficiency was enormously relied on the interfacial area of two phases. The important factor for the increasing area in LLE method was the shaking time, which should be sufficient for pollutant to transfer from the wastewater to the extract solvent. In this research, the shaking time was determined in the range of 0.5 min to 15 min, as demonstrated in Fig. 4.6.

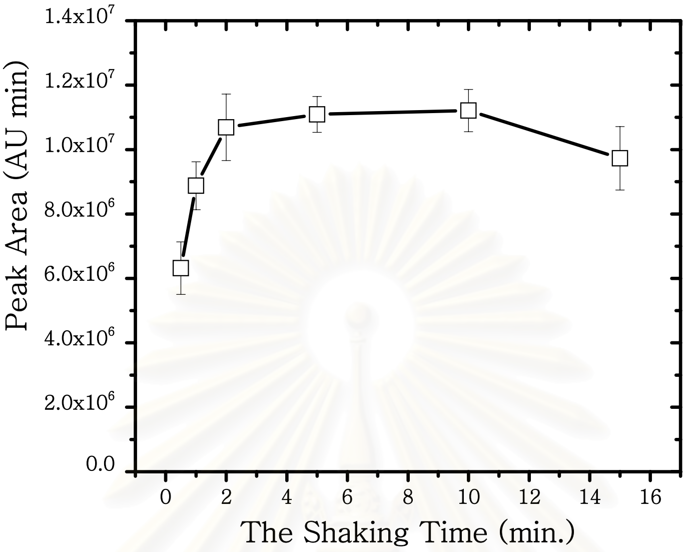


Figure 4.6 Effect of the shaking time on LLE based on 100 mL wastewater and 40 mL ethyl acetate

According to Fig.4.6, the increasing shaking time caused the increase in the mass of the organic extractant. This demonstrated the influence of the turbulent contacting between two phases. However, such impact was limited after 2 min and the obtained peak area started to decrease at 15 min. This was attributed to the slow separation rate of very small colloidal droplet, caused by too long shaking time, and insufficient fixed separation time. Noted that the horizontal shaking was more efficient than the circular motion (Komjarova and Blust, 2006).

In summary, the optimum extract condition for LLE was 40 mL ethyl acetate per 100 mL wastewater, one time extraction and 2 min shaking time.

4.2.2 Solid phase extraction (SPE)

With advantage over LLE, the modern technical SPE requiring less solvent was widely used for the pollutant analysis (Less *et al.*, 1998; Rouessac and Rouessac, 2000). Considering the SPE procedure, there were three parameters related to the extraction efficiency such as the type of the elution solvent, the volume of elution solvent and the flow rate of a sample loading.

4.2.2.1 Types of the elution solvent

The polymeric binding sorbent like Oasis HLB was used in this study, so it was necessary to determine the elution solvent, which is strong enough for the desorption process (Kloepfer *et al.*, 2004). Being varied with polarity, six elution solvents were investigated, including hexane, dichloromethane, ethyl acetate, hexane/dichloromethane mixture 1:1 (v/v), dichloromethane/ethyl acetate 1:1 (v/v), and ethyl acetate/methanol 1:1 (v/v). The results are shown in Fig. 4.7.

According to the compound identification resulted from GC/MS in the subsequent sections, it was shown that the highest SEC peak was indole groups. These compounds belong to the property of moderate polarity and they were well soluble in benzene, which is with polarity index 2.7. (Snyder and Kirkland, 1979) This number was closed to the dichloromethane’s polarity index (3.1) and considerably different from hexane and ethyl acetate (0.1 and 4.4, respectively). The results agreed well with the polarity index, for example, dichloromethane provided the highest peak area and was the best suitable elution solvent, as shown in Fig 4.7. Comparing with the LLE result in Fig. 4.3, dichloromethane used as the elution solvent in SPE provided higher precision/repeatability than as the extraction solvent in LLE. There was no problem resulting from the dichloromethane’s volatility. This was due to the low solvent volume used, leading to the cutting off of the evaporation step. The advantage of higher precision of SPE was cited in the literature (Kebbekus and Mitra, 1998).

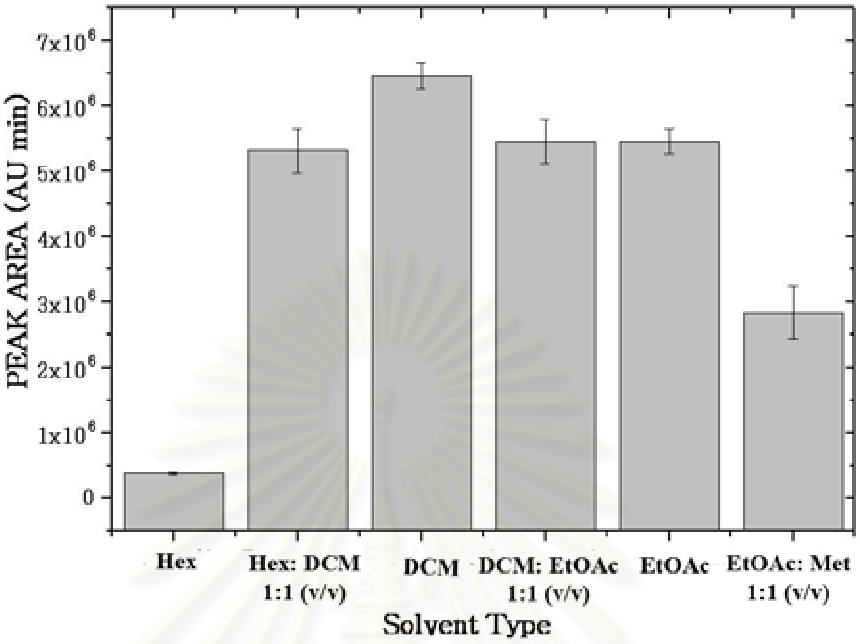


Figure 4.7 Effect of type of elution solvent on SPE based on 50 mL wastewater

4.2.2.2 <u>Volume of the elution solvent</u>

Another important factor for extracting the organics from the solid phase cartridge was the volume of the elution solvent. It should be sufficient to elute all organics trapped in the packed sorbent so as to prevent the sample loss. In general, the cartridge was not just used in one single time. It would be washed and reused again. From our preliminary study, Oasis HLB could be reused approximately 5 times before the problems of clogging and crack occur. Hence, to prevent the carry-over in the cartridge, the volume of the elution solvent should be sufficient to elute the organics as much as possible. In this research, the volume of dichlromethane varied in the range of 1-5 mL. The results are presented in Fig. 4.8.

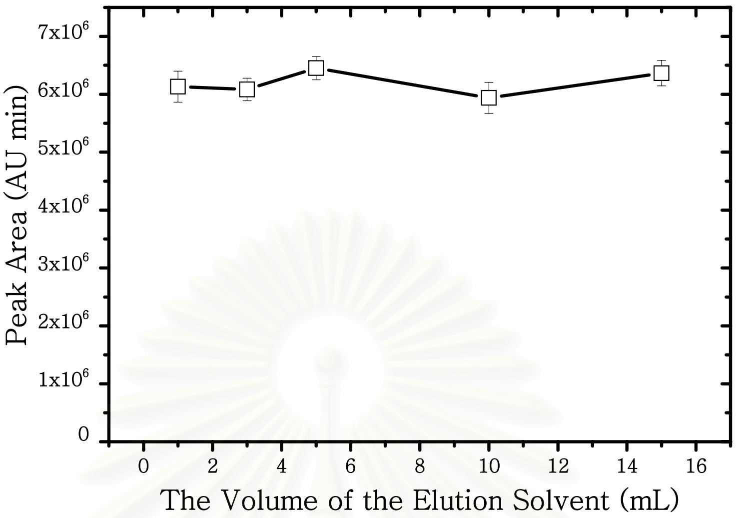


Figure 4.8 Effect of elution solvent volume on SPE based on 50 mL wastewater

From the results shown above, there was no effect of the solvent volume over the range of 1 – 15 ml dichloromethane. In other words, 1 ml of solvent was enough to elute all the organic from the solid adsorbent. In fact, there was the confirmation of such results by adding another 1 mL dichloromethane after the first 1 mL elution. No peaks were found in SEC chromatogram. Therefore, 1 ml of solvent was optimum and used for further experiments. These results agreed with the literature, which mentioned the environmental samples typically consuming 1.25 mL solvent per 50 mL samples by SPE, while it took 30 – 60 mL per 100 mL sample by LLE (Wercinski, 1999).

4.2.2.3 Flow rate of the sample loading

When the fluid flow through a circular tube, its flow rate was proportional to the pressure gradient, as shown in Eq.(4.3): (Bird *et al.*,1960)

$$Q = \frac{\pi(\Delta P)R^4}{8\mu L} \qquad (4.3)$$

Where Q = Volume flow rate
ΔP = Pressure gradient including gravitational force
R = Tubular radius
L = Tubular length
μ = Fluid viscosity

To reduce the human error from the flow rate measurement, the vacuum pressure was utilized rather than the sample flow rate in this study.

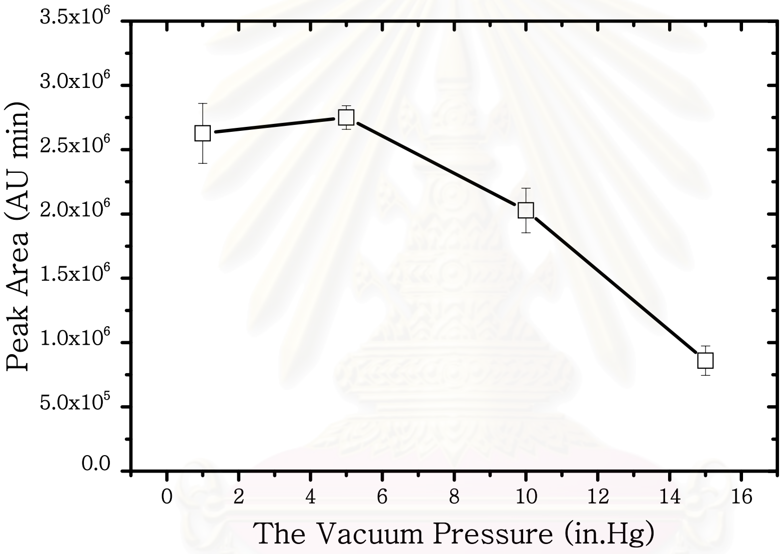


Figure 4.9 Effect of vacuum pressure on SPE based on 50 mL wastewater

According to the Fig.4.9, the increase of the vacuum pressure led to the reduction of extracting organic substances due to the less contacting time between the dichloromethane and the adsorbed organics substances. However, the decrease in the vacuum pressure from 5 to 1 in.Hg could not increase the number of extracted organics. Consequently, the eluted time should be minimized at the optimum vacuum pressure of 5 in of Hg per cm cartridge diameter. In conclusion, the optimum condition for SPE was 1 mL dichloromethane extract solvent and 5 in.Hg per cm cartridge diameter.

4.2.3 Comparison between LLE and SPE

Regardless of the typical advantage/disadvantage, both extraction methods were applied and compared to each other at their optimum conditions. The GC-MS chromatograms were obtained from two methods, as presented in Fig.4.10

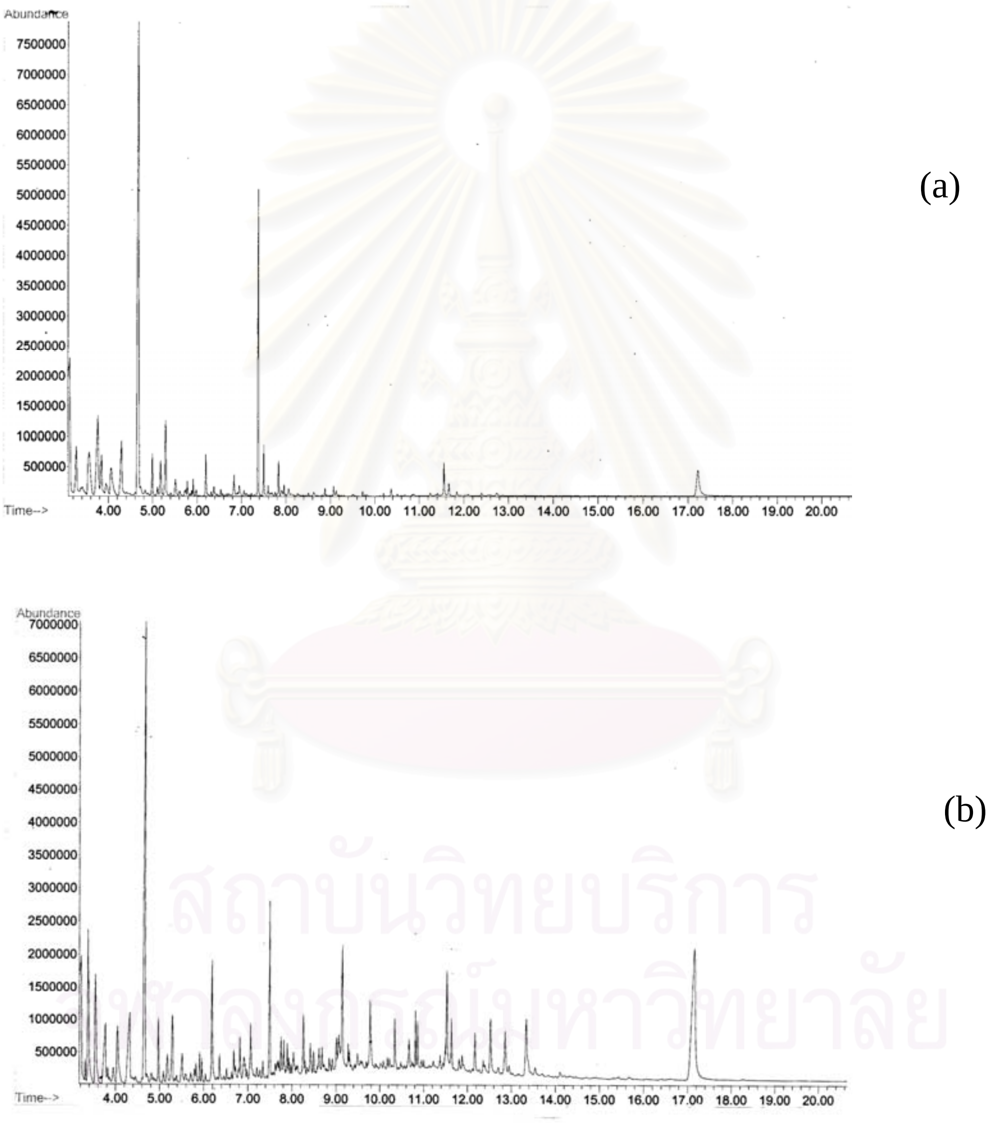


Figure 4.10 GC/MS chromatogram of extract from (a) LLE (b) SPE

As shown in Fig.4.10, the LLE provided the response of the first dominant species higher than SPE. However, the SPE presented the advantage over LLE in the number of organic species. This was more important for the target compound characterization. As a result, SPE was selected as the suitable extraction method in this study.

4.2.4 Identification by GC-MS

The wastewater was collected and analyzed every two weeks from November, 2004 to April, 2005. This sampling period were covered over both the cropping and leave shedding seasons. The samples were extracted by SPE with the different polarity solvents before fractionation by SEC, and then analyzed by GC-MS. The obtained mass spectrum was compared with WILEY275 and HPPEST-spectral library, and reference compounds. Based on their frequency of appearance during six months of the sampling period, the identified substances could be classified into 7 groups. Their average concentrations and percentage of each identified substance in relation to the total of compounds located were compiled as shown in Table 4.2 and Table 4.3 for the raw and treated wastewater, respectively. The chronic compounds (C) were used if they appeared more than 80% of samples being analyzed, the frequent compounds (F) with a frequency between 50% and 80%, and the accidental compounds (A) with the frequency below 50%. Two dominated species in the raw wastewater were 3-methylindole and 1,2- benzene dicarboxylic acid, bis(2-methylpropyl) ester or di-isobutyl phthalate (DIBP), which show the frequencies of 61.33% and 6.43%, respectively. These two species not only appeared in high concentration, but they were also found in every sample.

Table 4.2 Compounds found in RAW wastewater for 6 months monitoring

Substances	Occurrence	Range (mg L^{-1})	Average ±SD (mg L^{-1})	%
Acid				
Hexanoic acid	C	0.56-2.72	1.26±0.69	1.66
Heptanoic acid	C	0.35-2.49	1.45±0.64	1.92
Cyclohexanecarboxylic acid (or Benzoic acid, hexanydro-)	C	0.74-4.90	2.90±1.37	3.83
Octanoic acid (or Caprylic acid)	C	0.08-2.34	0.58±0.63	0.76
Boric acid	C	0.08-1.99	0.79±0.56	1.04
Nonanoic acid	F	0.08-1.80	0.46±0.67	0.60
Propionic acid	C	0.22-1.16	0.62±0.33	0.82
Benzoic acid, 2-amino- (or Anthranilic acid)	F	0.12-0.79	0.36±0.18	0.47
Dodecanoic acid (or Lauric acid)	C	0.08-0.45	0.15±0.11	0.20
α-methyl-2-aminobenzeneacetic acid	C	0.19-0.78	0.35±0.18	0.46
Tetradecanoic acid (or Myristic acid)	F	0.08-0.46	0.19±0.12	0.25
Palmitic acid	C	0.12-0.29	0.19±0.06	0.26
Octadecanoic acid (or Stearic acid)	F	0.16-0.87	0.33±0.27	0.44
3,5-dihydro-4-methylphenylacetic acid	A	0.61-0.86	0.76±0.11	1.01
Heptadecene-(8)-carbonic acid-(1)-	A	0.39-0.46	0.42±0.05	0.56
Indole derivatives				
1H-indole	C	0.14-1.42	0.50±0.35	0.66
3-methylindole (or skatole)	C	17.66-66.76	41.16±17.43	61.33
Oxindole (or 2H-indol-2-one, 1,3-dihydro-)	C	0.13-0.40	0.22±0.09	0.30
3-methyloxindole (or 3-methylindole-2(3H)-one)	C	0.13-1.28	0.53±0.37	0.70
1H-indole-3-ethanamine, N,N-dimethyl-	A	0.07-0.08	0.08±0.00	0.10
(1H)indole, 4-methoxy-3-cyanomethyl	A	0.10-0.11	0.10±0.00	0.13
1H-indole-3-ethanol (or Trytophol or 3-(2-hydroxyethyl)indole)	C	0.11-0.90	0.32±0.23	0.43
1H-indole-2,3-dione (or Isatin)	F	0.24-0.59	0.38±0.15	0.50
Indole-3-acetic acid	C	0.20-1.19	0.68±0.32	0.90
3-methyl-3-(3-methylindole-2-yl)-(3H)-indole	A	0.14-0.56	0.36±0.17	0.48
1-methyl-3-(2-(acetylamino)ethyl)indole	A	0.14-0.60	0.33±0.17	0.43
5-hydroxyindolacetic acid	F	0.11-0.16	0.12±0.03	0.16

Table 4.2 Compounds found in RAW wastewater for 6 months monitoring (cont.)

Substances	Occurrence	Range (mg L^{-1})	Average ±SD (mg L^{-1})	%
Phthalates				
1,2-benzenedicarboxylic acid, diethyl ester	F	0.07-0.33	0.17±0.10	0.22
1,2-benzenedicarboxylic acid, bis(2-methylpropyl) ester	C	0.71-11.85	4.46±3.73	6.43
1,2-benzenedicarboxylic acid, butyl cyclohexyl	F	0.10-0.37	0.24±0.09	0.31
1,2-benzenedicarboxylic acid, dibutyl ester	C	0.15-0.56	0.33±0.16	0.43
1,2-benzenedicarboxylic acid, dicyclohexyl ester	A	0.15-0.61	0.30±0.21	0.39
Alcohols and phenols				
4-methyl cathechol (or 1,2 Benzenediol, 4-methyl or 2-hydoxyl-4-methylphenol)	F	0.10-0.76	0.30±0.27	0.40
4-hydroxy-3-methoxybenzyl alcohol	A	0.08-0.12	0.10±0.01	0.13
3,5 dimethoxy-p-coumaric alcohol	A	0.08-0.08	0.08±0.00	0.11
9,10-dihydrotribenz0[a,c,e]cycloocten-9-ol	A	0.17-0.35	0.26±0.13	0.34
4-methylphenol (*p*-cresol)	C	0.33-3.18	1.66±1.02	2.19
2-methoxy-4-methylphenol	F	0.10-1.76	0.64±0.55	0.84
3-methoxyphenol	F	0.19-1.43	0.63±0.54	0.84
3,4-dimethoxyphenol	F	0.08-1.01	0.30±0.30	0.40
Phenol, 3,5-bis(1,1-dimethylethyl)-	F	0.08-0.21	0.13±0.05	0.17
4-(ethoxymethyl)-2-methoxyphenol	A	0.22-0.42	0.32±0.14	0.43
2-6-di-*tert*-butyl-4-methylphenol	F	0.10-0.50	0.22±0.16	0.29
Thiazoles				
2-hydroxybenzothiazole (or 2(3H)-Benzothiazolone)	A	0.08-0.08	0.08±0.00	0.11
2-mercaptothiazoline (or 4,5-hydro-2-mercaptothiazole or 2-thiazolidinethione or metabasal)	A	0.08-0.14	0.10±0.03	0.10
Thiocarbamates				
Zinc diethylthiocarbamate	C	0.08-0.17	0.12±0.03	0.16
Zinc dimethylthiocarbamate	A	0.10-0.10	0.10±0.00	0.13

Table 4.2 Compounds found in RAW wastewater for 6 months monitoring (cont.)

Substances	Occurrence	Range (mg L^{-1})	Average±SD (mg L^{-1})	%
Miscellaneous				
Ethanone, 1-(4-aminophenyl)- (or 1-acetyl-4-aminobenzene or 4-acetylphenylamine)	C	0.07-0.19	0.13±0.04	0.17
2H-1-benzopyran-2-one, 7-hydroxy-6-methoxy	A	0.11-0.11	0.11±0.00	0.15
5.alpha.-Estran-2-one	F	0.27-1.16	0.80±0.34	1.06
1,1,1a-trimethyl-1,1a-dihydrocycloprop[a]inden-6(6a)-one	A	0.09-0.09	0.09±0.00	0.12
4-Amino-5-acetyl-7-azatetracyclo[7.3.1.1(3,11).0(3,7)tetradec-4-en-6-one	A	0.33-1.26	0.79±0.66	1.05
Octadecane	A	0.10-0.17	0.12±0.03	0.16
Acetaldehyde, (3-chloro-5,5-dimethyl-2-cyclohexen-1-ylidene)-, (E)-	C	0.08-0.46	0.25±0.11	0.33
Isofraxidin (or 6,8-dimethoxy-7-hydroxycoumarin)	F	0.11-0.63	0.26±0.17	0.35
2-(2´-nitro-3´-thienyl)pyrimidine)	A	0.12-0.13	0.13±0.00	0.17
Tetramethyl thiurammonosulfide	A	0.01-0.31	0.16±0.15	0.21
Cyclopropaneoctanal, 2-octyl	A	0.13-0.13	0.13±0.00	0.17
8B, 13:8A, 14-diepoxy-14, 15-bisnorlabdane	A	0.12-0.49	0.25±0.13	0.33
8-Hydroquinone (or oxine or oxoquinoline or phenopyridine)	A	0.10-0.10	0.10±0.00	0.13
4-methyl-2-(3-thienyl)pyridine	A	0.08-0.08	0.08±0.00	0.11
3-cyano-6-(2-furyl)-4-(methylthio)-2-phenylpyridine	A	0.18-0.64	0.37±0.18	0.49
1-methoxy-3-methyl-9H-carbazole	A	0.11-0.11	0.11±0.00	0.15

Table 4-3 Compounds found in TREATED wastewater for 6 months monitoring

Substances	Occurrence	Range (mg L^{-1}) 10^{-1}	Average±SD (mg L^{-1}) 10^{-1}	%
Acid				
Heptanoic acid	A	0.84-0.84	0.84±0.00	0.77
Octanoic acid (or Caprylic acid)	A	0.67-0.67	0.67±0.00	0.62
Boric acid	A	0.74-0.74	0.74±0.00	0.69
Nonanoic acid	A	0.67-0.86	0.77±0.13	0.71
Propionic acid	F	0.31-1.29	0.99±0.35	0.91
Cyclopropaneacetic acid	A	0.89-0.89	0.89±0.00	0.82
Dodecanoic acid (or Lauric acid)	A	0.77-0.94	0.86±0.12	0.79
α-methyl-2-aminobenzeneacetic acid	A	0.88-0.88	0.88±0.00	0.81
Tetradecanoic acid (or Myristic acid)	A	0.85-0.94	0.90±0.05	0.84
Palmitic acid	C	0.31-1.73	1.13±0.38	1.04
Octadecanoic acid (or Stearic acid)	A	1.09-3.30	2.19±1.56	2.03
Dehydroabietic acid	A	2.18-2.18	2.18±0.00	2.02
Indole derivatives				
1H-indole	F	0.75-3.48	1.60±0.99	1.48
3-methylindole (or skatole)	C	2.13-21.89	8.53±5.58	7.89
Oxindole (or 2H-indol-2-one, 1,3-dihydro-)	A	0.80-0.80	0.80±0.00	0.74
3-methyloxindole (or 3-methylindole-2(3H)-one)	F	0.87-2.22	1.34±0.48	1.24
1H-indole-3-ethanol (or Trytophol or 3-(2-hydroxyethyl)indole)	A	0.69-1.12	0.96±0.24	0.89
3-methyl-3-(3-methylindole-2-yl)-(3H)-indole	A	1.04-4.10	2.57±2.16	2.38
Indole-3-acetic acid	A	1.76-13.91	7.84±8.59	7.25
Phthalates				
1,2-benzenedicarboxylic acid, diethyl ester	C	0.65-1.00	0.82±0.12	0.76
1,2-benzenedicarboxylic acid, bis(2-methylpropyl) ester	C	4.47-36.61	14.54±9.21	13.45
1,2-benzenedicarboxylic acid, butyl cyclohexyl	A	2.32-2.32	2.32±0.00	2.15
1,2-benzenedicarboxylic acid, dibutyl ester	C	1.19-5.35	2.47±1.54	2.28
1,2-benzenedicarboxylic acid, dicyclohexyl ester	C	0.89-2.68	1.54±0.65	1.43
1,2-benzenedicarboxylic acid, dioctyl ester	A	3.06-5.20	4.13±1.51	3.82

Table 4.3 Compounds found in TREATED wastewater for 6 months monitoring (cont.)

Substances	Occurrence	Range (mg L^{-1}) 10^{-1}	Average±SD (mg L^{-1}) 10^{-1}	%
Phenols				
Phenol	A	0.85-0.85	0.85±0.00	0.79
4-methylphenol (*p*-cresol)	A	0.82-0.82	0.82±0.00	0.76
3-methoxyphenol	F	0.65-1.31	0.91±0.25	0.84
Phenol, 3,5-bis(1,1-dimethylethyl)-	F	0.67-0.78	0.73±0.04	0.68
Phenol, 3,4,5-trimethoxy- (or Antiarol)	A	0.76-0.76	0.76±0.00	0.70
2-6-di-*tert*-butyl-4-methylphenol	A	1.32-1.32	1.32±0.00	1.22
2,5-di-*tert*-butyl-2,6-dinitrophenol	A	3.49-3.49	3.49±0.00	3.23
Thiazoles				
2-hydroxybenzothiazole (or 2(3H)-Benzothiazolone)	A	0.74-0.97	0.86±0.69	0.79
2-mercaptothiazoline (or 4,5-hydro-2-mercaptothiazole or 2-thiazolidinethione or metabasal)	F	1.10-2.78	1.99±0.09	1.84
Thiocarbamates				
Zinc diethylthiocarbamate	F	0.67-1.05	0.87±0.14	0.81
Zinc dimethylthiocarbamate	A	0.33-0.33	0.33±0.00	3.08
Miscellaneous				
2,6-di-*tert*-butyl-4-methylene-2,5-cyclohexadiene-1-one	A	0.66-0.92	0.79±0.13	0.73
Ethanone, 1-(4-aminophenyl)- (or 1-acetyl-4-aminobenzene or 4-acetylphenylamine)	F	0.78-1.70	1.09±0.36	1.01
1,4-nahthalenedione, 2-hydroxy-3-methyl-	A	0.79-0.79	0.79±0.00	0.73
7,9-di-*tert*-butyl-1-oxaspiro[4,5]deca-6,9-diene-2,8-dione	A	0.83-1.02	0.95±0.11	0.88
5.alpha.-Estran-2-one	A	1.50-1.50	1.50±0.00	1.39
4-Amino-5-acetyl-7-azatetracyclo[7.3.1.1(3,11).0(3,7)tetradec-4-en-6-one	A	7.35-7.35	7.35±0.00	6.80
Octadecane	F	0.70-1.81	1.20±0.45	1.11
Tetracosane	A	4.33-4.33	4.33±0.00	4.00
Quinazoline, 4-methyl	A	0.75-0.75	0.75±0.00	0.69

Table 4.3 Compounds found in TREATED wastewater for 6 months monitoring (cont.)

Substances	Occurrence	Range (mg L^{-1}) 10^{-1}	Average±SD (mg L^{-1}) 10^{-1}	%
Miscellaneous (Cont.)				
Benzaldehyde, 4-hydroxy-3-methoxy-	A	0.76-0.76	0.76±0.00	0.70
10,10-dimethylanthrone hydrazone	A	1.03-1.03	1.03±0.00	0.95
2-*tert*-butyl-3,3,5-trimethyl-4-(2-methyl-2-propenylidene)-1,2-diaza-3-sila-5-cyclopentene	A	2.50-2.50	2.50±0.00	2.31
Isofraxidin (or 6,8-dimethoxy-7-hydroxycoumarin)	A	0.81-0.81	0.81±0.00	0.75
8B, 13:8A, 14-diepoxy-14, 15-bisnorlabdane	A	2.08-2.08	2.08±0.00	1.92
3-cyano-6-(2-furyl)-4-(methylthio)-2-phenylpyridine	A	3.79-3.79	3.79±0.00	3.51

For the first dominant species, 3-methylindole (3MI) or called skatole, it was a microbial fermentation product of amino acid L-tryptophan (Tuomola *et. al.*, 2000). This amino acid was one of the Hevein structure, which was protein dissolved in the latex serum (Archer, 1960; Kajornchaikul, W., 1982). Consequently, it was possible that the raw material rubber latex was the source of 3MI. The degradation of the protein was guaranteed with the existence of 4-methylphenol or *p*-cresol (see Table. 4-2), because *p*-cresol could be formed during the degradation of proteins from aromatic amino acid (Reemtsma and Jekel, 1997). The 3-methylindole was malodorous compound (Hwang *et. al.*, 1994). This culprit might cause the Para rubber plant frequently to face with the odor claim from the neighborhood, apart from the odor issue of ammonia and hydrogen sulfide. In addition to the bad smelling problem, the chemical disinfection of indole-containing wastewater with dilute aqueous solution of chlorine, chlorine dioxide, and chloramines could also result in the formation of chlorinated aromatic products, which were known as carcinogen (Lin and Carson, 1984). Furthermore, the findings from a series of sophisticated immunological assays indicate that 3MI might be involved in the human lung disease (Kaster and Yost, 1997). In addition to human health concern, this compound was very lipophilic and might accumulate in adipose tissue of pigs, it leading to a severe reduction of the organoleptic quality of pork (Hansson, *et al.* 1980). Moreover, it has been shown to induce acute bovine pulmonary edema and emphysema in cattle and goats (Gu *et al.*, 2002; Carlson *et al.*, 1972) and it will be harmful to meat industry in view of heavy losses, if suffered with such compound (Deslandes *et al.*, 2001). Like 3-methylindole, 1H-indole could be naturally obtained from the biodegradation of tryptophan in the rubber serum (Schüssler and Nitschke, 1999). Because sulfuric acid was added in the skim crepe process, the sulfate-reducing bacteria were rich in the rubber trap pond. Under sulfate-reducing condition, sulfate serves as an electron acceptor resulting in the production of H_2S, and at the same time the organic compounds could be oxidized, serving as a source of carbon, *e.g.* 1H-indole. This compound was hydroxylated to form oxindole and then dehydrogenated at 2- and 3-position sequentially prior to the cleavage of the pyrrole ring between 2- and 3-positions and both isatin and anthranilic acid were finally formed, respectively (Gu. *et al*., 2002). With this, it is understood that the oxindole, isatin and anthranilic acid were detected in this study. Moreover, the degradation of indole could be found with the similar pathway under methanogenic condition (Gu and Berry, 1991) and denitrifying condition (Madsen and Bollag, 1989). In the literature, one microorganism capable of degrading indole was named as *Desulfobacterium indolicum* (Bak and widdel, 1986). The detection of 3-methyloxindole indicated that our dominant species (3MI) was hydroxylated at 2- position under methanogenic condition. Under this condition, the complete mineralization did not occur but it was obtained by sulfate-reducing bacteria. If sulfate was rich in the system, the pyrrole ring of 3-methyloxindole will be broken down at the place between 2- and 3-position to form α-methyl-2-aminobenzeneacetic acid and then it was mineralized to form H_2S and CO_2 in the long run (Gu *et al.*, 2002). Notice that not only 3MI causes unpleasant odor but its biodegraded products H_2S also result in the same odor problem. Thus, in the later section of this research the treatment process was proposed to solve this problem, *i.e.*, Fenton’s treatment. In addition to 1H-indole and 3-methylindole, the amino acid tryptophan could be biologically degraded to form indole-3-acetic acid, tryptophol and 5-hydroxyindolacetic acid as well (Kieslich, 1976; Mattivi *et al.*, 1999; Vaarmann et al., 2002). Other indole derivatives were sporadically detected with the possibility that these derivatives were microbially derived from biogenic matter (Reemtsma and Jekel, 1997).

The second dominant species DIBP and its derivatives were classified into a group of phthalic acid esters. These esters were often found as lab contaminants (Castillo and Barceló, 2001), so the blanks were run along with the samples to confirm the experimental results. The phthalates were used as a softener, which were added to the plastic (Kotowska *et al.*, 2006). Approximately 85% of whole production was used as plasticizers for polyvinyl chloride (PVC) resins, adhesives, and cellulose film coating (Vitali et al., 1997). Other applications are in the insect repellent, insecticide carriers, propellant, lacquer, paint, rubber, wire, cable and ink (Kotowska *et al.*, 2006; Bauer and Herrmann, 1997; Borch *et al*,. *article in press*; Saillenfait *et al., article in press*). Since phthalates were not chemically bound to the host polymers, they could be leached from the phthalate products and eventually migrate into the water environment (Fang *et. al.*, 2007; Yang *et al.*, 2005). In the production process, there were lots of the products made from phthalates including adhesive and PVC. Therefore, it was possible that the phthalates were leached from those mentioned sources. It seems the sources of phthalates were non-point sources. However, there was some literatures found DIBP in airborne extracted from the creeper/calendering stage (Fracasso et al., 1999). Moreover, the phthalate esters were used as the added emollients of the rubber and they could be leached into the water (Sarasa *et al.*, 2006). There were two reasons that made the appearance of DIBP in wastewater should be concerned. First, the phthalic acid esters were difficult to degrade biologically. The experimental results were in agreement with the report of Ejlertsson *et al.* (1997). Fig. 4.11 showed the chromatograms of the raw and treated wastewater. There were DIBP peaks at 7.35 min. appearing in both chromatograms. Since the DIBP was difficult to biodegrade, only biological treatments were not sufficient, thus it was recommended for the related industries to add more physical or chemical units for the post-treatment of the wastewater. The post treatment suitable for DIBP could also efficiently solve the problem of excessive COD to comply with the regulation-allowed value. Consequently, the Fenton’s oxidation treatment process was proposed in the further section in this research.

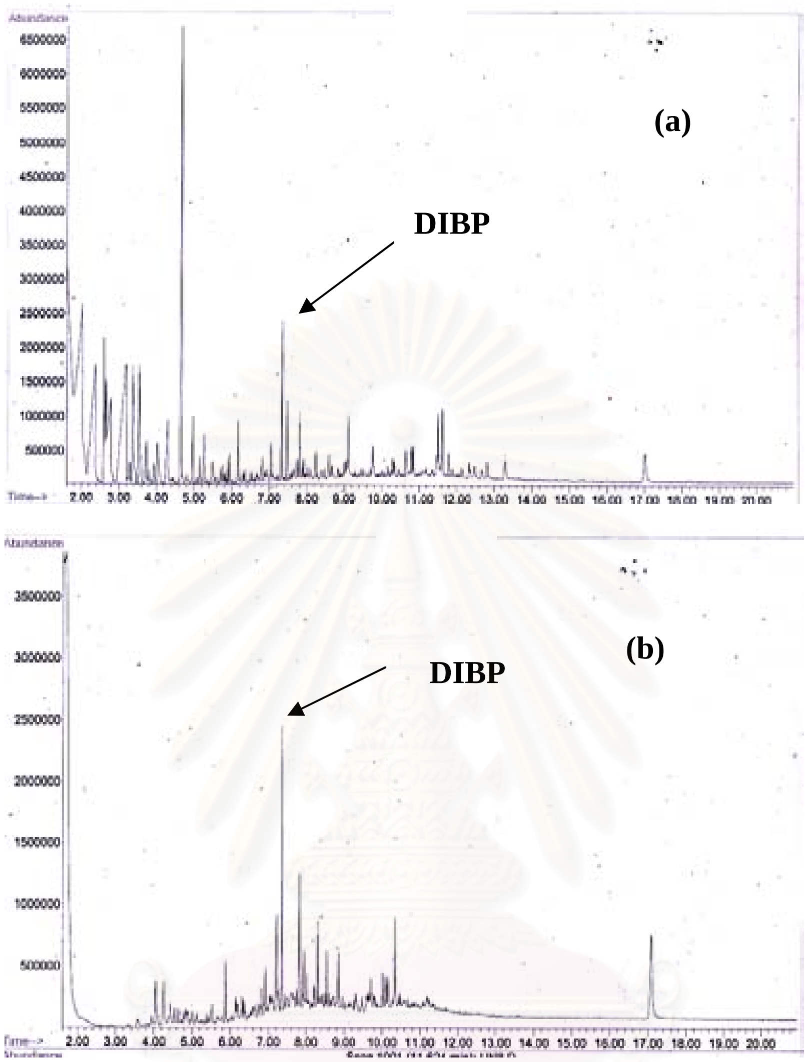


Figure 4.11 GC/MS chromatograms of the extract from (a) Raw (b) Treated wastewater

The second reason relates to the toxicity of DIBP. Because of their low water solubility and high octanol/water partition coefficients (log k_{ow} = 4.11 for DIBP) (Leyder and Boulanger, 1983), they tends to accumulate in the soil or sediment and in the biota living in the phthalate containing water (Chiou *et al.*, 2006). The United States Environmental Protection Agency (USEPA) and the China National Environmental Monitoring Centre had classified phthalate esters as a top priority pollutant for risk assessment (Wang *et. al.*, 1997; Kaneco *et al.*, 2006). They were one of endocrine disruptors (Li *et al.*, 2005) and some of them were considered as carcinogens, teratogens and mutagens (Giam *et al.*, 1982). Although the solubility of phthalates was very low, they were acutely and chronically toxic at concentrations below their aqueous solubility and the toxicity increased with increasing alkyl chain (Stables *et al.*, 1997).

The pH of the raw wastewater was found in the acidic zone. Without the question, many types of acid were found in the wastewater. The natural rubber latex contained various fatty acids, such as palmitic acid, tetradecanoic acid and stearic acid (Kawahara *et al.*, 2000). These saturated fatty acids including propionic acid derived from the microbial degradation of the carbohydrates in serum latex or the hydrolysis of lipid (Kajornchaikul, 1982). The aliphatic carboxylic acids (C_6-C_9) and cyclohexanecarboxylic acid were found as metabolic origin (Reemtsma and Jekel, 1997; Sekiyama *et al*., 2003). Together with the ammonia and boric acid, the lauric acid (or dodecanoic acid) might be added into the concentrated latex to preserve it from the biodegradation. By this method, the carboxylate group of the protein was changed into the carboxylate-boric acid chelate that the bacteria could not consume it. The advantage of this preservation method over the ammonia alone using was that it could prevent the thickening of the latex in the rubber production process (Kajornchaikul, 1982).

Phenols were liberated by anaerobic cleavage of the high molecular weight compounds and were not completely degraded within the anaerobic stage (Reemtsma *et al.*, 1997). As mentioned above, 4-methylphenol (*p*-cresol) was the product, which was formed during the degradation of proteins from aromatic amino acid. The microorganism, *Rhodococcus* and *Pseudomonas sp.*, were responsible for phenol degradation. The typical metabolic pathway occurred via the catechol derivatives (Martinez *et al.*, 2006). Thus, it was possible that 4-methyl cathechol was intermediates of the *p*-cresol decomposition. Other phenol derivatives, 3,5-bis(1,1-dimethylethyl)-phenol was used as antioxidants (Sarasa *et al.*, 2006). The 2-6-di-*tert*-butyl-4-methylphenol was commonly used as additives in rubber (Castillo and Barcelo, 2001). The sources of methoxyphenols were unclear, even through some researches found that they were the thermal degradation product from burning wood and appeared in the smoke (Kjällstrand *et. al.*,1998: Kjällstrand *et. al.*, 2000; Kjällstrand and Petersson, 2001).

To produce the low ammonia concentrated latex, the mixture of zinc diethylthiocarbamate, lauric acid and ammonia was applied into the latex rather than ammonia alone. The utilization of the low or high ammonia depended on the final product of the rubber (Kajornchaikul, 1982). The thiazole derivatives were added into the rubber as the secondary accelerator to promote the vulcanization. (Wolfe, 1971; Kajornchaikul, 1982; Puig *et al*., 1996). Although most of chemicals in the miscellaneous group could be not identified in terms of their sources, some could be done. Tetramethyl thiurammonosulfide could be used for many purposes, i.e. the mixture of preservatives, the vulcanizing agent or the secondary accelerator (Kajornchaikul, 1982; Caioli, 1997).

Comparing Table 4-2 with 4-3, 26 substances was disappeared or lower than the detection limit in the treated wastewater, while other 14 ones were the new species. However, most of them were detected sporadically. Of all these substances, phthalate group was the most recalcitrant. The efficient post-treatment method is required to manage those species in this group. Thus, the scope of this research was expanded to solve these problems through post treatment measure.

4.3 Wastewater treatment

According to the characterization results, one of the dominant species in water was non-biological and the other compound was the malodorous. This indicated that only biological unit was insufficient to treat the target wastewater, requiring fast and effective treatment method, like the advanced oxidation processes (AOPs). Fenton’s process, one of AOPs, has been proved to be effective and economical method (Al-tawabini, 2003). Compared with other AOPs, it does not need the energy input to active hydrogen peroxide and commonly requires the shorter reaction time (Lücking *et al.*, 1998; Zazo *et al.*, 2005). Consequently, Fenton’s process was applied in this study to treat the two identified dominant species.

4.3.1 Optimization of Fenton’s operating condition for the synthetic wastewater of DIBP

4.3.1.1 Effect of Initial H_2O_2 Concentration

In the treatment of a large volume of wastewater, the most important factor concerned is the cost. The major cost in Fenton’s treatment is the chemical cost, especially the H_2O_2. Based on such concern, the H_2O_2 dose should be determined properly. In this study, the initial concentration of H_2O_2 was determined by optimizing its molar ratio to DIBP. The molar ratio of H_2O_2 versus DIBP ranging from 0 to 20 was investigated. The results were depicted in Fig. 4.12

As shown in Fig. 4.12, no degradation of DIBP occurred in the system in the absence of H_2O_2. With H_2O_2, the decomposition rate of DIBP was very fast since its residual concentration remained unchanged after only 5 min. The degradation rate increased with increasing initial H_2O_2 concentration. This is due to more hydroxyl radicals and hydroperoxyl being produced according to Reactions (4.4) and (4.5), respectively.

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + \bullet OH + H_2O \qquad (k_1 = 58 \quad mol^{-1}dm^3s^{-1}) \qquad (4.4)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + \bullet OOH + H^+ \qquad (k_2 = 0.002 \quad mol^{-1}dm^3s^{-1}) \qquad (4.5)$$

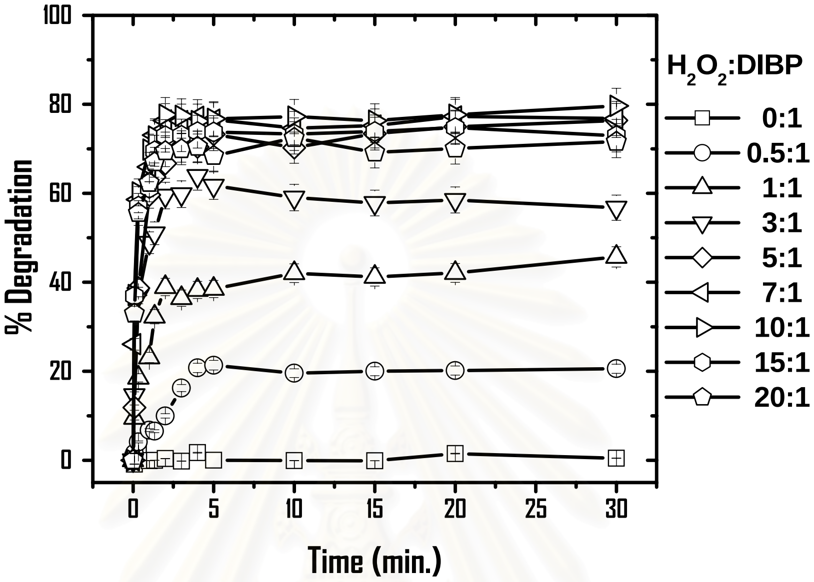


Figure 4.12 Effect of initial H_2O_2 concentration on DIBP degradation at pH = 3 and molar ratio of $[Fe^{2+}]$: [DIBP] = 3:1

However, it seems to reach the break point as the ratio was increased to the number of 10. Beyond this number, the increase of H_2O_2 concentration led to the decrease of DIBP degradation. The reason is attributed to the consumption of •OH and HO_2• by excess H_2O_2, as presented in Reactions (4.6) and (4.7) (Yang *et al.*, 2005; Christensen *et al.*, 1982). Note that the rate of •OH consumption can not be overlooked, if compared to its formation rate through Fenton reaction (Reaction (4.4))

$$\bullet OH + H_2O_2 \rightarrow HO_2 \bullet + H_2O \qquad (k_3 = 2.7x10^7 \, mol^{-1}dm^3s^{-1}) \qquad (4.6)$$

$$HO_2 \bullet + H_2O_2 \rightarrow \bullet OH + H_2O + O_2 \qquad (k_4 = 0.5 \pm 0.09 mol^{-1}dm^3s^{-1}) \qquad (4.7)$$

Furthermore, the excess hydroxyl radicals could be recombined by itself and hydroperoxyl radicals as well, as shown in Reactions (4.8) – (4.10). As a result, when the number of hydroxyl radical was reduced, the degradation efficiency decreased.

$$2\bullet OH \rightarrow H_2O_2 \qquad (k_5 = 4.2x10^9\ mol^{-1}dm^3s^{-1}) \qquad (4.8)$$

$$HO_2\bullet + \bullet OH \rightarrow H_2O + O_2 \qquad (k_6 = 1.0x10^{10}\ mol^{-1}dm^3s^{-1}) \qquad (4.9)$$

$$2HO_2\bullet \rightarrow H_2O_2 + O_2 \qquad (k_7 = 8.3x10^5\ mol^{-1}dm^3s^{-1}) \qquad (4.10)$$

According to Fig. 4.12, the difference of 3% was observed in the degradation of DIBP as the molar ratio was increased from 5 to 10. Since the difference is so slightly, the optimal ratio of 5 was selected throughout all other experiments.

4.3.1.2 Effect of Initial Fe^{2+} Concentration

Unlike hydrogen peroxide, Fe^{2+} was only the catalyst in homogeneous Fenton’s reaction, not the direct source of •OH. However, the reduction reaction of Fe^{3+} to Fe^{2+} (Reactions (4.5)) was relatively slower, as compared to the oxidation reaction of Fe^{2+} (Reactions (4.4)). For this reason, the suitable number of initial Fe^{2+} concentration becomes essential. In this study, the concentration ratio of Fe^{2+} versus DIBP varied between 0-15 for the DIBP degradation. The results were shown in Fig. 4.13.

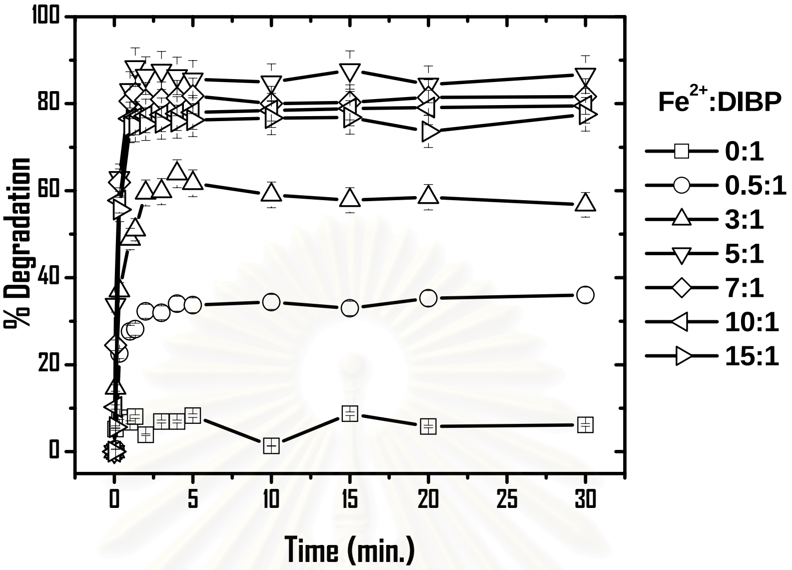


Figure 4.13 Effect of initial Fe^{2+} concentration on DIBP degradation at pH = 3 and molar ratio of $[H_2O_2]$: [DIBP] = 5:1

Without ferrous ion, there was a negligible DIBP degradation, with its removal efficiency less than 10%. This indicated that DIBP could be decomposed with pure H_2O_2 to some extent, even though the major degradation was contributed to Fenton's oxidation. The degradation increased significantly with the increasing in ferrous concentration. This was because the increasing in the initial Fe^{2+} concentration led to the more hydroxyl radicals for DIBP degradation. However, the negative effect appeared as the ratio was larger than 5, at which higher Fe^{2+} concentration results in lesser degradation of DIBP. The reason was that the •OH and HO_2• could be scavenged by the excess Fe^{2+} and Fe^{3+}, as shown in Reactions (4.11) - (4.13) (Gernjak *et al.,* 2006; Rivas *et al.,* 2001).

$$Fe^{2+} + HO\bullet \rightarrow Fe^{3+} + OH^{-} \qquad (k_8 = 4.3x10^8 mol^{-1}dm^3s^{-1}) \qquad (4.11)$$

$$Fe^{3+} + HO_2\bullet \rightarrow Fe^{2+} + O_2 + H^{+} \qquad (k_9 = 1.0x10^4 mol^{-1}dm^3s^{-1}) \qquad (4.12)$$

$$Fe^{2+} + HO_2\bullet + H^{+} \rightarrow Fe^{3+} + H_2O_2 \qquad (k_{10} = 1.2x10^6 mol^{-1}dm^3s^{-1}) \qquad (4.13)$$

Like the effect of excess H_2O_2, the ·OH consumption rate by the excess Fe^{2+} was considerably higher than its production from Fenton's reaction. Consequently, DIBP degradation was decelerated. Another possible reason was the occurrence of complexation reactions of Fe^{3+} by SO_4^{2-}. Because Fe^{2+} was added into the system as $FeSO_4$, it means that the more ferrous was added in the solution, the more sulfate was formed correspondingly. Such complexation reaction will compete with the formation reaction of peroxo complexes $[Fe^{3+}HO_2]^{2+}$, which was the intermediate pathway of Fe^{3+} reduced into Fe^{2+} (Laat *et al.*, 2004). Hence, the formation of Fe^{2+} decreased, leading to the decrease in DIBP degradation. In addition to above two reasons, the third was that the increasing in $Fe(OH)_3$ catalyzes the decomposition of H_2O_2 to O_2 and H_2O, leading to decreases of OH• production and the degradation of DIBP (Höfl *et al.*, 1997). With all these reasons, the optimal ratio of Fe^{2+} versus DIBP was controlled at 5 for further experiments.

4.3.1.3 Effect of pH

Undoubtedly, the pH was an important factor affecting the performance of Fenton's reaction (See reaction (4.4)) and the iron speciation in the solution. In this study, the pH range of 1-6 was investigated.

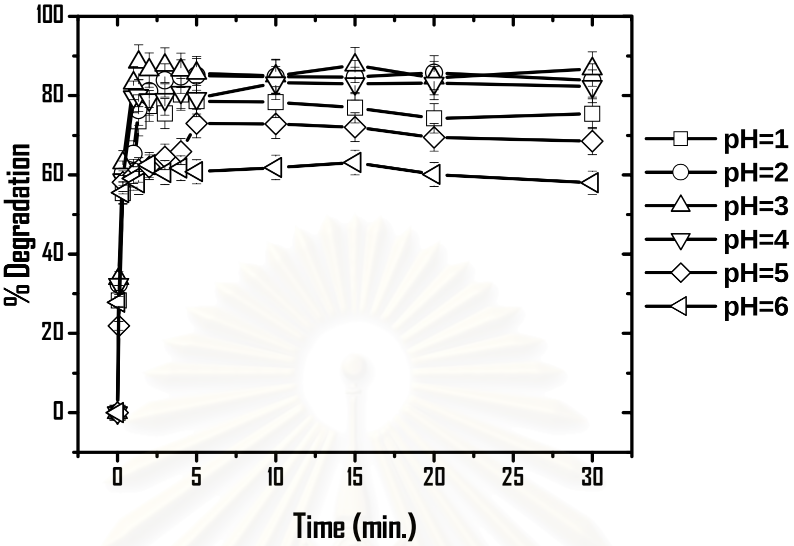


Figure 4.14 Effect of pH on DIBP degradation at molar ratio of [H_2O_2]: [Fe^{2+}]: [DIBP] = 5: 5: 1

Fig. 4.14 shows that effective oxidation occurred in the pH range of 2-4, with the highest DIBP destruction occurring at pH = 3, which is in agreement with some other reports (Pignatello, 1992; Christensen *et al.*, 1982; Gernjak *et al.*, 2006). The reason was due to the formation of dominating species of $Fe(OH)^+$. This form of iron species could be generated at pH= 2-4 and its activity is higher than the non-complex form of Fe^{2+} in Fenton's oxidation. This can serve to explain the optimal pH range for DIBP degradation (Malik and Saha, 2003). At pH > 3, the DIBP degradation declined with three possible reasons. First, the iron species started to precipitate as iron hydroxide, leading to the lower Fe^{2+} and then the lower number of ·OH for decomposing DIBP (Chiou *et al.,* 2006; Kwon *et al.*, 1999). Another reason was that the increasing in $Fe(OH)_3$ at high pH catalyzes the decomposition of H_2O_2 to O_2 and H_2O, thus decreasing the production of OH• and the degradation of DIBP (Höfl *et al.,* 1997). The last reason was that the oxidation potential of ·OH decreases with increasing pH (Kwon *et al.*,1999). On the other hand, the DIBP degradation was observed to decrease with decreasing pH when the solution pH was lower than 3, as can be explained in three aspects. First, at low pH, the hydrogen peroxide became stable probably because it solvated a proton to form an oxonium ion ($H_3O_2^+$). An oxonium ions made hydrogen peroxide electrophilic to enhance its stability and presumably to reduce substantially the reactivity with ferrous ion (Zhao *et al*., 2004). Second, the excess H^+ in the solution would consume •OH and form H_2O, as expressed in Reaction (4.14) (Chiou *et al.,* 2006).

$$\bullet OH + H^+ + e^- \rightarrow H_2O \qquad (k_{11} = 7x10^{-9} mol^{-1}dm^3s^{-1}) \qquad (4.14)$$

Third, the •OH might be scavenged by the excess sulfuric acid, shown in Reaction (4.15). (Laat *et al.*, 2004)

$$H_2SO_4 + \bullet OH \rightarrow SO_4{}^- \bullet + H^+ + H_2O \qquad (k_{12} = 1.4x10^7 mol^{-1}dm^3s^{-1}) \qquad (4.15)$$

With all these three reasons, hydroxyl radical concentration was reduced to a lower level in the system, leading to a lesser degradation of DIBP. Moreover, radical SO_4^- • produced from Reaction (4.15) would consume HO_2•, H_2O_2 and Fe^{2+}, as shown in Reactions (4.16) – (4.18) (Laat *et al.*, 2004); in turn, this may result in the decrease of •OH concentration as well.

$$SO_4{}^- \bullet + HO_2 \bullet \rightarrow SO_4{}^{2-} + H^+ + O_2 \qquad (k_{13} = 3.5x10^9 mol^{-1}dm^3s^{-1}) \qquad (4.16)$$

$$SO_4{}^- \bullet + H_2O_2 \rightarrow SO_4{}^{2-} + H^+ + HO_2 \bullet \qquad (k_{14} = 1.2x10^7 mol^{-1}dm^3s^{-1}) \qquad (4.17)$$

$$SO_4{}^- \bullet + Fe^{2+} \rightarrow Fe^{3+} + SO_4{}^{2-} \qquad (k_{15} = 3.0x10^8 mol^{-1}dm^3s^{-1}) \qquad (4.18)$$

Based on all experiments conducted in this study, it could be concluded that the optimal molar ratio for the treatment of DIBP was 5:5:1 H_2O_2: Fe^{2+}: DIBP with the pH controlled at 3. Moreover, the DIBP was removed by 87% approximately in 30 min. Compared with some other similar studies (Yang *et al., article in press*; Zhao *et al.; 2004),* the degradation of dimethyl phthalate (DMP) and diethyl phthalate (DEP) by dark Fenton's reaction were 30 and 43% at 120 min, respectively. Both compounds were treated under the same optimal conditions such as: pH = 3 and $[H_2O_2]$: $[Fe^{2+}]$ = 3:1. It was possible that the degradation efficiency was increased as the longer chain phthalate was applied.

4.3.1.4 Effect of Initial DIBP Concentration

As reported, the concentration of target pollutant is one of the important parameters in Fenton process (Muruganandham and Swaminathan, 2004). Thus, the effect of initial DIBP was investigated and the results were shown in Fig. 4.15.

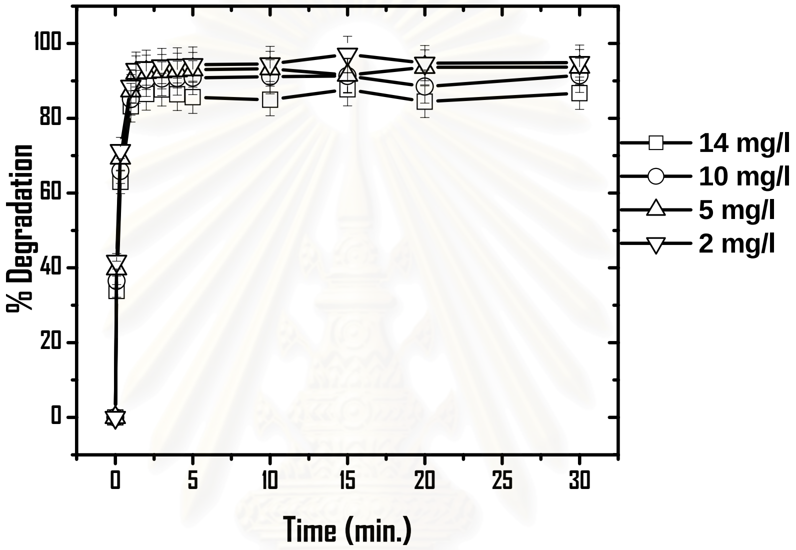


Figure 4.15 Effect of initial DIBP concentration on its degradation at pH = 3 and molar ratio of [H_2O_2]: [Fe^{2+}]: [DIBP] = 5: 5: 1

It was observed that the removal rate increased with decreasing DIBP concentration. This was because the steady-state hydroxyl radical, which was responsible for DIBP destruction, became decreasing as DIBP concentration increased. Consequently, the lower the hydroxyl radical concentration, the lesser the DIBP was degraded (Muruganandham and Swaminathan, 2004; Modirshahla *et al.*, 2007). This phenomenon was in agreement with other similar studies (Guedes *et al.*, 2003; Malik and Saha, 2003; Muruganandham and Swaminathan, 2004; Feng *et al.*, 2005; Modirshahla *et al.*, 2007).

4.3.1.5 Kinetic study for the synthetic DIBP wastewater

According to the degradation curves (Fig. 4.12 – 4.15), the DIBP decomposition could be divided into two stages. In the first stage, DIBP was degraded rapidly in the first few minutes and then the reaction became slowing down in the second stage. This can be attributed to the reaction of Fe^{2+}/H_2O_2 in the first stage and Fe^{3+}/H_2O_2 in the second stage (Malik and Saha, 2003). Undoubtedly, the first stage was more important and worth focusing than the second stage. For this reason, this study determines the rate of degradation reaction in the form of a power-law equation for the initial period reaction, which covers up to 80 -90% of the maximum DIBP reduction achieved. The initial rate of DIBP degradation was determined by drawing a tangent at time t = 0 on the concentration *v.s.* time curve. The data used to calculate the initial rate were from those plotted in Figs. 4.12-4.15.

The DIBP degradation was obtained by •OH produced from Fenton's reaction (Eq.(2.2) and (4.19))

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^- \qquad (2.2)$$

$$\bullet OH + Pollu\tan ts \rightarrow \mathrm{int}\, ermediates \qquad (4.19)$$

Consequently, the DIBP degradation was affected by 3 parameters, *i.e.* H_2O_2, Fe^{2+} and pollutant concentration. The partial orders influenced by each parameter were determined as followed;

a) Partial order by the H_2O_2 concentration

The rate equation could be generally written by

$$-\left(\frac{d[DIBP]}{dt}\right) = k_{H2O2}[H_2O_2]^a \qquad (4.20)$$

Take $\log_e$ to the both sides of equation, the equation becomes

$$\ln\left(-\frac{\Delta DIBP}{\Delta t}\right)_{initial} = \ln k_{H2O2} + a\ln[H_2O_2]_0 \qquad (4.21)$$

Where k_{H2O2} was apparent rate constant depending on H_2O_2 concentration; $[H_2O_2]$ was the hydrogen peroxide concentration (mg L^{-1}); a was partial order of H_2O_2; $\left(\frac{\Delta[DIBP]}{\Delta t}\right)_{initial}$ was the initial rate, *i.e.* the ratio between the change of DIBP concentration and time in the first min (used data from Fig.4.12 at 0, 1, 3, 5 of $[H_2O_2]$: [DIBP] molar ratio)

If plotted between ln $\left(-\frac{\Delta[DIBP]}{\Delta t}\right)_{initial}$ and ln $[H_2O_2]$, the slope would be the partial order of H_2O_2 effect, as shown in Fig.4.16.

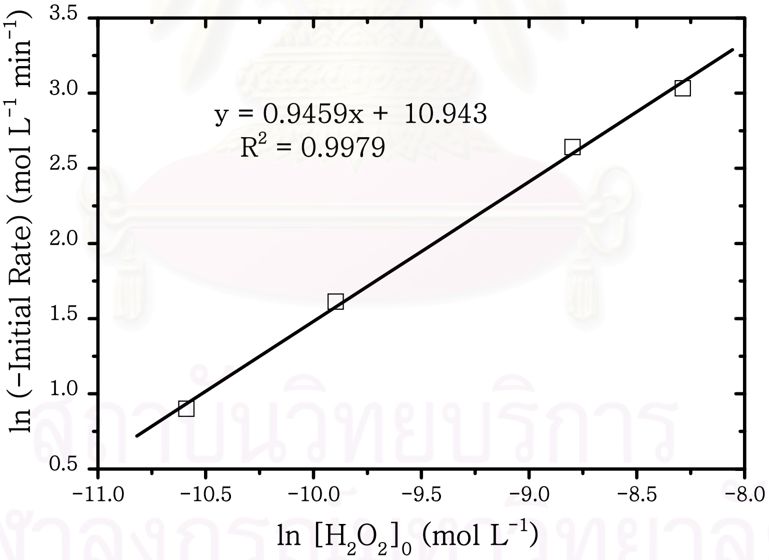


Figure 4.16 Initial rate of DIBP oxidation as a function of H_2O_2 concentration

As presented in Fig.4.19, the kinetic equation was rewritten to be

$$-\left(\frac{d[DIBP]}{dt}\right)_{initial} = 5.66x10^4[H_2O_2]_0^{0.95} \qquad (4.22)$$

b) Partial order by Fe^{2+} *concentration*

Similar to H_2O_2, the relevant equations are listed below:

$$-\left(\frac{d[DIBP]}{dt}\right) = k_{Fe2+}\left[Fe^{2+}\right]^b \qquad (4.23)$$

$$\ln\left(-\frac{\Delta[DIBP]}{\Delta t}\right)_{initial} = \ln k_{Fe2+} + b\ln\left[Fe^{2+}\right]_0 \qquad (4.24)$$

By using the data from Fig. 4.13 at 0.5, 3, 5 of [Fe^{2+}]: [DIBP] molar ratio, the initial rate was calculated determined by drawing a tangent at time t = 0 on the concentration *v.s.* time curve and Fig.4.17 was plotted.

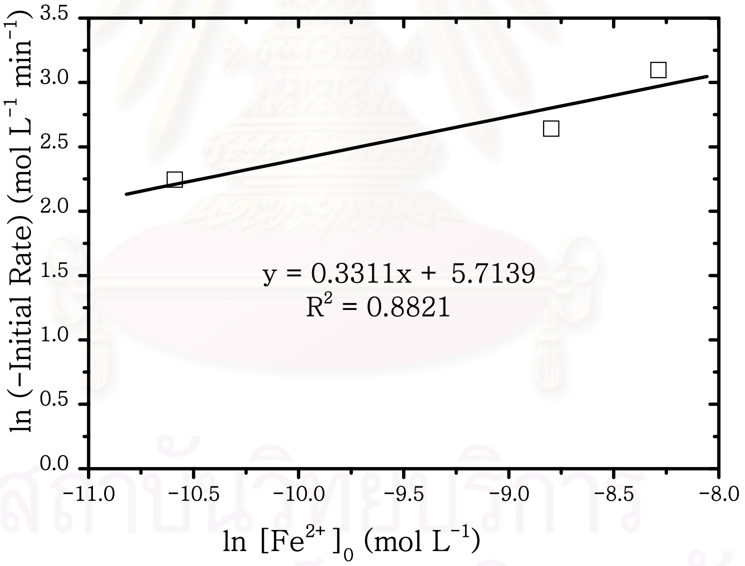


Figure 4.17 Initial rate of DIBP oxidation as a function of Fe^{2+} concentration

According to Fig.4.17, Eq.4.22 became

$$-\left(\frac{d[DIBP]}{dt}\right)_{initial} = 3.03x10^2\left[Fe^{2+}\right]_0^{0.33} \qquad (4.25)$$

c) Partial order by the initial DIBP concentration

Like the previous two parameters, the two equations with respect to DIBP are presented as follows:

$$-\left(\frac{d[DIBP]}{dt}\right) = k_{DIBP}[DIBP]^c \qquad (4.26)$$

$$\ln\left(-\frac{\Delta[DIBP]}{\Delta t}\right)_{initial} = \ln k_{DIBP} + c\ln[DIBP]_0 \qquad (4.27)$$

By using the data from Fig. 4.15 at 2, 5, 10, 14 mg L^{-1} DIBP, the initial rate was calculated determined by drawing a tangent at time t = 0 on the concentration *v.s.* time curve and Fig.4.18 was plotted.

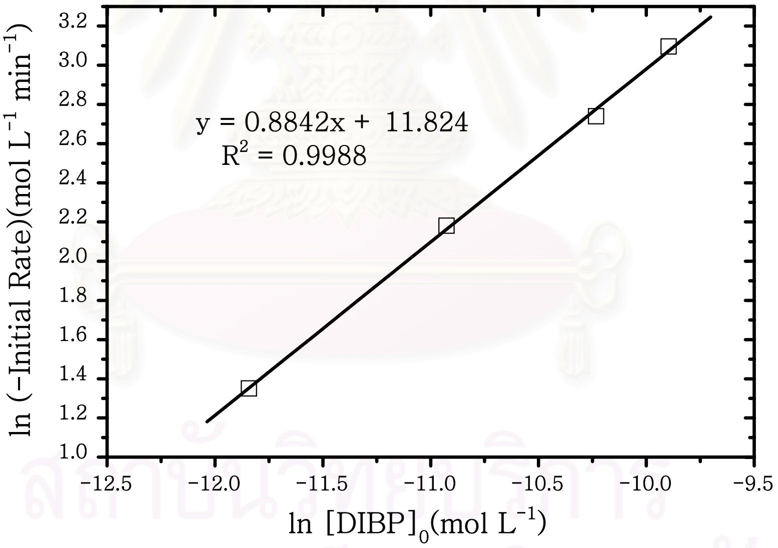


Figure 4.18 Initial rate of DIBP oxidation as a function of the initial DIBP concentration

Consequently, the partial rate equation could be expressed by:

$$-\left(\frac{d[DIBP]}{dt}\right)_{initial} = 1.36x10^5[DIBP]_0^{0.88} \qquad (4.28)$$

d) Determination of overall reaction rate constant

As mentioned previously, the initial rates of DIBP oxidation were linear-dependent on hydrogen peroxide, ferrous and initial DIBP concentrations. Eq. (4.29) represents the overall kinetic rate for DIBP oxidation by Fenton's process.

$$-\left(\frac{d[DIBP]}{dt}\right)_{Initial} = k[DIBP]_0{}^{0.88}[Fe^{2+}]_0{}^{0.33}[H_2O_2]_0{}^{0.95} \qquad (4.29)$$

Where k stands for the overall rate constants for DIBP degradation by Fenton's treatment ((L mol^{-1})$^{1.16}$ min^{-1}); $[DIBP]_0$ is the initial DIBP concentration (mol L^{-1}); $[Fe^{2+}]_0$ is the initial Fe^{2+} concentration (mol L^{-1}); $[H_2O_2]_0$ is the initial H_2O_2 concentration (mol L^{-1}) and $\left(\frac{d[DIBP]}{dt}\right)_{initial}$ is the initial DIBP degradation rate (mol L^{-1} min^{-1}).

By using a non-linear least squares method, which minimizing the sum of square error between the measured initial rates from the experiments and the calculated initial rates from Eq. (4.29), the k value could be determined and Eq. (4.29) became

$$-\left(\frac{d[DIBP]}{dt}\right)_{Initial} = 6.0x10^3[DIBP]_0{}^{0.88}[Fe^{2+}]_0{}^{0.33}[H_2O_2]_0{}^{0.95} \qquad (4.30)$$

Comparing the reaction order, H_2O_2 had the largest power (0.95). This could be inferred that the initial H_2O_2 concentration was the governing factor on the degradation rate of DIBP. In addition to the highest impact factor, H_2O_2 was also the main chemical cost in Fenton's reagent. Thus, it is essential to consider the initial concentration of H_2O_2 if the Fenton's process is applied.

4.3.2 Optimization of Fenton's operating condition for the synthetic wastewater of 3MI

Because of relatively fast degradation, 100 mg L^{-1} of 3MI was applied rather than 40 mg L^{-1}, which was the average concentration found in 6 months monitoring. Like DIBP, the effects of 4 variables were investigated.

4.3.2.1 Effect of pH

As presented in Eq. (4.4), the generation of •OH needs the supplement of H^+ or acid, so the solution pH was very important to the degradation of pollutant. Like DIBP, the pH range for 3MI degradation was varied between 1- 6. The results were depicted in the Fig.4.19.

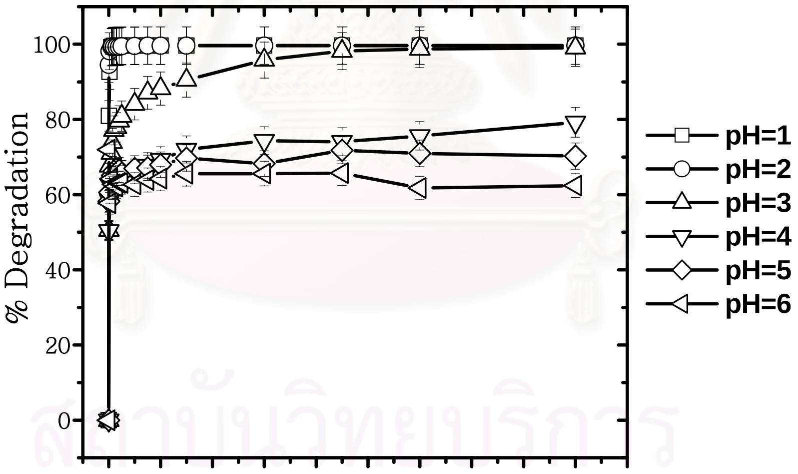


Figure 4.19 Effect of pH on 3MI degradation at molar ratio of [H_2O_2]: [Fe^{2+}]: [3MI] = 1: 1: 1

As presented in Fig. 4.19, at pH higher than 3 the results agreed with the DIBP experiments, *i.e.* the decrease in 3MI degradation with increasing pH. Consequently, the three same reasons were cited: the Fe^{2+} precipitation as iron hydroxide, the reduction of the •OH oxidation potential with increasing pH, and the decomposition of H_2O_2 catalyzed by $Fe(OH)_3$. The last reason plays the most important role in the 3MI system. Notice that the gap of the degradation between pH = 3 and pH = 4 was significant. It was attributed that at high pH the high Fe^{2+} concentration was applied in the 3MI system, leading to the larger number of $Fe(OH)_3$ and the large number of H_2O_2 being catalyzed and decomposed to form H_2O and O_2. Unlike DIBP, the 3MI was degraded to a larger degree at pH =1-2. This might be attributed that the 3MI was destructed by the concentrated acid. This could compensate the decreasing in the 3MI degradation caused by the lower pH. The effect of acid addition was referred to the section of the Fe^{2+} effect. Although the initial degradation rate at pH =1 was higher than at pH = 3, the difference in the number of degradation efficiency at 60 min was only 4% and there was no difference in both pH at 120 min. Furthermore, the acid was necessary to be added 100 times more, in order to reduce the pH from 3 to 1. For this reason, to save the acid cost, the optimum pH was selected at pH = 3.

4.3.2.2 Effect of Fe^{2+} Concentration

The suitable concentration of Fe^{2+} is obligatory. If it is too low, the degradation will be not complete. In contrast, the use of high Fe^{2+} concentration is not advisable in practice, because it incurs not only a higher cost of reagent but also the subsequent treatment requirement to remove the residual iron concentration in the effluent. (Badawy *et al.*, 2006) In this section, the concentration ratio of the catalyst Fe^{2+} versus 3MI was studied in the range of 0-3. The results were illustrated in Fig. 4.20.

The results showed that without the ferrous ion the 3MI was degraded by 20%. The two reasons might be the oxidation of 3MI by H_2O_2 alone and the degradation by the acid added. Therefore, the blank test of acid addition only was applied. The result showed that the 3MI could be degraded by the acid, which was used to adjust the pH from neutral pH down to pH=3, by about 10%. Therefore, the pure H_2O_2 accounts for the degradation of 3MI by the rest of 10%. However, the major degradation was contributed to Fenton's oxidation. The degradation increased with the increasing initial Fe^{2+} concentration, but the breaking point was found at 1.5, the molar ratio of

Fe^{2+} versus 3MI. Due to the degradation closed to 100%, more Fe^{2+} added becomes excess. This phenomenon was confirmed by the curve of the residual Fe^{2+}, as shown in Fig.4.21.

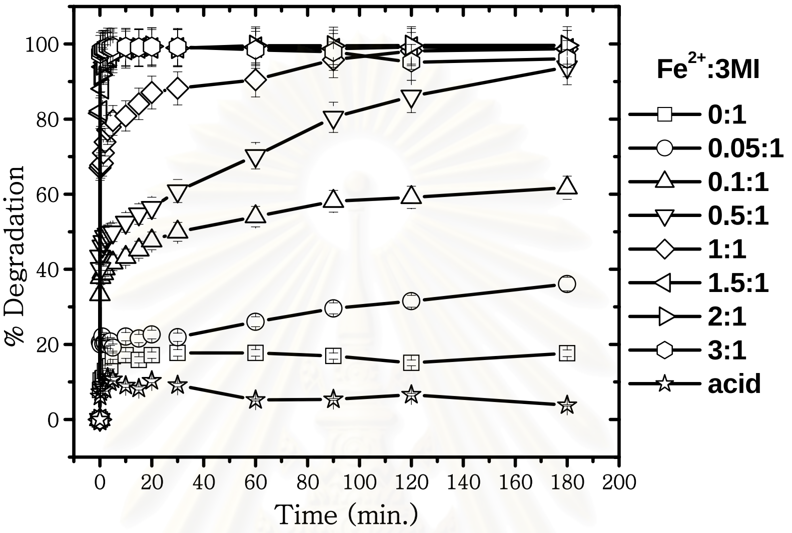


Figure 4.20 Effect of initial Fe^{2+} concentration on 3MI degradation at pH = 3 and $[H_2O_2]$: [3MI] = 1:1 molar ratio

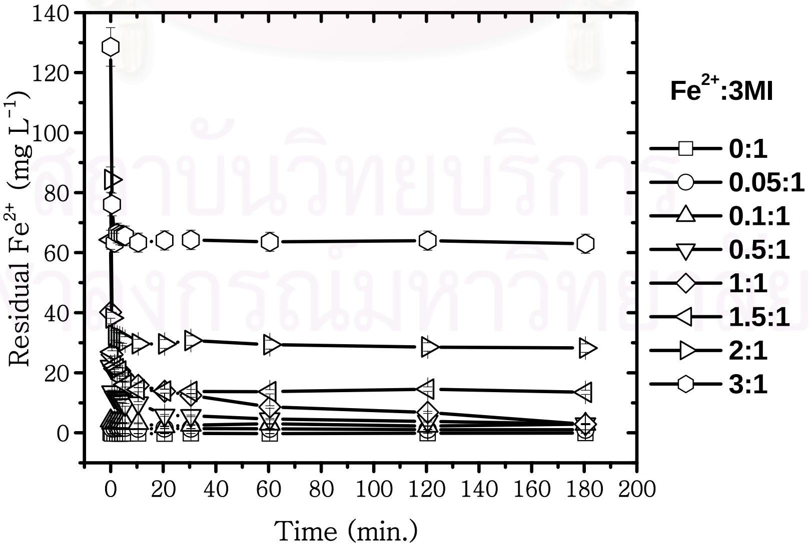


Figure 4.21 Effect of initial Fe^{2+} concentration on the Fe^{2+} residual at pH = 3 and $[H_2O_2]$: [3MI] = 1:1 molar ratio

Fig. 4.21 shows that Fe^{2+} was consumed and almost reduced to zero level if it was applied lower than 1.5. However, there's Fe^{2+} ions left in the system if it was added at the ratio more than 1.5. This excess Fe^{2+} to degrade the 3MI was not improved in its marginal benefit. In other words, the molar ratio of 1.5, Fe^{2+} versus 3MI, was sufficient to degrade 3MI, so it was selected as the optimum Fe^{2+} concentration.

4.3.2.3 Effect of H_2O_2 Concentration

As mentioned previously, the H_2O_2 consumption was a main component of the cost in the Fenton process. In addition, the excess of H_2O_2 remaining in the solution after treatment might also exceed the allowable limit of toxicity for industrial discharges to the municipal sewer system. Thus, it was necessary to determine the proper H_2O_2 concentration. In this research, different H_2O_2 concentrations were used based on the molar ratio of 0-2, its concentration versus 3MI.

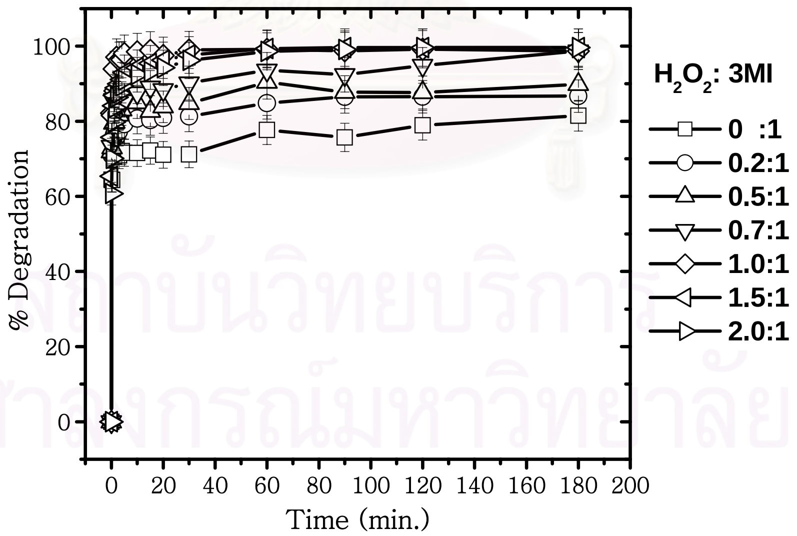


Figure 4.22 Effect of initial H_2O_2 concentration on 3MI degradation at pH = 3 and $[Fe^{2+}]$: [3MI] = 1.5:1 molar ratio

In the absence of H_2O_2, the degradation of 3MI by Fe^{2+} alone could reach up to 70%, as presented in Fig. 4.22. This indicated that the major degradation of 3MI was attributed to the reduction by Fe^{2+}. The decomposition rate was very fast and the equilibrium concentration was reached within the first 5 min. Like DIBP, the degradation increased with the increasing initial H_2O_2 concentration. However, the degradation rate started to decrease if the concentration of H_2O_2 was added at molar ratio more than 1. This was due to the same reasons mentioned in the DIBP section, *i.e.* the consumption of •OH by the excess H_2O_2 and the recombination of excess •OH. Nevertheless, the excess H_2O_2 in the range of this study was not adequate to cause the decrease in the degradation efficiency. Thus the degradation difference was not significant for the ratios of 1- 2. Thus, the optimum H_2O_2 ratio versus 3MI was selected at 1.

4.3.2.4 Effect of 3MI initial Concentration

Because the characteristics of wastewater from the concentrated latex industry fluctuated from day to day, the pollutant concentration is one of the important parameters in Fenton process. Thus, the effect of initial 3MI was studied and the results were presented in Fig.4.23.

It was pointed out that the removal rate was increased with the decreasing 3MI concentration. This was because hydroxyl radical, which was responsible for 3MI destruction, remained constant for all 3MI concentrations. The number of 3MI molecules was decreased while the hydroxyl radicals remained still the same. Consequently, the degradation efficiency became increasing with the decreasing initial 3MI concentration. Focused on the two lines of 50 and 100 mg L^{-1}, they were not different in both the efficiency and the rate of the degradation. It was implied that the initial 3MI concentration did not affect the oxidation efficiency when the 3MI concentration was less than 100 mg L^{-1}.

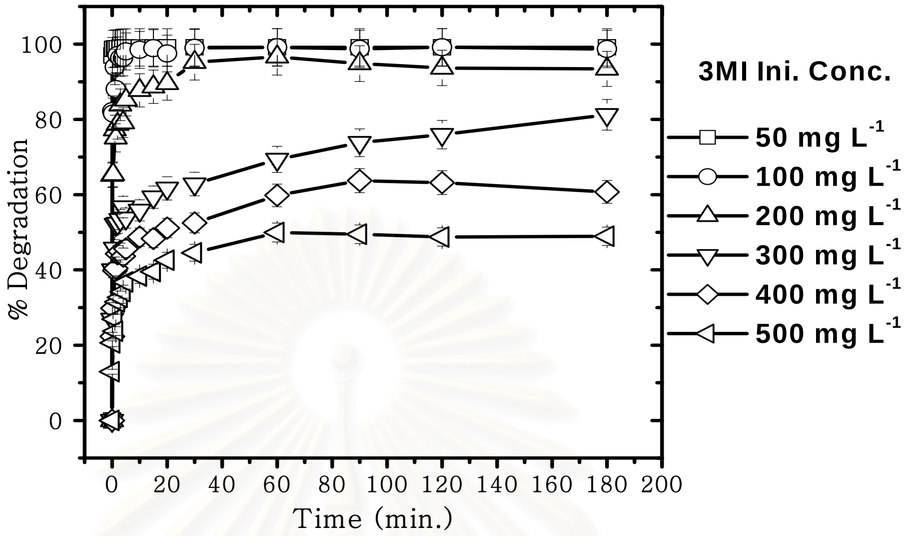


Figure 4.23 Effect of initial 3MI concentration on its degradation at pH = 3 and [H_2O_2]: [Fe^{2+}]: [3MI] = 1: 1.5: 1 molar ratio

In conclusion, the optimum of the 3MI degradation by Fenton's treatment was 1: 1.5: 1 for the molar ratio of [H_2O_2]: [Fe^{2+}]: [3MI] and pH = 3. The overall degradation was about 99% at 180 min.

4.3.2.5 Kinetic study for the synthetic 3MI wastewater

Like the DIBP degradation phenomena, the 3MI decomposition consisted of two phases, which were the fast and later slow phases. Concerning the removal rate, major degradation was contributed to the first period, which represents 90% of overall degradation achieved. Based on this, the kinetic equation was determined through the initial period of reaction. The initial rates were calculated from the data presented in Figs. 4.20 -4.23 and the results were shown in Fig. 4.24

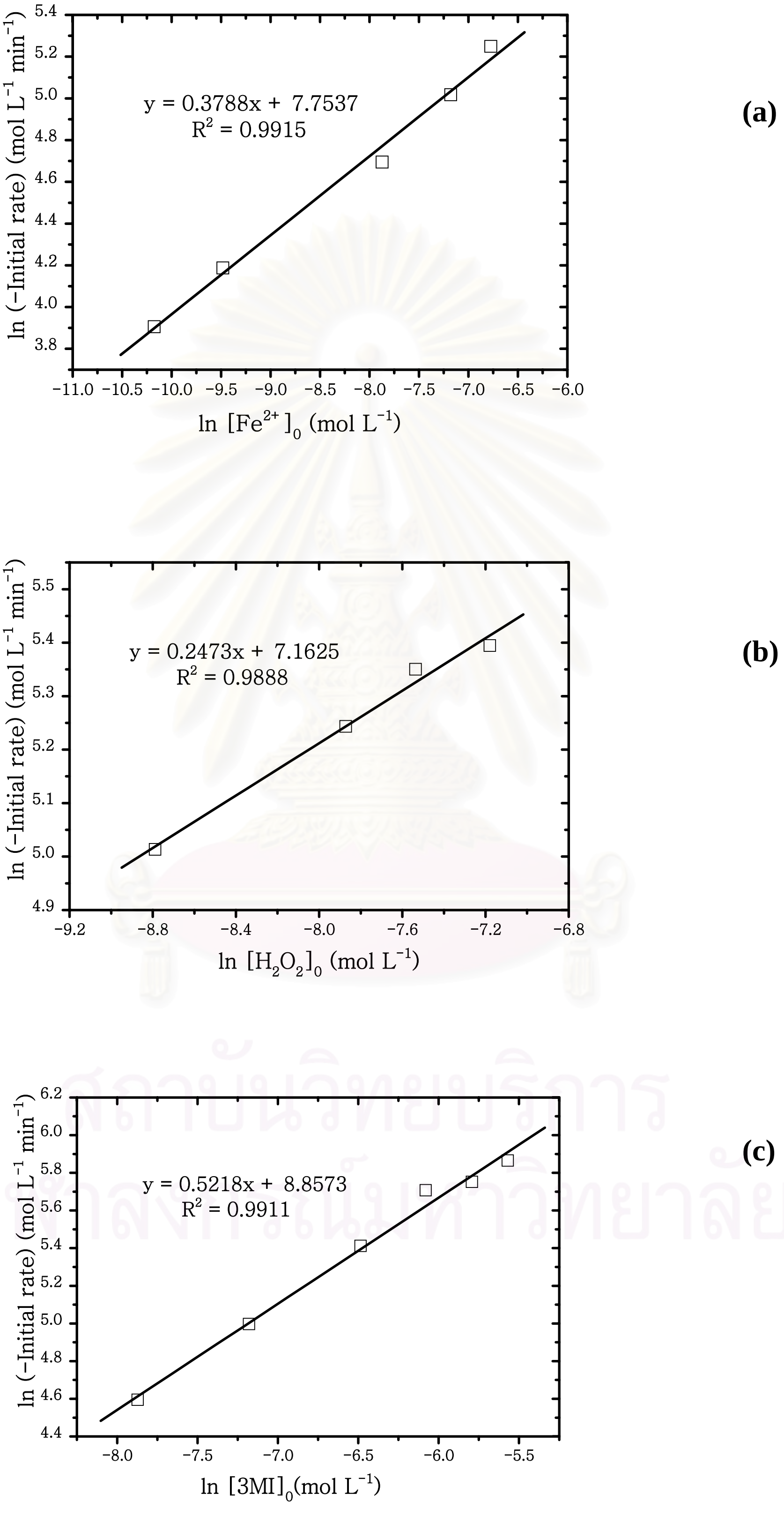


Figure 4.24 **Initial rate of 3MI treatment *v.s.* (a) $[Fe^{2+}]_0$ (b) $[H_2O_2]_0$ and (c) $[3MI]_0$**

According to Fig. 4.23, it appeared that the initial rates increased with the increasing concentration of each component. The overall initial rate equation could be written as follows:

$$-\left(\frac{d[3MI]}{dt}\right)_{initial} = k[H_2O_2]_0^{0.25}[Fe^{2+}]_0^{0.38}[3MI]_0^{0.52} \qquad (4.31)$$

Where k stands for the overall rate constants for 3MI degradation by Fenton's treatment (L mol^{-1})$^{0.15}$ min^{-1}; $[3MI]_0$ is the initial 3MI concentration (mol L^{-1}); $[Fe^{2+}]_0$ is the initial Fe^{2+} concentration (mol L^{-1}); $[H_2O_2]_0$ is the initial H_2O_2 concentration (mol L^{-1}) and $\left(\frac{d[3MI]}{dt}\right)_{initial}$ is the initial 3MI degradation rate (mol L^{-1} min^{-1}).

To determine the overall kinetic constant, the non-linear least square method was applied and the overall initial rate equation became:

$$-\left(\frac{d[3MI]}{dt}\right)_{initial} = 2.96x10^4[H_2O_2]_0^{0.25}[Fe^{2+}]_0^{0.38}[3MI]_0^{0.52} \qquad (4.32)$$

Comparing the kinetic constant of DIBP (k_{DIBP} = 6.0 x 10^3 (L mol^{-1})$^{1.16}$ min^{-1}), the degradation of 3MI was quite faster than DIBP. This indicated that the 3MI was easier to degrade than DIBP. One possible reason was that the degradation of 3MI includes the reduction by Fe^{2+}as well. Concerning the reaction order, the initial H_2O_2 concentration was the least impact factor on the 3MI degradation rate. This showed the cost-effective advantage of the 3MI treatment, since the main cost in Fenton's treatment was mainly due to the chemical cost, especially the H_2O_2 cost.

4.3.3 The synthetic mixtures

Because the composition in the real wastewater was more complicated than the synthetic wastewater, the obtained results were absolutely distinguished. The difference between synthetic wastewater and the real industrial wastewater was simplified by synthesizing the mixture of 3MI and DIBP. When one was dominant species, the other represented background species in the industrial wastewater.

4.3.3.1 *__Synthetic mixture as a RAW wastewater__*

According to the characterization study, the dominant species in raw wastewater was 3MI, so DIBP was considered as background species. In the real raw wastewater, the average concentration of 3MI was found at 40 mg L^{-1}, while DIBP was discovered at 4 mg L^{-1}. Consequently, the artificial wastewater was prepared at those concentrations and then the optimum conditions of single 3MI synthetic wastewater was applied to this mixture.

The difference between single 3MI and the mixture of 3MI+DIBP, considered as raw wastewater was shown in Fig. 4.25

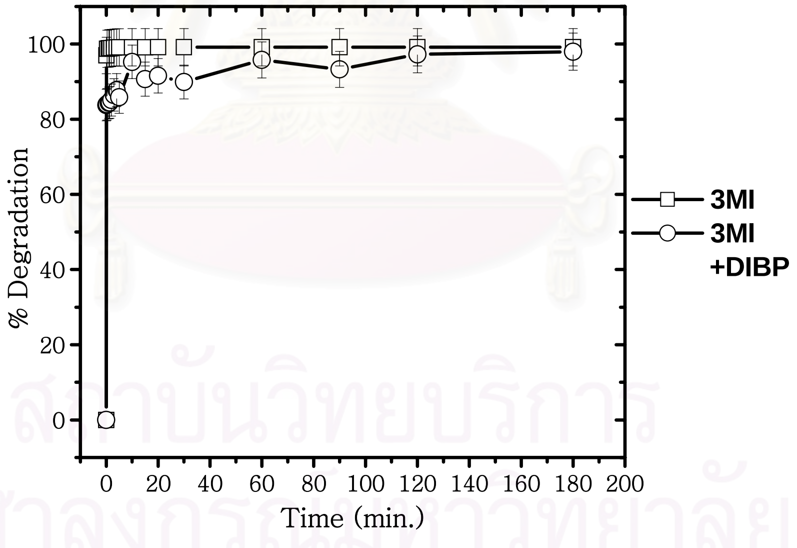


Figure 4.25 Difference between single 3MI and mixture 3MI+DIBP at [H_2O_2]: [Fe^{2+}]: [3MI] = 1: 1.5: 1 and pH =3

As shown in Fig. 4.25, it indicated that the 3MI was competed by DIBP in consuming hydroxyl radicals. The difference was quite high in the initial period of 60 min. Because of the incomparable concentration of DIBP, the difference between 3MI in single and mixture was only 10% in the first 30 min and 1% at 180 min.

4.3.3.2 <u>Synthetic mixture as a TREATED wastewater</u>

.Like the synthetic raw wastewater, the synthetic treated mixture was prepared with the target concentration found in the characterization part. Since the dominant species in treated wastewater was DIBP, the 3MI was regarded as background species. In characterization study, the averaged DIBP concentration was found approximately 1.5 mg L^{-1}, while the averaged 3MI concentration was around 1 mg L^{-1}. After preparing the solution, the Fenton's reagent was applied at the DIBP's optimum condition *i.e.* [H_2O_2]: [Fe^{2+}]: [DIBP] = 5: 5: 1 and pH = 3. The results were depicted in Fig. 4.26.

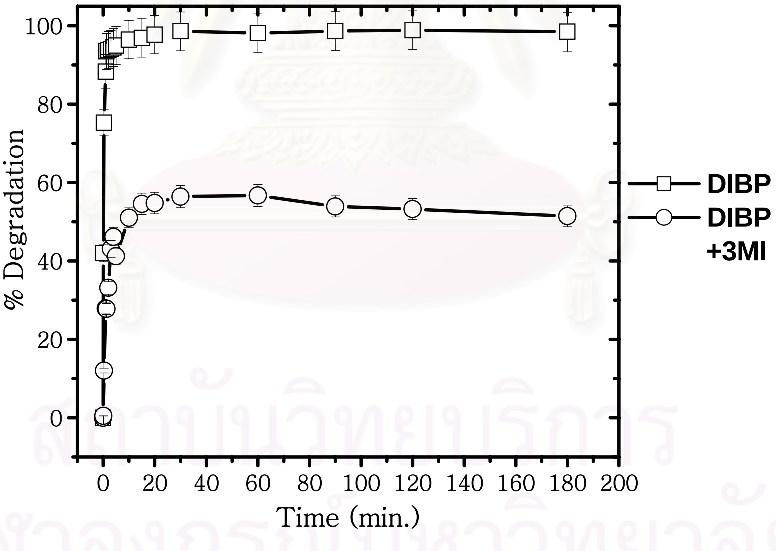


Figure 4.26 Difference between single DIBP and mixture of DIBP + 3MI at [H_2O_2]: [Fe^{2+}]: [DIBP]= 5: 5: 1 and pH =3

As presented in Fig.4.26, there was about 50% difference between single and the mixture DIBP at 180 min. This demonstrated that DIBP considerably competed with 3MI for consuming ·OH. This phenomenon was confirmed by the 3MI degradation curve in Fig. 4.27.

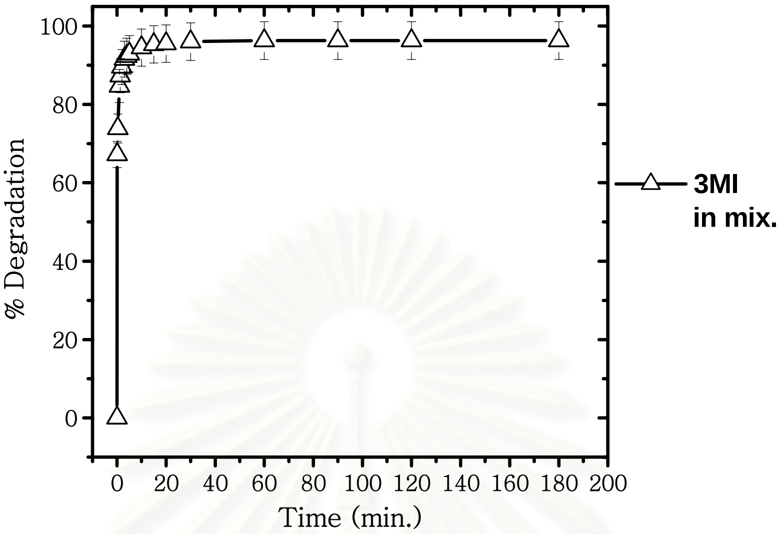


Figure 4.27 Degradation of 3MI in mixture at [H_2O_2]: [Fe^{2+}]: [DIBP]= 5: 5: 1 and pH = 3

Fig.4.27 shows that the degradation of 3MI was very fast and reached the steady-state within the first 10 min. The degradation efficiency was nearly 100%. This indicates that the 3MI was more active than DIBP in scavenging the hydroxyl radical and/or Fe^{2+}, as is consistent with both calculated overall kinetic constants.

4.3.3.3 Comparison between the Synthetic and Real Industrial Wastewater

After the synthetic wastewater experiments, the research continued to the genuine industrial wastewater. Since the concentration of 3MI and DIBP in the real industrial wastewater varied in each collecting day, the target concentrations in synthetic wastewater was prepared so that they have the same concentrations found in the real wastewater, in order to closely simulate the real one.

*a) Comparison in the RAW wastewate*r

Collected on the 17/7/06, the real raw wastewater provided 19 mg L^{-1} 3MI and 0.7 mg L^{-1} DIBP. To be able to compare with this real wastewater, the synthetic single and mixture raw wastewater was prepared with the same concentrations. After getting ready, both wastewaters were applied with the optimum conditions of single 3MI synthetic wastewater, *i.e.* 1:1.5:1 [H_2O_2]: [Fe^{2+}]: [3MI] and pH =3. The difference between the synthetic and raw wastewater was illustrated in Fig. 4.28.

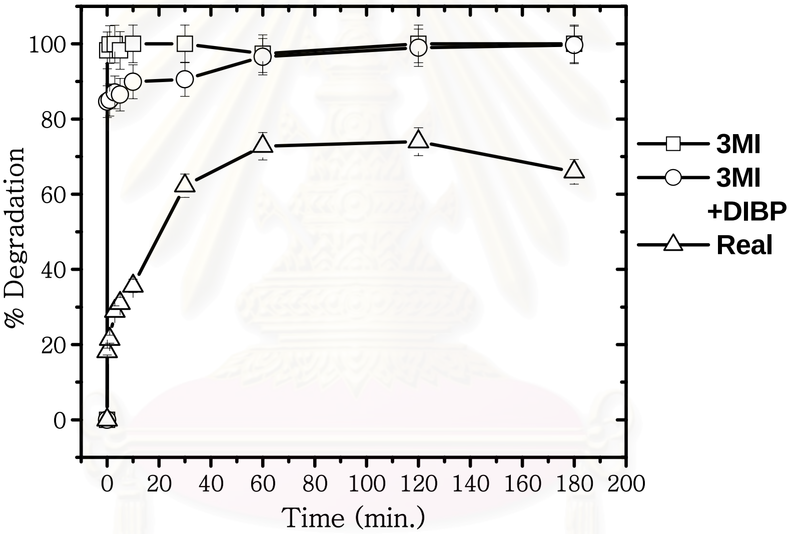


Figure 4.28 Comparison between 1) the synthetic single 3MI 2) the synthetic mixture of 3MI+DIBP and 3) the industrial raw wastewater

Although all lines of 3MI were 19 mg L^{-1}, they appeared in different matrix. At 180 min, both of synthetic wastewater was degraded by nearly 100%, while the real raw wastewater was only 70%. This was indicated that DIBP hardly affected to the 3MI degradation in real wastewater in the aspect of % degradation. However, it took part in the delay of the equilibrium time, which changing from 1min in single 3MI to 60 min in the real wastewater. The other background in real raw wastewater was responsible for 30% degradation difference. Comparing the performance of the synthetic mixture in Fig. 4.28 with those in Fig.4.25, they were different in equilibrium time, which was reduced from 120 min to 60 min. Both synthetic mixtures were not similar in the concentration of 3MI and DIBP. The ratio of 3MI/DIBP was increased from 4 (40 ppm/4 ppm) to 27 (19 ppm/0.7 ppm). Therefore, it might infer that the concentration ratio of DIBP versus 3MI was affected to the equilibrium time of the 3MI degradation.

b) Comparison in the TREATED wastewater

Like the raw wastewater, the target concentrations in synthetic wastewater were adjusted to be the same as found in the real treated wastewater. The real treated wastewater was collected on 19/8/06 with the 0.5 mg L^{-1} DIBP. The 3MI was not found in this wastewater; consequently, the synthetic mixture could not be prepared. After applying Fenton's reagent at optimum condition [H_2O_2]: [Fe^{2+}]: [DIBP] = 5: 5: 1 and pH = 3, the degradation of DIBP in synthetic single DIBP and the real treated wastewater was determined, as shown in Fig. 4.29.

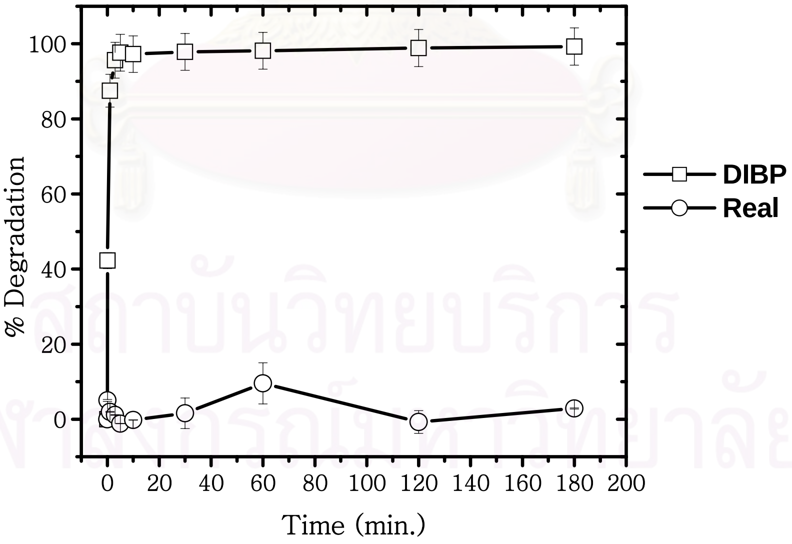


Fig. 4.29 Comparison between the synthetic single DIBP and the industrial treated wastewater

As shown in Fig.4.29, there exists the extremely difference between DIBP in the synthetic and in the real treated wastewater. The 0.5 mg L^{-1} DIBP could be degraded almost 100% in the solution of DIBP alone, but it was scarcely degraded in real industrial treated wastewater. It might due to the low concentration of Fenton's reagent, which was calculated from the low concentration of DIBP. It was not enough to produce sufficient hydroxyl radical to degrade all species in the wastewater. Moreover, the other reason might be the inert properties of DIBP, which might be more than other species in wastewater.

With this phenomenon, the optimum operating condition should be determined again, if Fenton's treatment would be applied to the real wastewater.

4.3.4 Optimization of Fenton's operating condition to the industrial RAW wastewater.

4.3.4.1 Effect of H_2O_2 concentration

The hydrogen peroxide concentration was varied in the range of 0 – 100, the molar ratio of its concentration versus 3MI. The results in 3MI degradation was illustrated in Fig. 4.30 Without H_2O_2, or Fe^{2+} alone, the 3MI has still been degraded by about 10%. This phenomenon could confirm the result from the synthetic wastewater that 3MI could be reduced by Fe^{2+} alone. However, the number of reductions was quite different. In the synthetic wastewater, 3MI could be reduced up to 70%, while in the real wastewater 3MI was merely about 10%. It was attributed to two reasons. First, the other species in the real wastewater competed with 3MI to consume Fe^{2+}. Second, the bivalent metallic ions could be used in the coagulation of the remained rubber particle in the wastewater {Kajornchaikul, 1982). When H_2O_2 concentration was increased, the degradation of 3MI was also increased and reached 100% at 20-fold 3MI. Consequently, more increase in the H_2O_2 concentration was not necessary. However, if the concentration of H_2O_2 was at the ratio more than 10, the initial rate of 3MI degradation was decelerated. This could be attributed to the same reasons described in the above section: (1) the competition to consume the hydroxyl radical by the excess H_2O_2 and (2) the recombination of the excess hydroxyl radicals and hydroperoxyl radicals, leading to the decrease in hydroxyl radical degradation of 3MI.

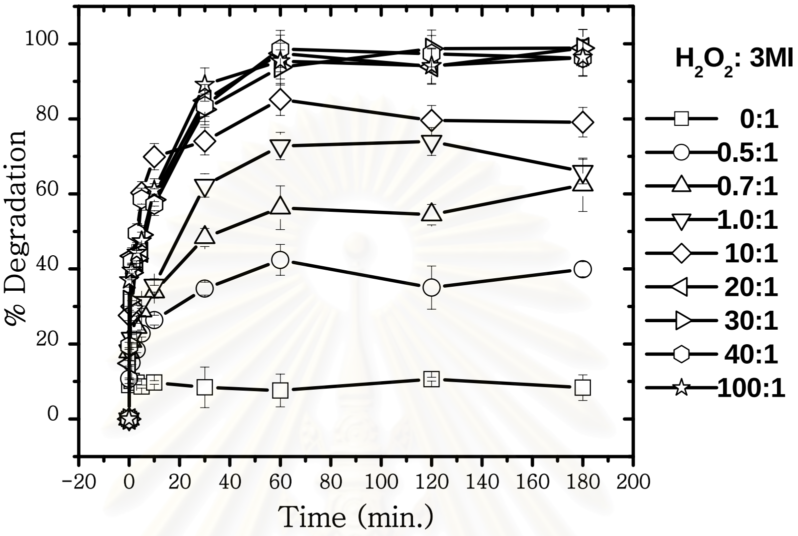


Figure 4.30 Effect of H_2O_2 concentration on 3MI degradation in industrial raw wastewater at 1.5:1 [Fe^{2+}]: [3MI] molar ratio, initial 3MI concentration = 19 mg L^{-1} and pH =3

In fact, the general term considered in the wastewater treatment system and represented as organics in the wastewater was the COD. To this, the %COD reduction was investigated and shown in Fig.4.31. It was found that the %COD reduction increased with increasing H_2O_2 concentration. Although the H_2O_2 concentration was used up to 100 molar ratio of H_2O_2 versus 3MI, the COD was removed only by 16%. In view of cost effective, the use of high H_2O_2 concentration like this was not attractive. The major cost of Fenton's treatment was contributed to the cost of H_2O_2. For this reason, the Fenton's treatment was recommended as the pretreatment system of 3MI, source of bad smelling, not used as the main treatment system. So, the optimum H_2O_2 concentration was selected at a molar ratio of 20.

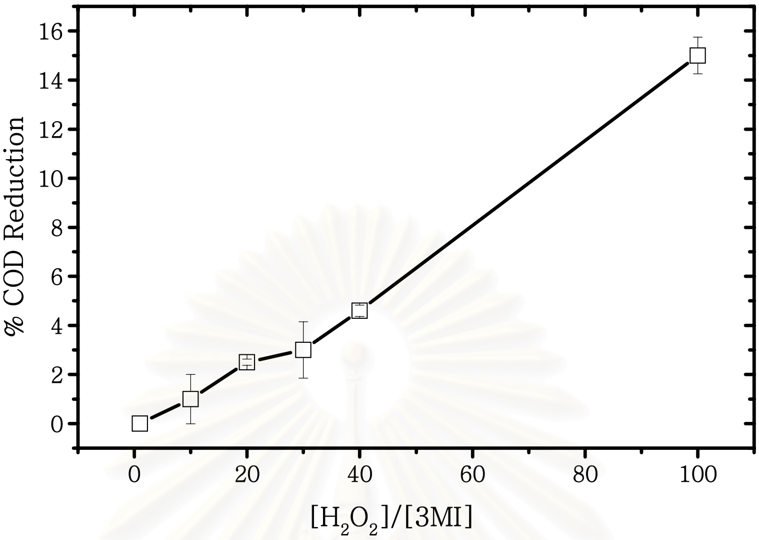


Figure 4.31 Effect of H_2O_2 concentration on %COD reduction in industrial raw wastewater at 1.5:1 [Fe^{2+}]: [3MI] molar ratio, initial 3MI concentration = 19 mg L^{-1} and pH =3

In addition to the reduction of COD, the utilization of 3MI as the pretreatment was more attractive, when the biodegradability index was concerned. Fig.4.32 indicated that Fenton’s oxidation could improve the biodegradability of the raw wastewater. This was useful for the subsequent biological treatment system if the Fenton’s treatment could be applied as the pretreatment process. The improvement in the biodegradability was also reported by other researchers, *i.e.* Lopez *et al.* (2004), Chamapro *et al.* (2001), Kajitvichyanukul and Suntronvipart (2006) and Tekin *et al.* (2006).

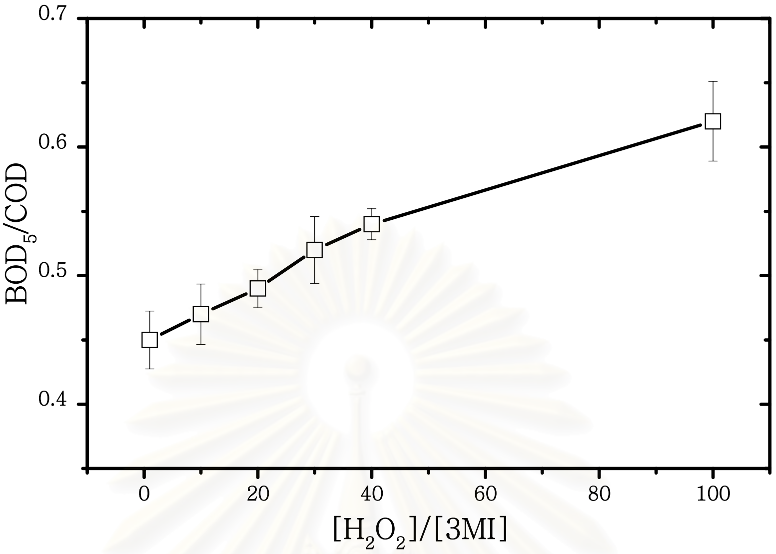


Figure 4.32 Effect of H_2O_2 concentration on the biodegradability in industrial raw wastewater at 1.5:1 [Fe^{2+}]: [3MI] molar ratio, initial 3MI concentration = 19 mg L^{-1} and pH =3

4.3.4.2 Effect of Fe^{2+} concentration

Likewise, the concentration of Fe^{2+} was investigated and varied from 0 to 20-fold of 3MI concentration. The results were depicted in Fig.4.33.

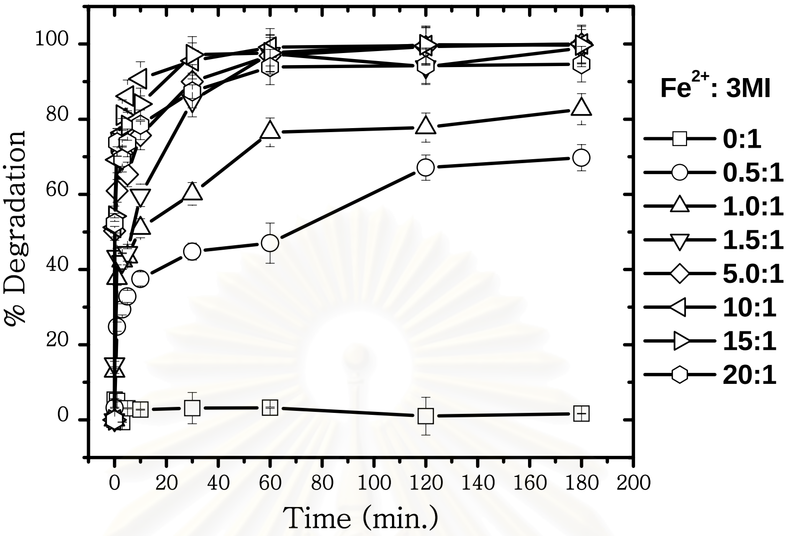


Figure 4.33 Effect of Fe^{2+} concentration on 3MI degradation in industrial raw wastewater at 20:1 [H_2O_2]: [3MI] molar ratio, initial 3MI concentration = 19 mg L^{-1} and pH =3

As shown in Fig.4.33, the degradation of 3MI at absence of Fe^{2+} could be negligible. Comparing with the synthetic 3MI wastewater, which provided the 10% degradation by H_2O_2 alone and the other 10% from acid addition, no degradation in the real wastewater might cause by (1) competition of other organics to consume the H_2O_2 and (2) competition with the coagulation of the remained rubber fragment in the wastewater to consume the acid. %Degradation was increased with the increasing Fe^{2+}. After the molar ratio of Fe^{2+} versus 3MI, 1.5, the increase in ferrous concentration hardly lifted up the 3MI degradation, but it elevated the initial rate of the degradation. This was due to its role being just as a catalyst. The initial rate would be increased if Fe^{2+} concentration was in range of 0 – 10. However, if the Fe^{2+} was added at a ratio more than 10, the initial rate would become decreasing. This might be resulted from the increasing in $Fe(OH)_3$, the •OH consumption by the excess Fe^{2+} and the occurrence of complexation reactions of Fe^{3+} by SO_4^{2-}, as mentioned previously. For all reasons, the optimum Fe^{2+} concentration was selected at a ratio of 10.

4.3.4.3 Effect of pH

The pH was one of parameters affecting Fenton’s reaction. In most research, this parameter has never been overlooked. For the raw wastewater, the pH varied from 1 to 5. Since the pH of the industrial wastewater had never exceeded 5 and Fenton’s reaction was favorably suitable for acid condition, it was not preferred to shift pH to 6, like the synthetic 3MI wastewater.

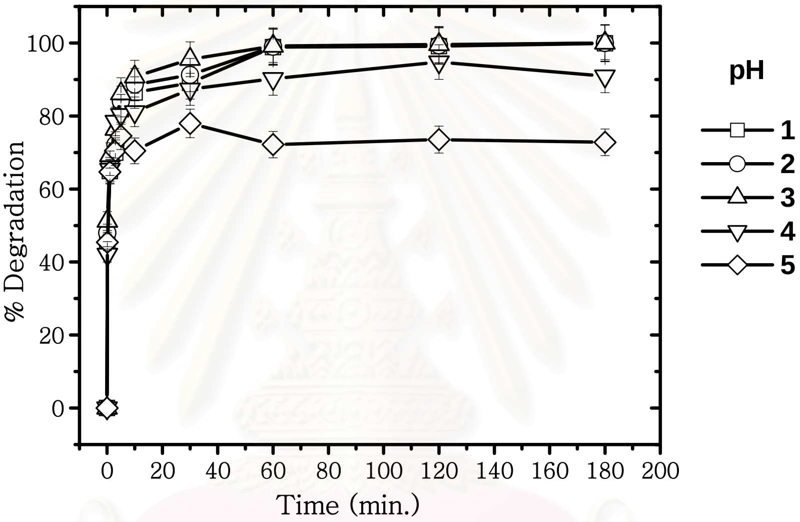


Figure 4.34 Effect of pH on 3MI degradation in industrial raw wastewater at 20:10:1 [H_2O_2]: [Fe^{2+}]: [3MI] molar ratio and initial 3MI concentration = 19 mg L^{-1}

According to Fig. 4.34, the 3MI could be degraded well at pH = 1-3 and the removal became diminishing at higher pH. As mentioned in the synthetic 3MI section, there were 3 possible reasons: (1) the precipitation of Fe^{2+} to $Fe(OH)_3$ at higher pH, hindering the reaction between Fe^{3+} and H_2O_2 and therefore the regeneration of Fe^{2+}; (2) the $Fe(OH)_3$ could catalyze the decomposition of H_2O_2 to H_2O and O_2, leading to lower amount of ·OH.; (3) the oxidation potential of ·OH decreases with increasing pH. Unlike the DIBP, the 3MI was still well degraded in both the synthetic and real wastewater even though the pH was less than 3. This indicated that the increase in %degradation by the acid destruction overcame the decrease in %degradation by the excess acid and the H_3O^+ formation. Another advantage of the acidic condition, beside promoting Fenton's oxidation, was the reduction of suspended solid. It was found that SS was removed by approximately 38% after 180 min. To save the number of the acid added, the optimum pH should be 3.

4.3.4.4 Effect of initial 3MI concentration

To avoid the side effect from the change of other species in wastewater, the 3MI concentration was adjusted by diluting with DI water for decreasing 3MI concentration, and spiking the standard 3MI for increasing 3MI concentration. The 3MI concentration was varied from 27.50 to 4.75 mg L^{-1}. The results were presented in Fig.4.35.

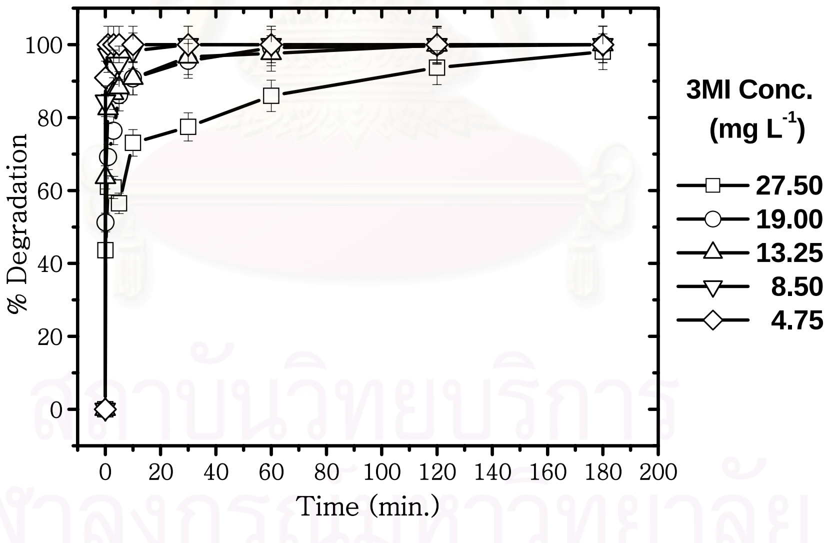


Figure 4.35 Effect of initial 3MI concentration on 3MI degradation in industrial raw wastewater at 20:10:1 [H_2O_2]: [Fe^{2+}]: [3MI] molar ratio and pH = 3

As shown in Fig. 4.35, the degradation of 3MI decreased with the increasing initial 3MI concentration. This was because the steady-state hydroxyl radical, which was responsible for 3MI destruction, became decreasing as 3MI concentration increased. Consequently, the lower the hydroxyl radical concentration, the lesser the 3MI was degraded. This phenomenon was similar to the synthetic wastewater. At the concentration of 27.5 mg L^{-1}, which was obtained by spiking the standard 3MI into the wastewater with 19 mg L^{-1} 3MI, the rate of degradation was decreased sharply. The rate was more declined than those from 8.5 to 19 mg L^{-1}, which was obtained by diluting the wastewater with DI water. This indicated that the concentration of 3MI itself affected the degradation rate more than other organics in wastewater.

4.3.4.5 Characteristics of the raw wastewater after the treatment

In the aspect of the regulation, the wastewater characteristics ware considered in the terms of lump parameters. Consequently, the raw wastewater after Fenton’s treatment was investigated and presented in Table 4.4

Table 4.4 Wastewater properties of raw wastewater after the treatment by Fenton’s oxidation

Parameter	Pre-treated raw wastewater	
	Before	**After**
SS (mg L^{-1})	1,582	980
COD (mg L^{-1})	11,963	10,583
BOD_5/COD	0.46	0.55

The iron precipitation permitted the removal of the suspended solids by approximately 38%. This was in agreement with some researcher (Barros *et al.,* 2006) Special for the rubber wastewater, the acid condition in Fenton’s treatment could coagulate the residual rubber particle in such wastewater. When the acid was added, the carboxylate anionic group ($R-CO_2$) surrounding the rubber particle was reacted with the H^+ and formed the fatty acid ($R-CO_2H$), as presented in Eq. (4.33). (Kajornchaikul, 1982)

$$R-CO_2^{\,-} \quad + \quad H^{+} \quad \longrightarrow \quad R-CO_2H \qquad (4.33)$$

This reduced the zeta potential and caused the coagulation of the rubber particle. Thus, the SS was reduced. As mentioned previously, the Fenton's reaction promoted the biodegradability index. At the optimum condition, it was increased from 0.46 to 0.55. This showed the possibility to use the Fenton's oxidation as the pretreatment system for the biological treatment.

4.3.5 Optimization of Fenton's operating condition to the industrial TREATED wastewater.

The re-optimization was very important to the treated wastewater, because the optimum condition obtained from the synthetic wastewater could not remove any DIBP from the real treated wastewater. In deeds, after passing the industrial biological treatment, the treated wastewater contained the high number of the non-biologically degraded substances. It needs the effective post-treatment to make the effluent meet the standard value required by law. Thus, the Fenton's abatement should be re-optimizing to fit with the real wastewater.

4.3.5.1 Effect of H_2O_2 concentration

Due to the low concentration of DIBP, the H_2O_2 concentration presented in the terms of ratio versus DIBP was high. For instance, the ratio was up to 500, despite only 31 mg L^{-1} concentration. Thus, in this section, the concentration of H_2O_2 would be presented in the form of concentration rather than ratio versus DIBP.

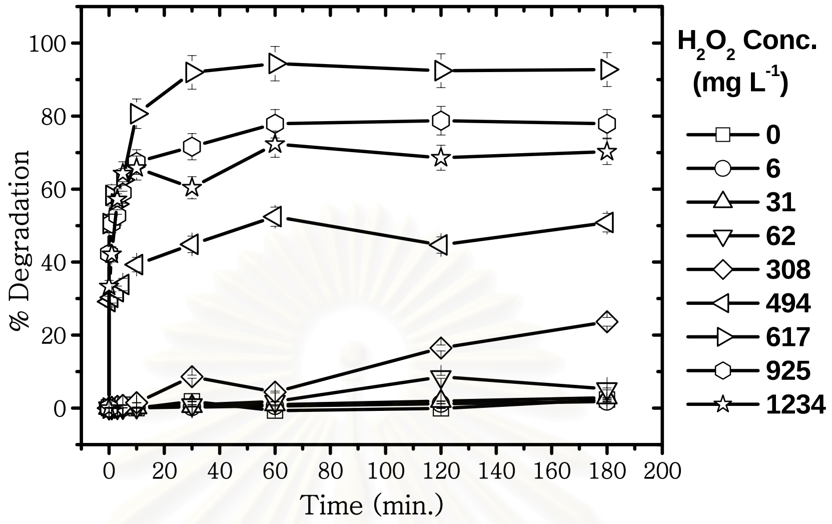


Figure 4.36 Effect of H_2O_2 concentration on DIBP degradation in industrial treated wastewater at $[Fe^{2+}]$ = 50 mg L^{-1}, initial DIBP concentration = 0.5 mg L^{-1} and pH = 3

The concentration of H_2O_2 was varied from 0 to 1234 mg L^{-1} in this study. Each concentration selected was equivalent to the integrated number of ratio. For example, 308 mg L^{-1} is 5000-folds of DIBP concentration, while 1234 mg L^{-1} equals to 20,000-folds. At zero concentration, there was no degradation of DIBP; it agrees with the experimental result from the DIBP synthetic wastewater that DIBP was inert to Fe^{2+}. DIBP was inactive to Fenton's reagent until the concentration of H_2O_2 increased to 308 mg L^{-1}. At this concentration, the degradation of DIBP was around 20%. The degradation kept increasing until the H_2O_2 concentration increased up to 617 mg L^{-1}. Beyond this concentration, the increasing in the H_2O_2 concentration reduced the DIBP degradation. The reasons were the same as mentioned in the synthetic part, *i.e.*, ·OH was consumed by the excess H_2O_2, the hydroperoxyl radicals and itself, leading to the decrease in the number of •OH for degrading the DIBP.

As mentioned in the raw wastewater section, the general lump term was very important in both aspects of being representative of all organics in wastewater and the regulation control. Thereby, the effect of H_2O_2 concentration on %COD reduction was also determined in this research, as shown in Fig. 4.37.

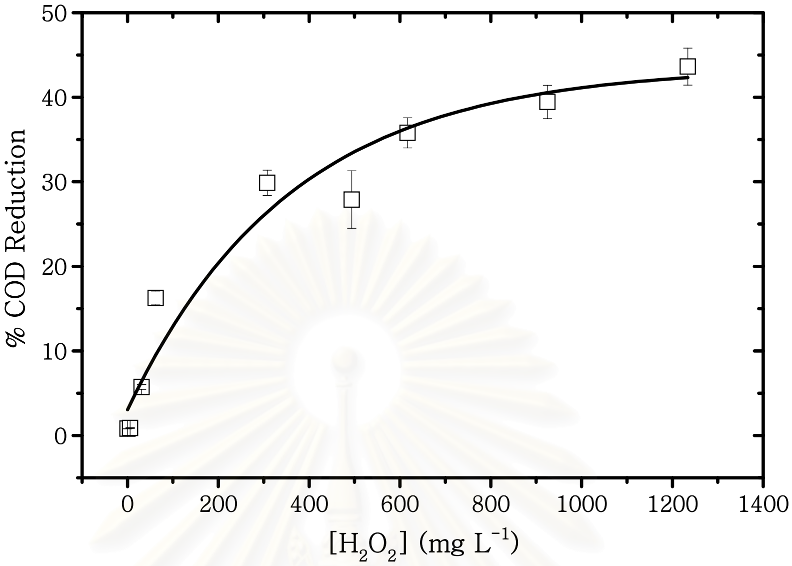


Figure 4.37 Effect of H_2O_2 concentration on %COD reduction in industrial treated wastewater at $[Fe^{2+}]$ = 50 mg L^{-1}, initial DIBP concentration = 0.5 mg L^{-1} and pH = 3

As presented in Fig. 4.37, the removal of COD increased with increasing H_2O_2 concentration. However, the slope trended to decrease at higher H_2O_2 concentration. Like the DIBP data, it owing to the competition reactions, Eq. (4.6) - (4.10). Noticed at 31 mg L^{-1}, COD was reduced by about 5%, while DIBP was rarely degraded. This confirmed the assumption in section 4.3.3.3 (b) that DIBP was more inert to the hydroxyl radical than other organic species in the treated wastewater. Because of its inertness, the DIBP degradation curve showed the breaking point at 617 mg L^{-1}, while COD reduction curve did not show such breaking point in the studied concentration range. Considering the cost-effectiveness, the H_2O_2 was the parameter with the highest weighing in overall chemical cost of Fenton's treatment. The increase by about 10% of COD removal seems not worthy, in view of 100% H_2O_2 addition from 617 to 1234 mg L^{-1}. For this reason, the optimum H_2O_2 concentration was chosen at 617 mg L^{-1} for further experiment.

4.3.5.2 Effect of Fe^{2+} concentration

Similar to the synthetic wastewater, the effect of Fe^{2+} was studied as well. It was varied in the range of 0 – 100 mg L^{-1}, equivalent to 0 – 1,000 ratio of Fe^{2+} versus DIBP. The results were shown in Fig. 4.38.

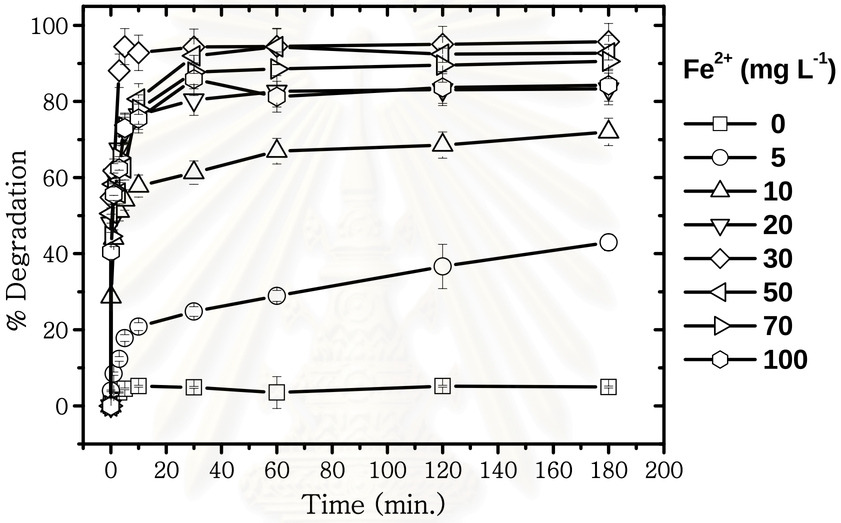


Figure 4.38 Effect of Fe^{2+} concentration on DIBP degradation in industrial treated wastewater at $[H_2O_2]$ = 617 mg L^{-1}, initial DIBP concentration = 0.5 mg L^{-1} and pH = 3

In the absence of ferrous ion, the H_2O_2 alone could degrade the DIBP with the removal efficiency less than 5% close to the result obtained from the synthetic section. The increase in Fe^{2+} concentration increased both the %degradation and the initial rate. The break point was at 30 mg L^{-1} and DIBP could be degraded by around 95% at 180 min. The removal percentage decreased when the concentration of ferrous ion was added more than the breaking point value. All phenomena were consistent to the synthetic wastewater and the raw wastewater study and all related reasons were as already mentioned in above sections. In view of the post-treatment, the COD should be concerned.

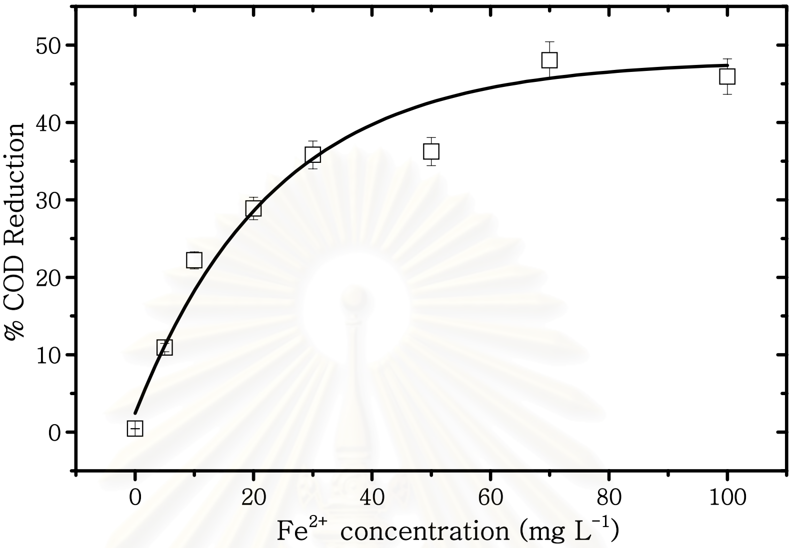


Figure 4.39 Effect of Fe^{2+} concentration on % COD reduction in industrial treated wastewater at [H_2O_2] = 617 mg L^{-1}, initial DIBP concentration = 0.5 mg L^{-1} and pH = 3

According to %COD reduction curve, the increase in Fe^{2+}concentration could lift up %COD reduction and would reach the steady-state at 70 mg L^{-1}. After that, the COD removal was retarded by the excess Fe^{2+}, as shown in Eq. (4.11)-(4.13), leading to the decline of %COD reduction. The optimum Fe^{2+} concentration 70 mg L^{-1} was worth of selection although %DIBP degradation was reduced only by about 5%. Note that the concentration of DIBP in wastewater was 0.5 mg L^{-1}, much lower than COD value. 5% decrease in DIBP degradation was incomparable with 10% increase in COD reduction. Moreover, the Fe^{2+} was inexpensive, if compared with H_2O_2.

4.3.5.3 Effect of pH

Again, the pH was investigated for the industrial treated wastewater as well. It was changed between1 to 5. The resulted was illustrated in Fig. 4.40.

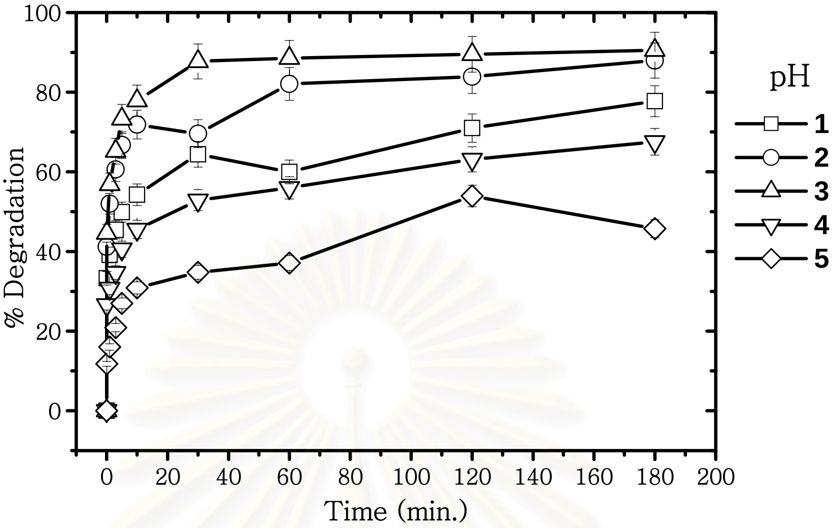


Figure 4.40 Effect of pH on DIBP degradation in industrial treated wastewater at [H_2O_2] = 617 mg L^{-1}, [Fe^{2+}] = 70 mg L^{-1} and initial DIBP concentration = 0.5 mg L^{-1}

The results were quite similar to those occurring in the synthetic wastewater. However, DIBP in the real treated wastewater was more sensitive to pH than itself in the synthetic wastewater. This might be resulted from its inert to hydroxyl radical. If the oxidizing potential was reduced from the changing pH, it was not enough to oxidize DIBP but it was sufficient for other less inert species in the wastewater. Consequently, the ·OH was seized by other species at low potential pH. Moreover, another difference in DIBP degradation obtained from the synthetic and the industrial wastewater was that the degradation at pH=4 was higher than pH = 1 for synthetic wastewater, while they was opposite for the industrial wastewater. In the real wastewater, the recycle of Fe^{3+} to Fe^{2+} could be promoted by ·R, as shown in Eq. (4.34) (Bautista *et al., article in press.*). However, at pH = 4 the iron started to precipitated $Fe(OH)_3$, so the recycle was prohibited. This made the degradation at pH = 4 was lower than pH = 1 for the industrial wastewater.

$$R\bullet + Fe^{3+} \longrightarrow Fe^{2+} + R^{+} \qquad (4.34)$$

In conclusion, the optimum operating condition for the industrial treated wastewater was 617 mg L^{-1} [H_2O_2], 70 mg L^{-1} [Fe^{2+}] and pH = 3 for 1 L wastewater contained 0.5 mg L^{-1} [DIBP].

4.3.5.4 *Effect of initial DIBP concentration*

Like the previous section, the last variable studied was the initial concentration of DIBP. The DIBP concentration found in the collected wastewater was 0.5 mg L^{-1}. It could not concentrate without changing in the composition in the wastewater. The spiking of the standard DIBP was impossible because of the much few differences in concentration between standard and wastewater. Thus, the wastewater was only diluted by DI water to 0.38, 0.25 and 0.10 mg L^{-1}.

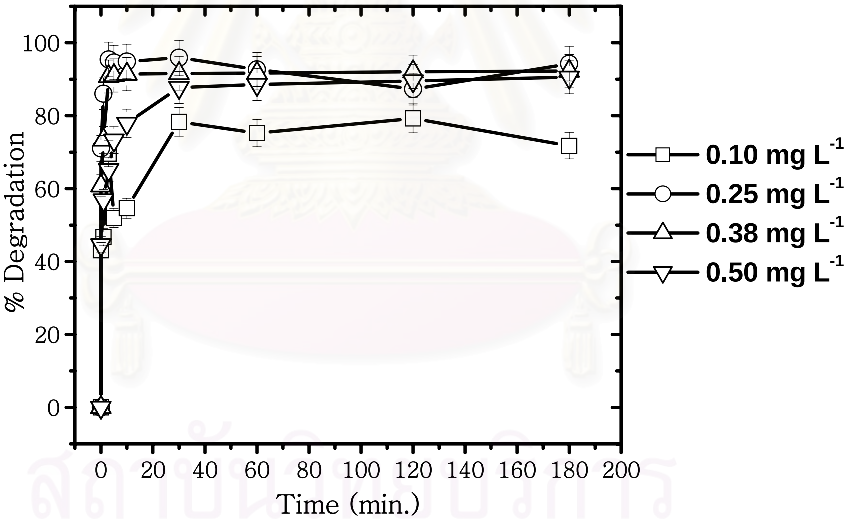


Figure 4.41 Effect of initial DIBP concentration on DIBP degradation in industrial treated wastewater on the DIBP degradation at [H_2O_2] = 617 mg L^{-1}, [Fe^{2+}] = 70 mg L-^{1} and pH =3

According to Fig.4.41, the DIBP was reached the steady-state in the shorter time when the initial DIBP concentration was decreased. However, the number of %removal was not improved. Unlike the synthetic wastewater, if the DIBP concentration was too low, the degradation became reduced in both number and initial rate (see the line with 0.1 mg L^{-1}). This might be resulted from the low concentration of DIBP and other species. This made ·OH become excess, leading to the high rate of competition reaction, as presented in Eq.(4.8).

4.3.5.5 Characteristics of the biological effluent after the Fenton's treatment

Before discharge to the public water resources, the lump parameters of the final effluent were important and they should be determined.

Table 4.5 Wastewater properties of the biological treated wastewater after the post-treatment by Fenton's oxidation

Parameter	**Post-treated biological effluent**	
	Before (mg L^{-1})	**After (mg L^{-1})**
SS	125	21
COD	224	116
BOD_5	34	19

According to Table 4.5, the Fenton's treatment at the optimum condition could remove the suspended solid by 83%. Moreover, it could reduce the BOD_5 and COD to a degree of complying with the discharge standards.

4.3.6 Kinetic study for the industrial wastewater

Since the characteristics of the industrial wastewater were so complicated, the reaction rate was different from the synthetic wastewater. The kinetic equation should be determined again to obtain the information reflecting the real nature of the wastewater.

4.3.6.1 Kinetic study for 3MI in the raw wastewater

As mentioned previously, the decomposition of 3MI could be divided into 2 steps. The first step was more important to the degradation quantity and therefore it deserved to focus on. The initial rate was determined by using the experimental results presented in Figs. 4.30 -4.33 and the plotting of the initial rate *v.s.* the concentration of each component was shown in Fig. 4.42.

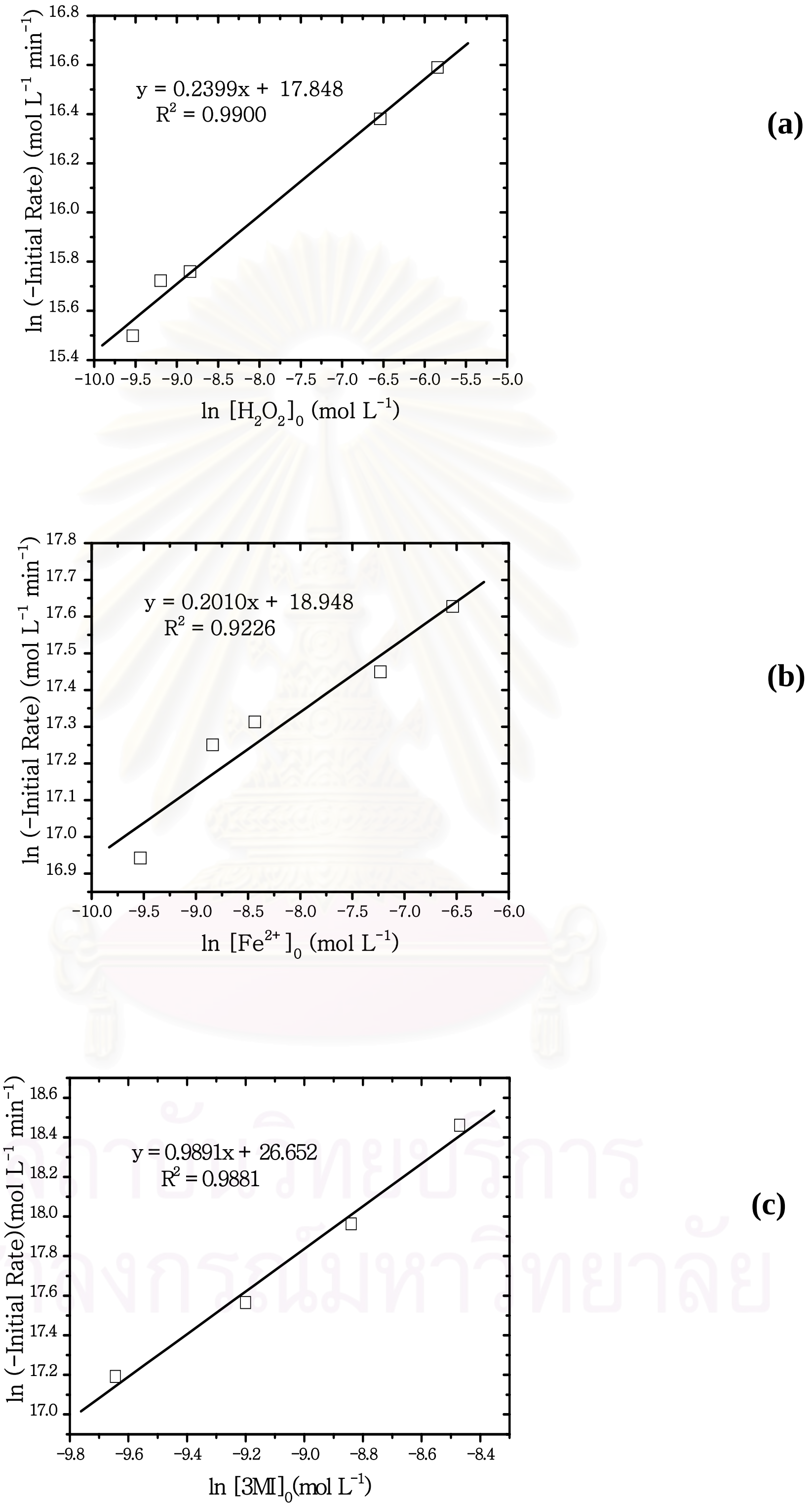


Figure 4.42 Initial rate of 3MI treatment in raw wastewater with respect to (a) $[H_2O_2]_0$; (b) $[Fe^{2+}]_0$; and (c) $[3MI]_0$

As shown in Fig. 4.42, the initial rates increased with the increasing concentration of each component. The overall initial rate equation could be written as follows:

$$-\left(\frac{d[3MI]}{dt}\right)_{initial} = k[H_2O_2]_0^{0.24}[Fe^{2+}]_0^{0.20}[3MI]_0^{0.99} \qquad (4.35)$$

Where k stands for the overall rate constants for 3MI degradation by Fenton’s treatment (L mol^{-1})$^{0.43}$ min^{-1}; $[3MI]_0$ is the initial 3MI concentration (mol L^{-1}); $[Fe^{2+}]_0$ is the initial Fe^{2+} concentration (mol L^{-1}); $[H_2O_2]_0$ is the initial H_2O_2 concentration (mol L^{-1}) and $\left(\frac{d[3MI]}{dt}\right)_{initial}$ is the initial 3MI degradation rate (mol L^{-1} min^{-1}).

To determine overall kinetic constant, the non-linear least square method was applied by minimizing the sum of square error and the overall initial rate equation was changed to be

$$-\left(\frac{d[3MI]}{dt}\right)_{initial} = 6.99x10^{-2}[H_2O_2]_0^{0.24}[Fe^{2+}]_0^{0.20}[3MI]_0^{0.99} \qquad (4.36)$$

Over COD and BOD_5 range of 10,700-27,600 mg L^{-1} and 3,400-7,000 mg L^{-1}, respectively.

Comparing with Eq. (4.32) of the synthetic wastewater, the kinetic constant was considerably reduced from 2.96 x 10^4 (L mol^{-1})$^{0.15}$ min^{-1} in the synthetic wastewater to 6.99x10^{-2} (L mol^{-1})$^{0.43}$ min^{-1} in the real wastewater. This indicates the important effect of the competition between 3MI and other organics to consume the hydroxyl radicals, leading to deceleration in the 3MI oxidation rate. In addition to the oxidation, the 3MI reduction by Fe^{2+} was also prohibited in the industrial wastewater. Because of these two reasons, the kinetic constant became decreased in the industrial wastewater. Focusing on the reaction order, the Fe^{2+} concentration became the least impact factor. It might result from the prohibition in 3MI reduction by Fe^{2+}. The order of H_2O_2 was scarcely changed, while the 3MI’s increased to nearly the first-order. The most important factor in the 3MI degradation was due to the 3MI itself. Thus, it was necessary to consider the concentration of 3MI if the Fenton’s treatment will be applied as a pretreatment system.

4.3.6.2 Kinetic study for DIBP in the treated wastewater

Similar to raw wastewater, the initial rate was determined as the function of H_2O_2, Fe^{2+} and 3MI by using the results from Figs.4.36-4.41.

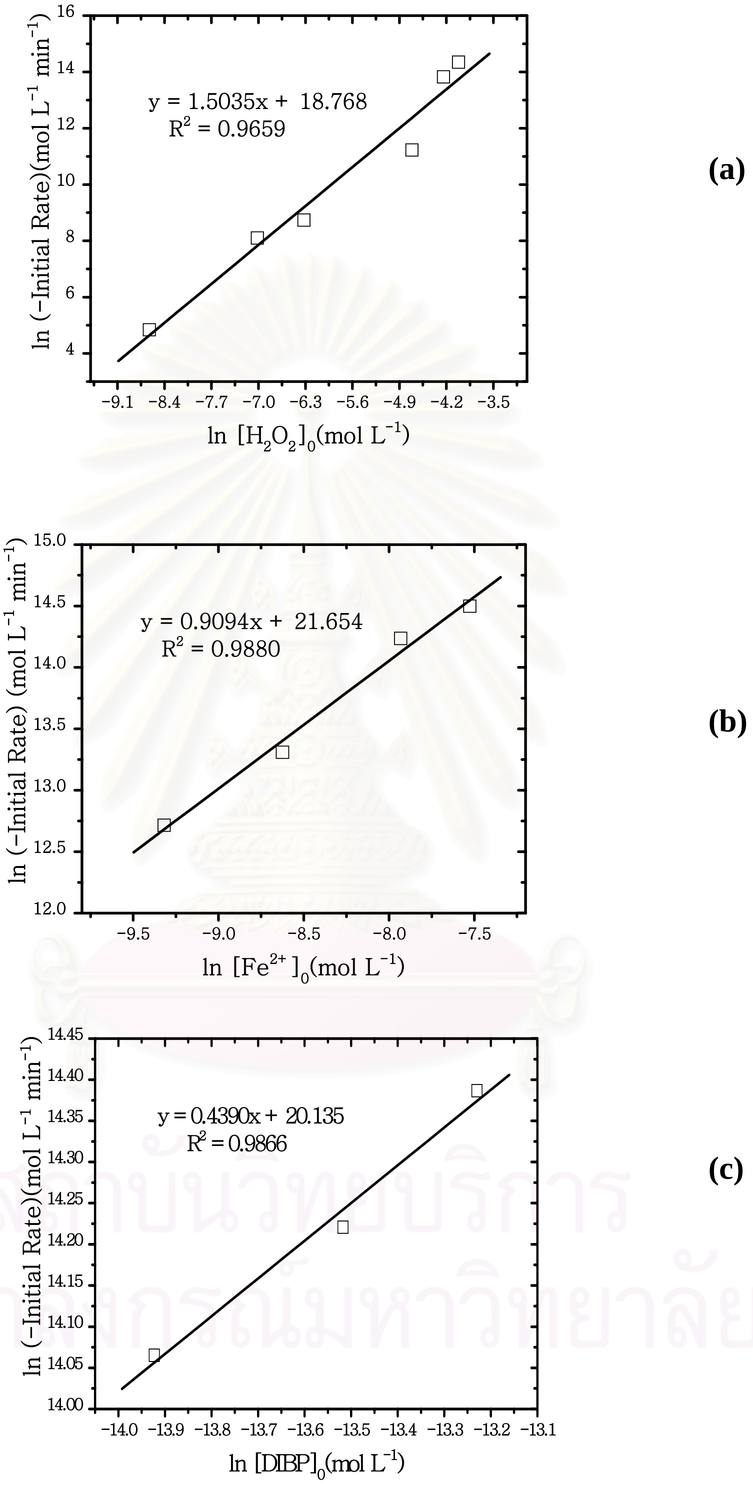


Figure 4.43 Initial rate of DIBP treatment in treated wastewater with respect to (a) $[H_2O_2]_0$; (b) $[Fe^{2+}]_0$; and (c) $[DIBP]_0$

According to Fig. 4.43, the initial rates increased with the increasing concentration of each component. The overall initial rate equation could be written as follows:

$$-\left(\frac{d[DIBP]}{dt}\right)_{initial} = k[H_2O_2]_0^{1.50}[Fe^{2+}]_0^{0.91}[DIBP]_0^{0.44} \qquad (4.37)$$

Where k stands for the overall rate constants for DIBP degradation by Fenton's treatment (L $mol^{-1})^{1.85}$ min^{-1}; $[DIBP]_0$ is the initial DIBP concentration (mol L^{-1}); $[Fe^{2+}]_0$ is the initial Fe^{2+} concentration (mol L^{-1}); $[H_2O_2]_0$ is the initial H_2O_2 concentration (mol L^{-1}) and $\left(\frac{d[DIBP]}{dt}\right)_{initial}$ is the initial DIBP degradation rate (mol L^{-1} min^{-1}).

To determine the overall kinetic constant, the non-linear least square method was applied by minimizing the sum of square error and the overall initial rate equation became

$$-\left(\frac{d[DIBP]}{dt}\right)_{initial} = 2.52x10^{-8}[H_2O_2]_0^{1.50}[Fe^{2+}]_0^{0.91}[DIBP]_0^{0.44} \qquad (4.38)$$

Over COD and BOD_5 range of 100-380 mg L^{-1} and 30-190 mg L^{-1}, respectively.

Comparing with the synthetic wastewater, the kinetic constant was substantially diminished from 6.0 x 10^3 (L $mol^{-1})^{1.16}$ min^{-1} in the synthetic wastewater to 2.52 $x10^{-8}$ (L $mol^{-1})^{1.85}$ min^{-1} in the industrial wastewater. Like the 3MI, it was attributed to the competition with other organics to consume the hydroxyl radicals. The difference up to the power of 11 was tremendous, while the 3MI's was just with the power of 6. This indicates the inert property of DIBP, if compared other non-biological species. Focusing on the reaction order, both Fe^{2+} and H_2O_2 increase in their numbers while the DIBP decreases its number. This demonstrated that the low concentration of DIBP was slightly affected in its degradation, whereas Fe^{2+} and H_2O_2 need to be supplied to the system in large number in order to sufficiently remove all organics in the wastewater before DIBP was degraded. The partial order of Fe^{2+}

increases nearly doubly. It might be due to the co-precipitation with the suspended solid. The highest impact factor still falls onto the H_2O_2 which has the largest number of power. Thereby, considering the cost concern, H_2O_2 should be regarded as the first for the Fenton’s post-treatment.

CHAPTER V

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORKS

5.1 Conclusions

This research could be divided into 2 parts; characterization and treatment.

5.1.1 Characterization study

The characteristics of the Para rubber wastewater were determined in order to provide the information for the further management efficiently. The compounds in the wastewater were identified by using the gas chromatography coupled with the mass spectrometry (GC/MS) after the fractionation by size exclusive chromatography (SEC). According to the experimental results, it was found that

a) In the analytical point of view, the optimum condition of the liquid-liquid extraction (LLE) was 40 mL ethyl acetate per 100 mL wastewater, one time extraction and 2 min shaking time if LLE was used as the extraction method for the dominant species.
b) The optimum condition of the solid phase extraction (SPE) was 1 mL dichloromethane extract solvent and 5 in.Hg per cm cartridge diameter, if SPE was used as the extraction method for the dominant species.
c) Although the LLE provided the response of the first dominant species higher than SPE, SPE presented the advantage over LLE in a number of organic species. This was more important for the characterization. As the results, SPE was selected as the suitable extraction method in this study.
d) The 6 months monitoring results showed the lump parameters of the raw wastewater were average BOD_5 = 5,517 mg L^{-1}, COD = 11,349 mg L^{-1}, SS = 1,519 mg L^{-1}, and pH = 4.92, while those of the treated wastewater were average BOD_5 = 108 mg L^{-1}, COD = 223 mg L^{-1}, SS = 165 mg L^{-1},

and pH = 8.27.

e) The average 281 m^3 day^{-1} wastewater was generated from many sources, especially the cleaning of equipments. The concentrated latex process released the wastewater between 2.7 – 5.5 m^3 ton production $^{-1}$, while the skim crepe and the rubber block emitted approximately 24.9 – 65.3 and 5.8 – 37.0 m^3 ton production^{-1}, respectively.

f) The organic substances in the raw wastewater could be divided into 7 groups; acids, indoles, phthalates, alcohols and phenols, thiazoles, thiocarbamates and others. The first and second dominant species in the raw wastewater were 3-methylindole (3MI) and diisobutyl phthalate (DIBP), respectively.

g) After the biological treatment, the number of found organics was reduced from 63 to 51 substances, *i.e.* 26 substances was removed from the raw wastewater/lower than the detection limit in the treated wastewater, while other 14 substances were the new comers. Most of compounds in the treated wastewater were detected sporadically. Among them, DIBP became the first dominant species in the treated wastewater. This presented DIBP including its phthalic acid esters was recalcitrant to biodegrade.

5.1.2 Wastewater treatment study

The unpleasant smelling was the biggest problem of the Para rubber latex industry. From the characterization results, one of this problem culprits appeared in the raw wastewater was the malodorous 3MI. It needs the fast treatment method to eliminate them. The economical and effective method, Fenton’s treatment was proposed in this research to treat the raw wastewater containing 3MI. Moreover, with its high oxidation potential, this method was also offered to treat the non-biodegradable DIBP in the treated wastewater. The wastewater treatment part was divided into 2 sub-divisions, *i.e.* the synthetic and industrial wastewater study. In the synthetic wastewater study, the 3MI and DIBP were prepared as the representatives of the raw and treated wastewater, respectively. They were applied with the Fenton’s reagent to determine the optimum operating conditions. Then, the results were compared with those obtained from the real industrial wastewater. According to the experimental data, it could be summarized that:

a) For the synthetic DIBP wastewater, the optimum operating condition was 5: 5: 1 [H_2O_2]: [Fe^{2+}]: [DIBP] molar ratio and pH =3. At the optimum condition, the DIBP could be removed up to 87% in 30 min, based on 14 mg L^{-1} of the initial DIBP concentration. The removal rate was increased with the decreasing initial DIBP concentration. The DIBP could be not degraded by the Fe^{2+} alone, but it could be eliminated by the single H_2O_2 with the removal efficiency around 10%.
b) For the synthetic 3MI wastewater, the optimum operating condition was 1: 1.5: 1 [H_2O_2]: [Fe^{2+}]: [3MI] molar ratio and pH =3. The 3MI degradation was occurred about 99% in 180 min, based on 100 mg L^{-1} of the 3MI initial concentration. However, the major degradation of 3MI was contributed to the reduction by Fe^{2+}, up to 70%, while the H_2O_2 alone could degrade the 3MI only 10%. Moreover, the 3MI could be also destroyed by the acid, which was used to adjust the pH, around 10%. The decreasing in the initial 3MI concentration promoted its removal rate.
c) When the optimum operating condition from the synthetic wastewater was applied to the industrial wastewater, the large difference in %degradation was noticed. For the raw wastewater, the degradation percentage of the industrial raw wastewater was 30% lower than the synthetic wastewater. The maximum degradation was reached within 1 min. for the synthetic and 60 min. for the real wastewater. According to the experimental results, it could be concluded that the DIBP was responsible for the equilibrium time expanded, while the reduction in %degradation was in charge of other species in the wastewater. For the treated wastewater, the 0.5 mg L^{-1} DIBP could be removed nearly 100% in the synthetic wastewater, but it was scarcely degraded in the industrial wastewater. It was attributed to the DIBP's inert property comparing with other species in the industrial wastewater. Since the large difference between the synthetic and real

industrial was observed, the operating conditions of the industrial wastewater would be optimized again.

d) For the raw industrial wastewater, the conditions were optimized as the ratio of Fenton’s reagent to the 3MI concentration, because the dominant species in the raw wastewater was 3MI. Based on the 3MI and COD removal, the optimum condition was selected at 20:10:1 [H_2O_2]: [Fe^{2+}]: [3MI] molar ratio and pH = 3. The 3MI could be removed up to 100%, while the COD was approximately 12%. The decreasing in the initial 3MI concentration promoted its removal rate. The suspended solids were reduced about 38% from the iron precipitation and acid addition. Because it promoted the biodegradability index (BOD_5/COD) about 0.1, this method was recommended to apply as the pre-treatment of the subsequent biological treatment.

e) For the treated biological wastewater, the conditions were optimized by considering the DIBP concentration, because the dominant species in the raw wastewater was DIBP. Based on the DIBP and COD removal, the optimum condition was selected at 617 mg L^{-1} [H_2O_2], 70 mg L^{-1} [Fe^{2+}] and pH = 3 for 1 L wastewater contained 0.5 mg L^{-1} [DIBP]. The decreasing in the initial DIBP concentration promoted its removal rate. However, if the DIBP concentration was lower than 0.25 mg L^{-1}, the removal rate became decreased. At the optimum conditions, the DIBP was degraded about 90%, while the COD was removed around 48%. This was enough to allow the wastewater quality meet the standard required by law. Thereby, the Fenton’s treatment was suitable to apply as the post-treatment.

f) The empirical kinetic equation of the initial degradation rate could be expressed as follows;

For the single DIBP:

$$-\left(\frac{d[DIBP]_0}{dt}\right)_{Initial} = 6.0x10^3 [DIBP]_0^{0.88} [Fe^{2+}]_0^{0.33} [H_2O_2]_0^{0.95}$$

For the single 3MI:

$$-\left(\frac{d[3MI]}{dt}\right)_{initial} = 2.96x10^{4}\left[H_2O_2\right]_0^{0.25}\left[Fe^{2+}\right]_0^{0.38}\left[3MI\right]_0^{0.52}$$

For the DIBP in the treated wastewater:

$$-\left(\frac{d[DIBP]}{dt}\right)_{initial} = 2.52x10^{-8}\left[H_2O_2\right]_0^{1.50}\left[Fe^{2+}\right]_0^{0.91}\left[DIBP\right]_0^{0.44}$$

For the 3MI in the raw wastewater:

$$-\left(\frac{d[3MI]}{dt}\right)_{initial} = 6.99x10^{-2}\left[H_2O_2\right]_0^{0.24}\left[Fe^{2+}\right]_0^{0.20}\left[3MI\right]_0^{0.99}$$

5.2 Suggestions for future work

This study was related to the characterization of the wastewater from the concentrated latex industry, which was the upstream of other Para rubber industries. It should be extended to other industrial types of the natural rubber, *e.g.* ribbed smoked sheet, air dried sheet, rubber glove, and STR rubber block, etc. Especially the STR, its 6 different grades covers 60% of the export market of the natural rubber. Moreover, if it will be possible, the sampling site should be expanded to each step of the production process so as to obtain the exact sources of the pollutants.

For the proposed treatment, it is necessary to work more on the continuous process before applied to the industry. The kinetic results from this study can be used to design the continuous reactors by calculating from mass balance. The continuous stirring tank reactor (CSTR) is recommended, because it is closed to the present industrial system that it will reduce the construction cost. The reaction product should be determined so as to ensure the product is not toxic to environment. According to the experimental results, the 3MI could be reduced by the Fe^{2+} alone up to 70%. The treatment of 3MI by the Fe^{2+} alone is worth to study. To reduce the reagent cost, the Fenton-like treatment, such as the iron coated sand, might be studied. From the nature of the rubber, it is possible the residual rubber particle in the wastewater can be flocculated by ferric, leading to the reduction of the suspended solid. This will be another advantage of Fenton’s like process.

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APPENDICES

APPENDIX A

1, 10-Phenanthroline standard method for ferrous concentration determination

General Discussion

The 1, 10-phenanthroline complex with iron (II) was first discovered by Blau (1898). A spectrophotometric determination of iron dependent on the formation of the iron (II)-1, 10-phenanthroline complex was developed by Fortune and Mellon (1938). The iron (II)-1, 10-phenanthroline complex is reddish orange color.

Instrumentation

1) Spectrophotometer (HP 8452A Dioade Array and Specord S100): The wavelength used for ferrous analysis is 510 nm.
2) Acid-washed glassware: All glassware have to be washed with conc. HCl and rinsed with DI water to remove the iron oxide deposited.
3) Membrane filter: A 0.45 µm cellulose acetate membrane is used to remove ferric hydroxide suspended in a sample solution.

Reagents

All reagents are prepared in Milli-Q water. Reagents are stored in glass bottles. The hydrochloric acid and ammonium acetate solutions are kept for a long time, if their bottles are closed tightly enough. However, the standard ferrous solution is not stable. Thus, it should be prepared daily.

1) Hydrochloric acid, HCl: 20 mL concentrated hydrochloric acid is diluted to 1000 mL by the DI water.
2) Ammonium acetate buffer solution, $NH_4C_2H_3O_2$: 500 g $NH_4C_2H_3O_2$ is dissolved in 300 mL of DI water. Then, 1400 mL concentrated acetic acid is filled up to the mark of 2000 mL volumetric flask.

3) Phenanthroline solution, $C_{12}H_8N_2.H_2O$: 5 g of 1, 10-phenathroline monohydrate is mixed with 1 mL concentrated hydrochloric acid. Then, it is added with DI water to make the volume be 1000 mL.
4) Stock ferrous ion solution: 20 mL of concentrated H_2SO_4 was slowly added to 50 mL DI water and 0.25 g of ferrous sulfate ($FeSO_4.7H_2O$) was added. Then, DI water was used to make the mark of 1000 mL. The stock solution is 500 mg L^{-1}as Fe^{2+}.
5) Standard solution: 1 mL concentrated H_2SO_4 is slowly added to 25 mL DI water. Then, it is added by 5 mL stock ferrous ion solution and diluted to 50 mL with DI water. The standard is 50 mg L^{-1}.

Procedure

1) Calibration curves: The standard ferrous (Fe^{2+}) solutions will be prepared in the range 0 to 50 mg L^{-1} as Fe^{2+}. The 25 mL HCl solution is prepared in 6 of 50 mL volumetric flasks. Then, they are added by 10 mL of phenanthroline solution and 5 mL of ammonium acetate solution with vigorous stirring. The 1, 2, 3, 4, 5 mL of 50 mg L^{-1} as Fe^{2+} standard solution are then added to those flasks, respectively. After that, they are diluted to 50 mL with DI water and mixed thoroughly. Next, it is let leave for 10 min before measured the absorbance by a spectrophotometer at 510 nm.
2) Sample analysis: To determine ferrous ion in wastewater sample, 25 mL HCl stock solution is prepared in 50 mL volumetric flask. Then, 10 mL phenanthroline solution and 5 mL ammonium acetate solution are added with vigorous stirring. The 2 mL sample is filled and diluted to 50 mL with DI water. After that, it has to stand for 10 min. Do not expose to sunlight (color development is rapid in the presence of excess phenanthroline). Next, it is let leave for 10 min before measured the absorbance by a spectrophotometer at 510 nm.

Precision and accuracy

Precision and accuracy depends on the method of sample collection and storage, the method of color measurement, the iron concentration, and the presence of interfering color, turbidity and foreign ions.

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APPENDIX B

Table B-1 Effect of the organic type on LLE based on 20 mL solvent and 100 mL wastewater

Types of organic solvent	Average peak area (AU unit)
Hex	2.14×10^6
Hex: DCM 1:1 (v/v)	6.78×10^6
DCM	1.01×10^7
DCM: EtOAc 1:1 (v/v)	9.10×10^6
EtOAc	9.00×10^6
EtOAc: MeOH 1:1 (v/v)	8.02×10^6

Table B-2 Effect of the solvent volume on LLE based on 100 mL wastewater

Volume of Ethyl Acetate (mL)	**Average peak area (AU unit)**
20	9.00×10^{6}
40	1.27×10^{7}
60	1.22×10^{7}
80	1.24×10^{7}
100	1.21×10^{7}

Table B-3 Effect of number of successive extractions on LLE based on 100 mL wastewater and 40 mL ethyl acetate

Number of successive extractions	Average peak area (AU unit)
1	1.07×10^{7}
2	9.19×10^{6}
3	4.69×10^{6}
4	4.33×10^{6}

Table B-4 Effect of the shaking time on LLE based on 100 mL wastewater and 40 mL ethyl acetate

Shaking Time (min)	**Average peak area (AU unit)**
0.5	6.32×10^{6}
1	8.88×10^{6}
2	1.07×10^{7}
5	1.11×10^{7}
10	1.12×10^{7}
15	9.73×10^{6}

Table B-5 Effect of the type of elution solvent on SPE based on 50 mL wastewater

Types of elution solvent	Average peak area (AU unit)
Hex	3.72×10^5
Hex:DCM 1:1 (v/v)	5.31×10^6
DCM	6.45×10^6
DCM:EtOAc 1:1 (v/v)	5.46×10^6
EtOAc	5.45×10^6
EtOAc:MeOH 1:1 (v/v)	2.84×10^6

Table B-6 Effect of the elution solvent volume on SPE based on 50 mL wastewater

Volume of elution solvent (mL)	Average peak area (AU unit)
1	6.13×10^6
3	6.08×10^6
5	6.45×10^6
10	5.94×10^6
15	6.36×10^6

Table B-7 Effect of the vacuum pressure on SPE based on 50 mL wastewater

Vacuum Pressure (in. Hg)	Average peak area (AU unit)
1	2.63×10^6
5	2.75×10^6
10	2.03×10^6
15	8.59×10^5

Table B-8 Average concentration of compounds found in the RAW wastewater for 6 months monitoring during November 2004 to April 2005 (mg L^{-1} x 10^{-1})

Substances	9/11/2004	24/11/2004	9/12/2004	24/12/2004	10/1/2005	24/1/2005	24/2/2005	9/3/2005	24/3/2005	8/4/2005	22/4/2005
Acids											
Hexanoic acid	15.78±0.79	13.11±1.05	8.84±0.53	5.62±0.22	11.99±0.84	9.62±0.77	6.26±0.50	10.19±0.61	7.04±0.28	27.21±1.90	22.68±1.81
Heptanoic acid	16.65±0.98	14.64±0.59	12.13±0.73	3.49±0.24	9.93±0.30	7.30±0.51	15.78±0.63	22.18±1.33	24.88±1.74	19.92±0.60	12.31±0.86
Cyclohexanecarboxylic acid	24.67±1,.48	32.51±1.63	29.58±1.77	7.40±0.44	10.77±0.75	15.59±0.77	30.45±1.52	48.91±2.93	47.56±2.85	39.39±2.76	31.28±1.88
Octanoic acid	8.54±0.43	5.77±0.23	2.94±0.09	0.83±0.02	1.24±0.06	4.08±0.24	1.98±0.08	5.95±0.18	4.00±0.08	23.40±1.77	4.52±0.27
Boric acid	10.23±0.41	8.93±0.54	4.49±0.22	1.64±0.08	4.00±0.28	7.04±0.21	9.87±0.59	19.90±1.01	14.31±0.72	0.84±0.06	5.46±0.16
Nonanoic acid	-	4.31±0.13	-	0.84±0.03	0.78±0.05	1.63±0.08	-	-	-	17.95±1.08	1.64±0.08
Proionic acid	8.23±0.58	7.15±1.50	3.32±0.13	2.83±0.14	2.97±0.18	8.92±0.45	11.62±0.81	9.69±0.39	-	5.44±0.33	2.16±0.11
Benzoic acid,2-amino-	4.21±0.08	3.12±0.12	3.33±0.17	1.18±0.05	-	3.98±0.20	3.14±0.13	-	7.86±0.31	2.73±0.16	2.42±0.12
Dodecanoic acid	2.42±0.02	1.23±0.02	0.96±0.05	0.78±0.04	0.77±0.03	1.11±0.03	1.39±0.03	1.42±0.07	4.50±0.23	1.23±0.05	1.10±0.03
a-methyl-2-aminobenzeneacetic acid	5.34±0.21	3.12±0.12	1.93±0.14	2.03±0.16	2.11±0.11	4.50±0.36	4.36±0.17	2.64±0.18	7.75±0.62	2.24±0.11	2.08±0.17
Tetradecanoic acid	-	-	1.86±0.09	0.84±0.03	-	1.83±0.09	1.60±0.06	1.83±0.09	4.62±0.18	1.25±0.06	1.08±0.05
Palmitic acid	2.18±0.11	2.21±0.02	1.42±0.07	1.24±0.10	1.43±0.07	2.88±0.17	2.69±0.05	-	2.54±0.20	1.52±0.08	1.26±0.08
Octadecanoic acid	-	3.31±0.14	-	1.63±0.08	-	2.14±0.11	-	-	8.74±0.44	2.20±0.11	1.81±0.09
3,5-Dihydroxy-4-methylphenylacetic acid	-	-	7.12±0.43	-	-	8.24±0.66	8.58±0.43	6.07±0.36	-	-	-
Heptadecene-(8)-carbonic acid-(1)-	-	-	-	-	-	4.59±0.32	3.88±0.19	-	-	-	-

Table B-8 Average concentration of compounds found in the RAW wastewater for 6 months monitoring during November 2004 to April 2005 (mg L^{-1} x 10^{-1}) (cont.)

Substances	9/11/2004	24/11/2004	9/12/2004	24/12/2004	10/1/2005	24/1/2005	24/2/2005	9/3/2005	24/3/2005	8/4/2005	22/4/2005
Indole derivatives											
1H-Indole	4.12±0.21	3.90±0.23	2.17±0.05	2.00±0.10	3.83±0.19	5.59±0.45	4.12±0.16	1.39±0.05	14.23±0.71	5.34±0.21	3.12±0.16
3-methylindole	176.62±5.51	271.79±6.09	371.46±8.86	196.41±3.98	394.46±8.76	336.72±12.68	395.44±13.16	620.33±35.12	667.61±24.76	667.44±36.01	429.13±44.43
Oxindole	2.76±0.06	2.65±0.08	1.31±0.07	1.46±0.07	1.41±0.08	2.67±0.13	1.89±0.09	3.99±0.08	1.67±0.08	3.43±0.25	1.39±0.07
3-methyloxindole	7.32±0.44	7.12±0.36	1.53±0.09	1.32±0.08	2.87±0.14	2.26±0.09	3.44±0.17	8.06±1.24	12.81±0.74	8.48±0.23	3.34±0.17
1H-Indole-3-ethanamine, N,N-dimethyl-	0.81±0.03	0.71±0.05	-	0.76±0.04	-	-	-	-	-	-	-
(1H)Indole,4-methoxy-3-cyanomethyl	0.97±0.05	-	1.05±0.05	1.01±0.03	-	-	-	-	-	-	-
1H-Indole-3-ethanol	5.12±0.10	3.11±0.19	1.49±0.07	1.12±0.06	1.51±0.08	3.09±0.09	3.54±0.18	3.73±0.19	8.99±0.28	2.34±0.12	1.60±0.10
1H-indole-2,3-dione	-	-	-	5.94±0.30	-	5.02±0.25	4.18±0.13	2.44±0.12	-	2.83±0.14	2.40±0.02
Indole-3-acetic acid	-	6.81±0.34	6.76±0.34	2.43±0.17	11.93±0.60	8.94±0.72	9.01±0.45	7.12±0.24	9.14±0.56	3.82±0.19	2.00±0.14
3-methyl-3-(3-methylindole-2-yl)-(3H)-indole	-	-	-	3.64±0.18	1.37±0.10	3.85±0.19	-	-	5.55±0.28	-	-
1-methyl-3-(2-(acetylamino)ethyl)indole	-	-	-	-	1.39±0.70	3.03±0.12	3.61±0.18	-	6.00±0.24	2.31±0.12	-
5-hydroxyindolacetic acid	-	-	-	-	1.09±0.05	1.55±0.03	-	1.07±0.05	-	-	-

Table B-8 Average concentration of compounds found in the RAW wastewater for 6 months monitoring during November 2004 to April 2005 (mg L^{-1} x 10^{-1}) (cont.)

Substances	**9/11/2004**	**24/11/2004**	**9/12/2004**	**24/12/2004**	**10/1/2005**	**24/1/2005**	**24/2/2005**	**9/3/2005**	**24/3/2005**	**8/4/2005**	**22/4/2005**
Phthalates											
1,2-benzenedicarboxylic acid, diethyl ester	2.87±0.14	1.11±0.07	1.04±0.17	0.68±0.03	0.81±0.04	-	-	-	3.29±0.16	2.00±0.08	1.58±0.47
1,2-benzenedicarboxylic acid, bis(2-methylpropyl) ester	1.97±0.04	0.70±0.03	7.48±0.37	1.63±0.07	4.07±0.28	4.21±0.21	1.18±0.09	1.24±0.06	9.48±0.66	5.20±0.47	11.85±0.95
1,2-benzenedicarboxylic acid, butyl cyclohexyl ester	2.11±0.04	3.12±0.09	-	-	1.04±0.06	-	3.13±0.16	2.92±0.15	3.70±0.19	1.77±0.02	1.60±0.18
1,2-benzenedicarboxylic acid, dibutyl ester (7.803)	5.12±0.31	3.11±0.16	1.63±0.20	1.53±0.10	2.25±0.11	3.83±0.11	2.39±0.12	1.77±0.20	5.59±0.28	3.40±0.10	5.53±0.43
1,2-benzenedicarboxylic acid, dicyclohexyl ester	-	-	-	-	1.61±0.05	2.61±0.23	-	-	6.07±0.98	1.53±0.08	-
Thiazole											
2(3H)-Benzothiazolone	-	-	-	0.82±0.05	0.77±0.04	-	-	-	-	-	
2-mercaptothiazoline	-	-	-	-	1.35±0.05	-	0.99±0.13	0.78±0.04	-	-	
Thiocarbamates											
Zinc diethylthiocarbamate	1.10±0.03	1.09±0.08	-	-	1.68±0.12	1.38±0.07	1.22±0.11	0.80±0.5	1.39±0.07	1.10±0.13	0.81±0.12
Zinc dimethylthiocarbamate	-	-	-	1.01±0.16	-	-	-	-	-	-	

Table B-8 Average concentration of compounds found in the RAW wastewater for 6 months monitoring during November 2004 to April 2005 (mg L^{-1} x 10^{-1}) (cont.)

Substances	9/11/2004	24/11/2004	9/12/2004	24/12/2004	10/1/2005	24/1/2005	24/2/2005	9/3/2005	24/3/2005	8/4/2005	22/4/2005
Alcohol and phenols											
4-methyl cathechol	-	-	3.03±0.41	0.97±0.05	1.31±0.07	2.23±0.18	7.61±0.54	-	-	-	
4-hydroxy-3-methoxybenzyl alcohol	-	-	-	0.77±0.05	-	0.91±0.09	1.18±0.19	1.03±0.05	1.13±0.08	0.99±0.09	1.02±0.08
3,5 Dimethoxy-p-coumaric alocohol	-	-	-	0.83±0.08	-	-	-	-	-	-	
9,10-Dihydrotribenzo[a,c,e] cycloocten-9-ol	-	-	-	1.67±0.17	-	3.48±0.67	-	-	-	-	
Phenol, 4-methyl-	19.91±1.81	18.71±1.31	11.02±0.67	3.32±0.24	7.76±0.23	27.89±1.34	5.36±0.21	30.43±2.52	31.78±1.91	16.87±1.84	8.96±0.54
2-methoxy-4-methylphenol	8.21±0.51	-	4.52±0.42	2.51±0.23	0.97±0.05	6.79±65	-	-	-	3.97±0.20	17.59±2.11
3-methoxyphenol	6.31±0.23	-	-	2.39±0.33	3.09±0.15	14.26±3.45	13.70±0.69	-	-	2.57±0.43	1.89±0.11
3,4-dimethoxyphenol	4.14±0.29	1.91±0.11	-	0.80±0.12	-	1.57±0.12	2.09±0.06	-	10.09±0.20	2.28±0.26	1.33±0.13
Phenol, 3,5-bis(1,1-dimethylethyl)	1.10±0.15	-	1.31±0.11	0.77±0.08	-	1.08±0.21	2.13±0.11	-	-	-	1.04±0.09
4-(ethoxymethyl)-2-methoxyphenol	-	-	-	2.23±0.23	-	-	-	-	-	-	4.21±0.43
2-6-di-tert-butyl-4-methylphenol	-	-	-	-	1.03±0.07	1.66±0.32	1.72±0.09	1.60±0.18	4.98±0.34	-	

Table B-8 Average concentration of compounds found in the RAW wastewater for 6 months monitoring during November 2004 to April 2005 (mg L^{-1} x 10^{-1}) (cont.)

Substances	9/11/2004	24/11/2004	9/12/2004	24/12/2004	10/1/2005	24/1/2005	24/2/2005	9/3/2005	24/3/2005	8/4/2005	22/4/2005
Miscellaneous											
Ethanone, 1-(4-aminophenyl)-	-	-	-	1.27±0.21	1.04±0.13	1.93±0.16	1.46±0.15	0.67±0.04	1.82±0.12	0.94±0.11	1.33±0.11
2H-1-Benzopyran-2-one, 7-hydroxy-6-methoxy-	-	-	-	1.11±0.07	-	-	-	-	-	-	
5.alpha.-Estran-2-one	-	-	-	-	11.57±1.32	7.22±0.98	-	9.27±1.21	9.31±2.10	-	2.65±0.21
1,1,1a-trimethyl-1,1a-dihydrocycloprop[a]inden-6(6a)-one	-	-	-	-	0.92±0.02	-	-	-	-	-	
4-Amino-5-acetyl-7-azatetracyclo[7.3.1.1(3,11).0(3,7)]tetradec-4-en-6-one	-	-	-	-	-	-	12.56±1.34	-	-	3.28±0.34	
Octadecane								0.97±0.01	1.24±0.11	1.02±0.10	1.66±0.11
Acetaldehyde, (3-chloro-5,5-dimethyl-2-cyclohexen-1-ylidene)-, (E)-	3.12±0.54	2.61±0.17	1.71±0.11	0.84±0.05	-	4.75±0.78	2.64±0.22	1.24±0.11	3.34±0.35	2.63±0.21	1.93±0.16
Isofraxidin	2.70±0.23	2.50±0.21	-	1.14±0.11	-	1.82±0.18	-	-	6.32±0.99	1.96±0.11	1.80±0.12
2-(2'-nitro-3'-thienyl)pyrimidine	-	-	-	1.23±0.11	1.28±0.12	-	-	-	-	-	
Tetramethyl thiurammonosulfide	2.11±0.26	-	-	0.12±0.09	-	3.12±0.21	-	-	-	-	
Cyclopropaneoctanal, 2-octyl	-	-	-	1.25±0.14	-	-	-	-	-	-	

Table B-8 Average concentration of compounds found in the RAW wastewater for 6 months monitoring during November 2004 to April 2005 (mg L^{-1} x 10^{-1}) (cont.)

Substances	9/11/2004	24/11/2004	9/12/2004	24/12/2004	10/1/2005	24/1/2005	24/2/2005	9/3/2005	24/3/2005	8/4/2005	22/4/2005
Miscellaneous											
8B, 13:8A,14-Diepoxy-14,15-bisnorlabdane	-	-	-	1.78±0.15	1.91±0.13	4.92±0.54	2.71±0.21	1.97±0.02	4.10±0.56	1.62±0.13	1.23±0.12
8-Hydroxyquinoline	-	-	-	-	0.95±0.07	-	-	-	-	-	
4-Methyl-2-(3-thienyl)pyridine	-	-	-	-	0.80±0.06	-	-	-	-	-	
3-cyano-6-(2-furyl)-4-(methylthio)-2-phenylpyridine	-	-	-	-	3.31±0.21	6.38±0.45	3.90±0.32	2.71±0.24	5.71±0.67	1.91±0.12	1.80±0.14
1-methoxy-3-methyl-9H-carbazole	-	-	-	-	-	-	1.14±0.12	-	-	-	

Table B-9 Average concentration of compounds found in the TREATED wastewater for 6 months monitoring during November 2004 to April 2005 (mg L^{-1} x 10^{-1})

Substances	**9/11/2004**	**24/11/2004**	**9/12/2004**	**24/12/2004**	**10/1/2005**	**24/1/2005**	**24/2/2005**	**9/3/2005**	**24/3/2005**	**8/4/2005**	**22/4/2005**
Acids											
Heptanoic acid	-	-	-	-	-	-	-	0.84±0.07	-	-	-
Octanoic acid	-	-	-	-	0.67±0.02	-	-	-	-	-	-
Boric acid	-	-	-	-	-	-	-	0.74±0.03	-	-	-
Nonanoic acid	-	-	-	-	-	0.67±0.03	-	0.86±0.04	-	-	-
Propionic acid	0.31±0.02	0.65±0.04	-	0.88±0.05	1.29±0.13	1.07±0.11	-	1.06±0.11	-	-	-
Cyclopropaneacetic acid	-	-	-	0.89±0.07	-	-	-	-	-	-	-
Dodecanoic acid	-	-	-	-	0.77±0.09	-	-	0.94±0.10	-	-	-
a-methyl-2-aminobenzeneacetic acid	-	-	-	-	-	-	-	-	-	-	0.88±0.11
Tetradecanoic acid	-	-	-	-	0.94±0.10	-	-	0.85±0.12	-	-	0.92±0.12
Palmitic acid	0.31±0.03	0.69±0.05	0.82±0.05	1.10±0.11	1.13±0.12	1.24±0.11	1.73±0.14	0.91±0.11	1.21±0.12	-	1.11±0.11
Octadecanoic acid	-	3.30±0.31	-	-	-	1.09±0.09	-	-	-	-	-
Dehydroabietic acid	-	-	-	2.18±0.21	-	-	-	-	-	-	-

Table B-9 Average concentration of compounds found in the TREATED wastewater for 6 months monitoring during November 2004 to April 2005 (mg L^{-1} x 10^{-1}) (cont.)

Substances	**9/11/2004**	**24/11/2004**	**9/12/2004**	**24/12/2004**	**10/1/2005**	**24/1/2005**	**24/2/2005**	**9/3/2005**	**24/3/2005**	**8/4/2005**	**22/4/2005**
Indole derivatives											
1H-Indole	-	0.75±0.09	0.77±0.04	0.88±0.05	1.90±0.16	0.97±0.08	-	3.48±0.21	-	1.42±0.11	-
3-methylindole	2.13±0.21	3.59±0.21	4.96±0.34	4.16±0.21	5.57±0.45	7.13±0.92	9.27±1.21	13.53±2.11	6.90±0.98	8.29±0.98	21.89±2.11
Oxindole	-	-	-	-	0.80±0.09	-	-	0.80±0.09	-	-	-
3-methylindole-2(3H)-one	1.12±0.11	-	-	-	2.22±0.17	1.25±0.11	-	1.01±0.10	1.12±0.11	-	0.87±0.17
1H-Indole-3-ethanol	-	0.69±0.07	-	1.08±0.11	1.12±0.09	-	-	-	-	-	-
3-methyl-3-(3-methylindole-2-yl)-(3H)-indole	-	-	-	-	-	-	4.10±0.34	1.04±0.09	-	-	-
Indole-3-acetic acid	-	-	-	-	13.91±1.23	-	-	1.76±0.12	-	-	-

Table B-9 Average concentration of compounds found in the TREATED wastewater for 6 months monitoring during November 2004 to April 2005 (mg L^{-1} x 10^{-1}) (cont.)

Substances	9/11/2004	24/11/2004	9/12/2004	24/12/2004	10/1/2005	24/1/2005	24/2/2005	9/3/2005	24/3/2005	8/4/2005	22/4/2005
Phthalates											
1,2-benzenedicarboxylic acid, diethyl ester	-	0.65±0.03	-	0.89±0.0.9	0.81±0.07	0.83±0.09	-	1.00±0.11	-	-	0.75±0.08
1,2-benzenedicarboxylic acid, bis(2-methylpropyl) ester	-	4.47±0.78	20.01±2.01	13.97±1.74	11.98±1.67	11.01±1.18	-	10.13±1.27	12.32±2.35	10.40±1.27	36.61±3.51
1,2-benzenedicarboxylic acid, butyl cyclohexyl ester	-	-	-	-	-	-	2.32±0.21	-	-	-	-
1,2-benzenedicarboxylic acid, dibutyl ester	-	1.19±0.11	-	2.47±0.56	1.66±0.11	-	5.35±0.59	1.39±0.11	-	-	2.74±0.21
1,2-benzenedicarboxylic acid, dicyclohexyl ester	-	-	-	1.57±0.15	1.28±0.12	2.68±0.25	1.79±0.18	1.04±0.12	-	-	0.89±0.07
1,2-benzenedicarboxylic acid, dioctyl ester	-	5.20±1.09	-	3.06±0.48	-	-	-	-	-	-	-
Thiazoles											
2-Thiazolidinethione	-	-	-	-	2.01±0.25	2.05±0.20	2.78±0.28	1.10±0.11	-	-	-
2(3H)-Benzothiazolone	0.85±0.06	-	-	0.97±0.11	0.74±0.09	-	-	-	-	0.85±0.15	-
Thiocarbamate											
Zinc diethylthiocarbamate	-	0.67±0.04	-	0.82±0.09	0.82±0.10	1.05±0.11	-	-	0.87±0.09	-	1.01±0.13
Zinc dimethylthiocarbamate	-	-	-	-	-	3.33±0.31	-	-	-	-	-

Table B-9 Average concentration of compounds found in the TREATED wastewater for 6 months monitoring during November 2004 to April 2005 (mg L^{-1} x 10^{-1}) (cont.)

Substances	9/11/2004	24/11/2004	9/12/2004	24/12/2004	10/1/2005	24/1/2005	24/2/2005	9/3/2005	24/3/2005	8/4/2005	22/4/2005
Phenol											
Phenol	-	-	-	-	0.85±0.11	-	-	-	-	-	-
4-methylphenol	-	-	-	-	0.82±0.10	-	-	-	-	-	-
3-methoxyphenol	-	0.65±0.12	-	0.82±0.09	1.09±0.12	0.70±0.08	1.31±0.11	-	0.91±0.08	-	-
Phenol, 3,5-bis(1,1-dimethylethyl)	-	0.67±0.05	-	0.73±0.10	0.73±0.11	0.75±0.10	-	0.78±0.05	-	0.73±0.11	-
Phenol, 3,4,5-trimethoxy-	-	-	-	-	0.76±0.09	-	-	-	-	-	-
2-6-di-tert-butyl-4-methylphenol	-	-	-	-	-	1.32±0.12	-	-	-	-	-
2,5-di-tertl-butyl-2,6-dinitrophenol	-	-	-	-	-	-	3.49±0.38	-	-	-	-

Table B-9 Average concentration of compounds found in the TREATED wastewater for 6 months monitoring during November 2004 to April 2005 (mg L^{-1} x 10^{-1}) (cont.)

Substances	9/11/2004	24/11/2004	9/12/2004	24/12/2004	10/1/2005	24/1/2005	24/2/2005	9/3/2005	24/3/2005	8/4/2005	22/4/2005
Miscellaneous											
2,6-di-t-butyl-4-methylene-2,5-cyclohexadiene-1-one	0.66±0.06	-	0.92±0.08	-	-	-	0.80±0.13	-	-	-	0.66±0.07
Ethanone, 1-(4-aminophenyl)-	-	1.09±0.11	-	1.00±0.12	-	1.70±0.11	0.87±0.36	-	-	0.78±0.09	-
1,4-naphthalenedione, 2-hydroxy-3-methyl-	-	-	0.79±0.15	-	-		-	-	-	-	-
7,9-ditert-butyl-1-oxaspiro[4.5]deca-6,9-diene-2,8-dione	-	-	-	-	1.02±0.11	-	0.83±0.09	-	-	1.01±0.12	-
5.alpha.-Estran-2-one	-	-	-	-	1.50±0.14	-	-	-	-	-	-
4-Amino-5-acetyl-7-azatetracyclo[7.3.1.1(3,11).0(3,7)]tetradec-4-en-6-one	-	-	-	7.35±0.87	-	-	-	-	-	-	-
Octadecane	0.70±0.09	-	1.01±0.13	-	1.49±0.17	1.81±0.21	0.98±0.12	-	-	-	0.70±0.08
Tetracosane	-	-	-	-	-	4.33±0.78	-	-	-	-	-
Quinazoline, 4-methyl	-	-	-	0.75±0.11	-	-	-	-	-	-	-

Table B-9 Average concentration of compounds found in the TREATED wastewater for 6 months monitoring during November 2004 to April 2005 (mg L^{-1} x 10^{-1}) (cont.)

Substances	**9/11/2004**	**24/11/2004**	**9/12/2004**	**24/12/2004**	**10/1/2005**	**24/1/2005**	**24/2/2005**	**9/3/2005**	**24/3/2005**	**8/4/2005**	**22/4/2005**
Miscellaneous											
Benzldehyde,4-hydroxy-3-methoxy-	-	-	-	-	-	-	0.76±0.11	-	-	-	-
10,10-dimethylanthrone hydrazone	-	-	1.03±0.12	-	-	-	-	-	-	-	-
2-*tert*-Butyl-3,3,5-trimethyl-4-(2-methyl-2-propenylidene)-1,2-diaza-3-sila-5-cyclopentene	-	-	-	-	-	2.50±0.21	-	-	-	-	-
Isofraxidin (or 6,8-dimethoxy-7-hydroxycoumarin)	-	-	-	0.81±0.15	-	-	-	-	-	-	-
8B, 13:8A,14-Diepoxy-14,15-bisnorlabdane	-	-	-	2.08±0.24	-	-	-	-	-	-	-
3-cyano-6-(2-furyl)-4-(methylthio)-2-phenylpyridine	-	-	-	3.79±0.54	-	-	-	-	-	-	-

Table B-10 Effect of the initial H_2O_2 concentration on DIBP degradation at pH = 3 and molar ratio of $[Fe^{2+}]$: [DIBP] = 3:1

Time	Average % DIBP degradation at different H_2O_2 molar ratio								
(min)	**0**	**0.5**	**1**	**3**	**5**	**7**	**10**	**15**	**20**
0	0	0	0	0	0	0	0	0	0
0.083	0	1.55	9.53	14.64	11.83	26.07	37.13	36.90	32.97
0.333	1.59	4.13	18.53	37.04	38.69	58.58	60.21	57.11	55.57
1	0	6.77	23.11	48.90	59.63	65.92	69.81	61.14	62.35
1.333	0	6.54	32.27	51.02	63.65	73.07	72.77	69.55	66.98
2	0.38	9.97	38.94	59.48	66.71	76.34	77.65	72.93	69.47
3	0	16.23	36.42	59.81	70.53	76.21	77.37	73.03	69.92
4	1.70	20.77	38.28	63.91	70.44	77.18	76.22	73.85	70.48
5	0	21.36	38.51	61.71	73.26	76.54	76.73	73.78	68.39
10	0	19.59	42.05	59.04	70.24	74.65	77.23	73.30	72.47
15	0	20.02	41.20	57.83	73.42	75.19	76.30	73.88	69.17
20	1.50	20.17	42.10	58.50	74.95	77.28	77.65	74.75	70.07
30	0.45	20.58	45.71	56.77	76.38	76.82	79.64	72.95	71.61

Table B-11 Effect of the initial Fe^{2+} concentration on DIBP degradation at pH = 3 and molar ratio of $[H_2O_2]$: [DIBP] = 5:1

Time (min)	**Average % DIBP degradation at different Fe^{2+} molar ratio**						
	0	**0.5**	**3**	**5**	**7**	**10**	**15**
0	0	0	0	0	0	0	0
0.083	5.20	0.58	14.64	33.81	24.48	10.28	5.65
0.333	7.78	22.55	37.04	62.98	61.91	57.76	55.68
1	6.76	27.62	48.90	83.18	80.58	76.55	74.76
1.333	8.06	28.16	51.02	88.41	82.32	76.68	74.99
2	3.89	32.26	59.48	86.46	80.81	77.20	75.33
3	6.94	31.93	59.81	87.65	80.95	77.44	75.61
4	6.94	34.02	63.91	86.40	81.29	77.71	75.86
5	8.29	33.68	61.71	85.62	81.80	78.02	76.23
10	1.32	34.41	59.04	84.93	80.01	78.43	76.70
15	8.72	32.97	57.83	87.73	80.31	78.86	76.85
20	5.79	35.26	58.50	84.43	81.44	79.11	73.61
30	6.15	36.02	56.77	86.72	81.65	79.51	77.56

Table B-12 Effect of pH on DIBP degradation at molar ratio of [H_2O_2]: [Fe^{2+}]: [DIBP] = 5: 5: 1

Time (min)	**Average % DIBP degradation at different pH**					
	1	**2**	**3**	**4**	**5**	**6**
0	0	0	0	0	0	0
0.083	28.31	32.36	33.81	32.39	21.91	27.86
0.333	55.39	60.45	62.98	58.75	58.09	55.49
1	60.92	65.29	83.18	79.67	59.88	59.08
1.333	73.52	76.36	88.41	80.07	61.26	57.95
2	77.40	81.08	86.46	79.01	61.94	62.53
3	75.47	83.86	87.65	79.04	64.55	60.57
4	80.30	84.82	86.40	80.88	65.88	61.68
5	78.63	85.11	85.62	79.33	72.94	60.78
10	78.35	84.77	84.93	83.22	72.82	61.85
15	76.93	84.71	87.73	83.03	72.05	63.10
20	74.26	85.75	84.43	83.15	69.49	60.11
30	75.42	83.81	86.72	82.35	68.50	58.02

Table B-13 Effect of the initial DIBP concentration on its degradation at pH = 3 and molar ratio of [H_2O_2]: [Fe^{2+}]: [DIBP] = 5: 5: 1

Time (min)	**Average % DIBP degradation at different initial DIBP concentration**			
	14	**10**	**5**	**2**
0	0	0	0	0
0.083	33.81	36.45	39.76	41.75
0.333	62.98	65.88	69.34	71.33
1	83.18	85.12	87.32	88.54
1.333	88.41	90.15	92.05	93.05
2	86.46	90.34	92.27	93.54
3	87.65	90.58	92.46	93.98
4	86.40	90.72	92.75	94.13
5	85.62	90.84	92.97	94.32
10	84.93	91.10	93.26	94.52
15	87.73	91.30	93.41	94.62
20	84.43	91.37	93.62	94.74
30	86.72	91.50	93.67	94.86

Table B-14 Kinetic calculation for the synthetic DIBP wastewater

(a) Initial concentration *v.s.* initial rate

Reactants	**Initial concentration (mol L^{-1})**	**Initial rate (mol L^{-1} min^{-1})**
H_2O_2	2.52×10^{-5}	2.46
	5.04×10^{-5}	5.02
	1.51×10^{-4}	14.02
	2.52×10^{-4}	20.74
Fe^{2+}	2.52×10^{-5}	9.43
	1.51×10^{-4}	14.02
	2.52×10^{-4}	22.10
DIBP	7.19×10^{-6}	3.86
	1.80×10^{-5}	8.85
	3.60×10^{-5}	15.48
	5.04×10^{-5}	22.10

(b) Reaction order

Reactants	**Reaction order**
H_2O_2	0.95
Fe^{2+}	0.33
DIBP	0.88

Table B-15 Effect of pH on 3MI degradation at molar ratio of [H_2O_2]: [Fe^{2+}]: [3MI] = 1: 1: 1

Time	Average % 3MI degradation at different pH					
(min)	1	2	3	4	5	6
0	0	0	0	0	0	0
0.083	80.93	94.52	50.57	50.33	58.22	71.94
0.333	92.65	98.14	67.65	58.44	60.57	57.71
1	99.16	99.25	70.99	62.16	63.88	64.21
1.333	99.29	99.45	73.88	61.84	65.05	63.87
2	99.56	99.27	77.08	63.39	66.27	62.74
3	99.56	99.28	77.89	63.04	65.69	62.12
4	99.63	99.29	79.63	64.45	66.57	63.11
5	99.63	99.44	80.86	65.80	65.68	63.12
10	99.63	99.52	84.05	66.20	66.98	62.68
15	99.63	99.62	87.09	67.73	67.12	63.88
20	99.63	99.61	88.21	69.28	67.92	64.23
30	99.63	99.64	90.46	72.00	69.71	65.53
60	99.63	99.64	95.81	74.34	68.24	65.59
90	99.63	99.64	98.16	74.07	71.79	65.72
120	99.63	99.64	98.72	75.61	70.95	61.76
180	99.63	99.64	99.07	79.21	70.26	62.40

Table B-16 Effect of the initial Fe^{2+} concentration on 3MI degradation at pH = 3 and $[H_2O_2]$: [3MI] = 1:1 molar ratio

Time	Average % 3MI degradation at different Fe^{2+} molar ratio								
(min)	0	0.05	0.1	0.5	1	1.5	2	3	Acid
0	0	0	0	0	0	0	0	0	0
0.083	7.87	20.58	33.29	43.48	67.05	81.56	91.70	97.39	6.12
0.333	10.39	20.00	37.84	40.19	67.65	82.16	91.89	98.18	7.28
1	10.87	22.10	39.21	46.14	68.24	88.08	94.41	98.52	9.28
1.333	11.04	20.19	38.88	47.34	70.99	93.93	97.88	98.65	8.57
2	12.90	20.46	40.15	48.69	73.88	95.06	98.18	98.65	7.95
3	13.78	19.92	41.82	49.32	77.08	96.29	98.19	99.27	11.17
4	14.19	20.76	41.83	49.76	77.89	96.39	98.54	99.04	9.90
5	16.88	19.13	41.71	49.88	79.63	98.06	97.19	99.28	10.68
10	17.14	22.09	43.22	52.49	80.86	98.50	98.99	99.24	9.02
15	15.88	21.56	45.20	54.71	84.05	98.93	98.91	99.12	8.26
20	17.12	22.64	47.60	56.39	87.09	98.92	99.38	99.29	10.30
30	17.74	21.92	49.97	60.85	88.21	98.99	98.85	99.21	9.16
60	17.75	26.05	54.04	70.24	90.46	99.16	99.60	98.46	5.21
90	16.91	29.59	58.11	80.48	95.81	98.74	99.51	97.89	5.37
120	15.10	31.50	59.17	86.05	98.16	99.18	99.62	95.12	6.59
180	17.65	36.10	61.72	93.86	98.72	98.72	99.63	96.10	3.80

Table B-17 Effect of the initial Fe^{2+} concentration on the Fe^{2+} residual at pH = 3 and [H_2O_2]: [3MI] = 1:1 molar ratio

Time	Average residual Fe^{2+} concentration (mg L^{-1}) at Fe^{2+} molar ratio							
(min)	0	0.05	0.1	0.5	1	1.5	2	3
0	0	2.01	4.01	22.11	40.15	64.27	84.32	128.55
0.5	0	1.42	3.29	13.54	26.04	26.93	38.21	76.08
1.5	0	1.48	3.29	11.85	21.39	22.30	32.50	63.30
2.5	0	1.68	3.28	11.39	20.81	21.32	31.87	66.53
3.5	0	1.57	3.30	10.74	20.61	20.54	31.63	65.93
4.5	0	1.67	3.22	10.40	19.05	17.96	31.31	65.61
5.5	0	1.63	3.17	9.29	18.08	16.02	30.51	65.59
10.5	0	1.29	3.13	9.90	15.83	14.36	29.64	63.37
20.5	0	1.40	2.12	5.80	13.83	13.87	29.60	64.10
30.5	0	1.38	2.57	5.66	12.44	13.75	30.71	64.25
60.5	0	1.33	2.95	4.55	8.58	13.67	29.34	63.60
120.5	0	1.03	2.24	3.79	6.80	14.53	28.56	64.01
180.5	0	0.98	2.87	2.90	2.84	13.47	28.21	62.99

Table B-18 Effect of the initial H_2O_2 concentration on 3MI degradation at pH = 3 and $[Fe^{2+}]$: [3M] = 1.5:1 molar ratio

Time	**Average % 3MI degradation at different H_2O_2 molar ratio**						
(min)	**0**	**0.2**	**0.5**	**0.7**	**1**	**1.5**	**2**
0	0	0	0	0	0	0	0
0.083	64.45	70.99	71.87	73.30	82.16	65.37	60.73
0.333	64.35	71.36	72.96	80.79	81.56	75.72	70.11
1	70.59	76.27	79.52	85.76	93.93	84.12	79.84
1.333	71.94	77.03	79.80	84.98	88.08	86.90	83.60
2	73.04	75.87	82.12	85.18	97.06	88.90	86.36
3	70.93	77.29	81.70	84.47	96.29	89.95	87.50
4	72.05	79.37	83.08	86.23	96.39	91.10	89.37
5	71.58	79.21	85.76	85.41	98.06	92.96	90.94
10	71.52	80.71	84.98	87.52	98.50	94.27	92.44
15	72.18	80.29	82.69	89.05	98.93	95.40	93.18
20	71.07	80.84	83.84	88.37	97.52	96.24	94.25
30	71.17	81.30	84.76	90.18	98.99	97.65	96.19
60	77.67	84.83	90.43	93.61	99.16	99.37	98.62
90	75.70	86.51	87.74	92.39	98.74	99.64	99.11
120	78.95	86.55	87.65	94.88	99.18	99.64	99.64
180	81.47	86.71	89.85	98.71	98.72	99.64	99.64

Table B-19 Effect of the initial 3MI concentration on its degradation at pH = 3 and [H_2O_2]: [Fe^{2+}]: [3M] = 1: 1.5: 1 molar ratio

Time	**Average % 3MI degradation at different initial 3MI concentration**					
(min)	**50**	**100**	**200**	**300**	**400**	**500**
0	0	0	0	0	0	0
0.083	96.96	82.17	65.20	26.89	22.32	12.93
0.333	98.76	81.56	65.41	39.96	29.83	20.62
1	98.84	93.94	77.28	45.75	39.82	26.92
1.333	98.86	88.09	75.13	52.08	40.42	23.73
2	98.93	97.07	78.73	52.34	44.27	31.53
3	99.05	96.29	83.88	53.37	44.91	32.72
4	99.11	96.39	79.13	56.73	43.67	34.23
5	99.12	98.07	85.19	53.77	45.60	36.77
10	99.13	98.50	87.74	55.82	48.73	38.33
15	99.14	98.93	88.68	59.34	48.34	39.53
20	99.14	97.52	89.59	61.68	51.13	42.57
30	99.14	99.00	95.21	62.82	52.51	44.56
60	99.14	99.17	96.63	69.38	59.82	49.94
90	99.14	98.75	94.85	73.82	63.75	49.48
120	99.14	99.18	93.68	75.95	63.21	48.75
180	99.14	98.72	93.43	81.24	60.73	48.96

Table B-20 Kinetic calculation for the synthetic 3MI wastewater

(a) Initial concentration *v.s.* initial rate

Reactants	**Initial concentration (mol L^{-1})**	**Initial rate (mol L^{-1} min^{-1})**
H_2O_2	1.52×10^{-4}	150.44
	3.81×10^{-4}	189.29
	5.34×10^{-4}	210.65
	$7.62 \times 10\text{-}^{4}$	220.21
Fe^{2+}	3.81×10^{-5}	49.683
	7.62×10^{-5}	65.858
	3.81×10^{-4}	109.39
	7.62×10^{-4}	151.01
	1.14×10^{-3}	190.41
3MI	3.81×10^{-4}	99.011
	7.62×10^{-4}	147.9
	1.52×10^{-3}	224.04
	2.29×10^{-3}	301.11
	3.05×10^{-3}	314.68
	3.81×10^{-3}	352.31

(b) Reaction order

Reactants	**Reaction order**
H_2O_2	0.25
Fe^{2+}	0.38
3MI	0.52

Table B-21 The difference between the single 3MI and the mixture of 3MI and DIBP at [H_2O_2]: [Fe^{2+}]: [3MI] = 1: 1.5: 1 and pH =3

Time	**Average % 3MI degradation**	
(min)	**Single 3MI**	**Mixture of 3MI and DIBP**
0	0	0
0.083	96.96	83.75
0.333	98.76	83.99
1	98.84	84.36
1.333	98.86	84.47
2	98.93	85.11
3	99.05	86.45
4	99.11	87.74
5	99.12	85.87
10	99.13	95.25
15	99.14	90.68
20	99.14	91.55
30	99.14	89.88
60	99.14	95.77
90	99.14	93.26
120	99.14	97.24
180	99.14	97.97

Table B-22 The difference between the single DIBP and the mixture of DIBP + 3MI at $[H_2O_2]$: $[Fe^{2+}]$: [DIBP]= 5: 5: 1 and pH =3

Time	Average % DIBP degradation		Average % 3MI
(min)	Single DIBP	Mixture of DIBP and 3MI	degradation
0	0	0	0
0.083	42.03	0.48	67.22
0.333	75.28	12.02	73.88
1	88.29	27.90	84.72
1.333	93.45	27.76	87.34
2	93.84	33.17	89.56
3	94.05	43.10	91.57
4	94.45	46.17	92.30
5	94.97	41.22	92.91
10	96.48	51.02	94.50
15	96.91	54.57	95.33
20	97.76	54.79	95.52
30	98.64	56.43	96.01
60	98.14	56.70	96.31
90	98.65	53.91	96.31
120	98.87	53.26	96.31
180	98.49	51.46	96.31

Table B-23 The comparison between 1) the synthetic single 3MI 2) the synthetic mixture of 3MI+DIBP and 3) the industrial raw wastewater

Time	Average % 3MI degradation		
(min)	Single 3MI	Mixture of 3MI and DIBP	Raw wastewater
0	0	0	0
0.083	98.27	84.63	18.15
1	99.83	85.07	21.45
3	99.95	87.09	28.89
5	98.26	86.50	31.01
10	100.00	89.92	35.62
30	100.00	90.56	62.27
60	97.39	96.58	72.77
120	100.00	98.98	73.99
180	100.00	99.71	65.96

Table B-24 The comparison between the synthetic single DIBP and the industrial treated wastewater

Time	Average % DIBP degradation	
(min)	Single DIBP	Treated wastewater
0	0	0
0.083	42.26	5.02
1	87.51	1.97
3	95.64	1.15
5	97.64	0
10	97.27	0
30	97.86	1.60
60	98.14	9.56
120	98.87	0
180	99.27	2.87

Table B-25 Effect of H_2O_2 concentration on 3MI degradation in the industrial raw wastewater at 1.5:1 [Fe^{2+}]: [3MI] molar ratio, the initial 3MI concentration = 19 mg L^{-1} and pH =3

Time (min)	Average % 3MI degradation at different H_2O_2 molar ratio								
	0	**0.5**	**0.7**	**1**	**10**	**20**	**30**	**40**	**100**
0	0	0	0	0	0	0	0	0	0
0.083	9.02	10.74	17.97	18.15	27.60	14.85	31.63	19.50	37.03
1	10.15	15.00	20.76	21.45	30.04	43.46	39.07	41.96	39.57
3	9.67	18.40	24.45	28.89	43.66	42.13	42.78	49.57	44.37
5	8.66	22.80	28.87	31.01	60.28	44.46	49.12	58.59	47.46
10	9.72	26.36	33.93	35.62	69.92	59.75	58.46	57.11	61.00
30	8.45	34.75	48.38	62.27	74.08	84.90	82.51	83.48	89.15
60	7.59	42.41	56.32	72.77	85.19	97.47	93.72	98.65	95.42
120	10.61	35.03	54.46	73.99	79.58	93.95	98.76	97.35	94.15
180	8.33	39.92	62.46	65.96	79.11	98.92	98.88	96.15	96.36

Table B-26 Effect of H_2O_2 concentration in the industrial raw wastewater at 1.5:1 [Fe^{2+}]: [3MI] molar ratio, the initial 3MI concentration = 19 mg L^{-1} and pH =3

(a) on %COD reduction

[H_2O_2]/[3MI]	**%COD Reduction**
1	0
10	1
20	2.5
30	3
40	4.6
100	15

(b) on the biodegradability index

[H_2O_2]/[3MI]	**BOD_5/COD**
1	0.45
10	0.47
20	0.49
30	0.52
40	0.54
100	0.62

Table B-27 Effect of Fe^{2+} concentration on 3MI degradation in the industrial raw wastewater at 20:1 [H_2O_2]: [3MI] molar ratio, the initial 3MI concentration = 19 mg L^{-1} and pH =3

Time (min)	**Average % 3MI degradation at different Fe^{2+} molar ratio**							
	0	**0.5**	**1**	**1.5**	**5**	**10**	**15**	**20**
0	0	0	0	0	0	0	0	0
0.083	5.37	3.22	13.01	14.85	50.28	51.21	54.18	52.34
1	5.05	24.78	37.71	43.46	60.94	69.20	73.85	73.83
3	0	29.39	42.33	42.13	71.01	76.38	81.08	69.42
5	3.07	32.86	43.40	44.46	65.30	86.13	78.34	73.69
10	2.71	37.48	51.01	59.75	75.67	90.73	84.03	78.52
30	3.12	44.79	60.15	84.90	90.04	95.53	97.14	87.39
60	3.24	47.05	76.52	97.47	96.90	99.15	97.64	93.89
120	0.98	67.15	77.79	93.95	99.33	99.56	99.80	94.25
180	1.66	69.75	82.67	98.92	100	100	99.71	94.64

Table B-28 Effect of pH on 3MI degradation in the industrial raw wastewater at 20:10:1 [H_2O_2]: [Fe^{2+}]: [3MI] molar ratio and the initial 3MI concentration = 19 mg L^{-1}

Time	**Average % 3MI degradation at different pH**				
(min)	**1**	**2**	**3**	**4**	**5**
0	0	0	0	0	0
0.083	45.83	47.99	51.21	42.09	45.43
1	64.89	67.04	69.20	65.38	64.64
3	69.93	72.08	76.38	78.50	70.49
5	81.83	83.98	86.13	80.36	74.54
10	86.42	88.57	90.73	81.13	70.44
30	89.07	91.23	95.53	87.32	77.95
60	98.83	98.93	99.15	90.20	72.16
120	99.13	99.35	99.56	94.75	73.54
180	99.89	99.95	100	90.92	72.79

Table B-29 Effect of the initial 3MI concentration on 3MI degradation in the industrial raw wastewater at 20:10:1 [H_2O_2]: [Fe^{2+}]: [3MI] molar ratio and pH = 3

Time (min)	**Average % 3MI degradation at different initial 3MI concentration**				
	27.50	**19.00**	**13.25**	**8.50**	**4.75**
0	0	0	0	0	0
0.083	43.63	51.21	63.57	84.47	90.92
1	61.02	69.20	82.44	97.23	100
3	60.83	76.38	86.58	93.79	100
5	56.48	86.13	88.22	94.87	100
10	73.03	90.73	90.78	98.27	100
30	77.43	95.53	96.63	100	100
60	85.95	99.15	97.56	100	100
120	93.69	99.56	99.86	100	100
180	98.06	100	100	100	100

Table B-30 Effect of the H_2O_2 concentration in the industrial treated wastewater at $[Fe^{2+}]$ = 50 mg L^{-1}, the initial DIBP concentration = 0.5 mg L^{-1} and pH = 3

(a) on DIBP degradation

Time (min)	**Average % DIBP degradation at different H_2O_2 concentration**								
	0	**6**	**31**	**62**	**308**	**494**	**617**	**925**	**1,234**
0	0	0	0	0	0	0	0	0	0
0.083	0.19	0.00	0.00	0.00	0.01	29.16	50.55	42.31	33.31
1	0.23	0.01	0.02	0.03	0.15	30.31	58.27	50.63	42.11
3	-0.15	0.03	0.05	0.09	0.45	31.86	55.90	52.73	57.18
5	0.93	0.05	0.08	0.15	0.75	33.83	62.51	59.02	64.24
10	-0.02	0.10	0.16	0.30	1.49	39.30	80.64	67.41	65.76
30	1.81	0.30	0.48	0.90	8.61	44.85	91.97	71.60	60.38
60	-0.70	0.60	0.96	1.78	4.40	52.44	94.37	77.89	72.30
120	-0.11	1.19	1.90	8.56	16.47	44.68	92.42	78.73	68.56
180	2.32	1.78	2.84	5.26	23.66	50.82	92.72	77.89	70.24

(b) on the %COD reduction

$[H_2O_2]_0$ (mg L^{-1})	%COD Reduction
0	0.82
6	0.87
31	5.74
62	16.26
308	29.88
494	27.91
617	35.79
925	39.44
1234	43.62

Table B-31 Effect of the Fe^{2+} concentration in the industrial treated wastewater at $[H_2O_2]$ = 617 mg L^{-1}, the initial DIBP concentration = 0.5 mg L^{-1} and pH = 3

(a) on the DIBP degradation

Time (min)	**Average % DIBP degradation at different Fe^{2+} concentration**							
	0	**5**	**10**	**20**	**30**	**50**	**70**	**100**
0	0	0	0	0	0	0	0	0
0.083	2.10	3.96	28.66	47.99	54.79	50.55	44.59	40.52
1	3.38	8.47	44.07	60.65	66.00	58.27	56.85	55.60
3	3.55	12.35	51.18	67.50	88.07	55.90	65.19	62.40
5	4.49	17.83	54.11	72.26	94.41	62.51	73.29	73.00
10	5.19	20.85	57.78	76.49	92.78	80.64	77.87	75.51
30	4.88	24.81	61.32	80.39	94.31	91.97	87.73	85.86
60	3.51	28.91	66.93	82.67	94.48	94.37	88.56	81.26
120	5.19	36.65	68.54	83.10	95.02	92.42	89.52	83.69
180	4.98	42.99	72.01	83.30	95.70	92.72	90.53	84.24

(b) on %COD reduction

$[Fe^{2+}]_0$ (mg L^{-1})	%COD Reduction
0	0.45
5	10.92
10	22.20
20	28.90
30	35.81
50	36.25
70	48.04
100	45.92

Table B-32 Effect of pH on the DIBP degradation in the industrial treated wastewater at [H_2O_2] = 617 mg L^{-1}, [Fe^{2+}] = 70 mg L-^{1} and the initial DIBP concentration = 0.5 mg L^{-1}

Time (min)	**Average % DIBP degradation at different pH**				
	1	**2**	**3**	**4**	**5**
0	0	0	0	0	0
0.083	33.27	41.20	44.59	26.62	11.80
1	39.12	51.98	56.85	30.72	16.04
3	45.44	60.59	65.19	34.68	20.90
5	49.89	66.72	73.29	40.56	26.97
10	54.24	71.86	77.87	45.54	30.84
30	64.41	69.58	87.73	52.88	34.76
60	59.98	82.08	88.56	55.98	37.10
120	70.97	83.89	89.52	63.13	53.94
180	77.73	87.96	90.53	67.55	45.73

Table B-33 Effect of the initial DIBP concentration degradation in the industrial treated wastewater on the DIBP degradation at [H_2O_2] = 617 mg L^{-1}, [Fe^{2+}] = 70 mg L-^{1} and pH =3

Time (min)	**Average % DIBP degradation at different initial DIBP concentration**			
	0.1	**0.25**	**0.38**	**0.50**
0	0	0	0	0
0.083	43.10	34.55	36.60	44.59
1	46.68	68.47	56.92	56.85
3	69.61	89.63	85.01	65.19
5	51.92	87.76	85.48	73.29
10	54.62	88.34	86.10	77.87
30	78.28	90.71	86.39	87.73
60	75.21	87.63	86.48	88.56
120	79.26	92.23	87.13	89.52
180	71.72	86.93	87.39	90.53

Table B-34 Kinetic calculation for 3MI in the RAW wastewater

(a) Initial concentration *v.s.* initial rate

Reactants	Initial concentration ($mol\ L^{-1}$)	Initial rate ($mol\ L^{-1}\ min^{-1}$)
H_2O_2	7.24×10^{-5}	-5.38×10^{6}
	1.01×10^{-4}	-6.73×10^{6}
	1.45×10^{-4}	-6.99×10^{6}
	1.45×10^{-3}	-1.30×10^{7}
	2.90×10^{-3}	-1.60×10^{7}
Fe^{2+}	7.24×10^{-5}	-2.28×10^{7}
	1.45×10^{-4}	-3.10×10^{7}
	2.17×10^{-4}	-3.30×10^{7}
	7.24×10^{-4}	-3.79×10^{7}
	1.45×10^{-3}	-4.52×10^{7}
3MI	2.10×10^{-4}	-1.04×10^{8}
	1.45×10^{-4}	-6.32×10^{7}
	1.01×10^{-4}	-4.25×10^{7}
	6.48×10^{-5}	-2.93×10^{7}

(b) Reaction order

Reactants	Reaction order
H_2O_2	0.24
Fe^{2+}	0.20
3MI	0.99

Table B-35 Kinetic calculation for DIBP in the TREATED wastewater

(a) Initial concentration *v.s.* initial rate

Reactants	Initial concentration (mol L^{-1})	Initial rate (mol L^{-1} min^{-1})
H_2O_2	1.80×10^{-4}	-1.26×10^{2}
	8.98×10^{-4}	-3.30×10^{3}
	1.80×10^{-3}	-6.23×10^{3}
	8.98×10^{-3}	-7.54×10^{4}
	1.44×10^{-2}	-1.01×10^{6}
	1.80×10^{-2}	-1.71×10^{6}
Fe^{2+}	8.98×10^{-5}	-3.33×10^{5}
	1.80×10^{-4}	-6.03×10^{5}
	3.59×10^{-4}	-1.52×10^{6}
	5.39×10^{-4}	-1.98×10^{6}
3MI	8.98×10^{-7}	-1.28×10^{6}
	1.35×10^{-6}	-1.50×10^{6}
	1.80×10^{-6}	-1.77×10^{6}

(b) Reaction order

Reactants	Reaction order
H_2O_2	1.50
Fe^{2+}	0.91
3MI	0.44

APPENDIX C

List of accepted journal papers and conference papers

Journal publication

Wongniramaikul, W., Liao, C-H. and Kanatharana, P. 2007. Diisobutyl phthalate degradation by Fenton treatment. *Journal of Environmental Science and Health, Part A* 42 (5): 567-572.

Conference paper publication list

1. Wongniramaikul, W., Mitra, S., Thavarungkul, P. and Kanatharana, P. 2004. Preliminary study on characterization of hazardous organic substances in wastewater from Para industry. *The 2nd Asian International Conference on Ecotoxicology and Environmental Safety (SECOTOX 2004),* Songkhla, THAILAND. September 26-29, 2004

2. Wongniramaikul, W., Liao, C.-H., Thavarungkul, P. and Kanatharana, P. 2007. 3-Methylindole degradation by Fenton treatment. *The 2nd International Conference on Advances in Petrochemicals and Polymers* (ICAPP 2007), Bangkok, THAILAND. Scheduled on June 25-28, 2007.

BIOGRAPHY

Mr. Worawit Wongniramaikul was born on April 21, 1979 in Bangkok, Thailand. He attended Suankularb Vittayalai School in Bangkok and graduated in 1995. He received his Bachelor’s Degree and Master’s Degree in Chemical Technology from Faculty of Science, Chulalongkorn University in 1999 and 2002, respectively. After that, he pursued his Philosophy of Doctoral Degree studies in the International Postgraduate Programs in Environmental Management, Inter-Department of Environmental Management, Chulalongkorn University, Bangkok, Thailand in April 2002.