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THESIS

TREATMENT OF PARACETAMOL IN BANGKOK'S SEWAGE BY ACTIVATED SLUDGE PROCESS AND ITS ATTENUATION IN RECEIVING CANAL

SIRIPORN POLTAM

A Thesis Submitted in Partial Fulfillment of
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Pharmaceutical substances have been detected in sewage treatment plant as well as receiving waters in many parts of the world. In this study, the occurrence and removal of Paracetamol were investigated in the a sewage treatment plant of Bangkok city (Din Daeng Water Environment Control Plant). It appeared that the concentrations of Paracetamol in sewage, settled sewage, effluent and disposal sludge were in ranges of 500-800 ng/L, 440-750 ng/L, and 170-288 ng/L and 14.5-18.2 ng/g dried sludge, respectively. The proximate Paracetamol levels as in the discharge water were found in the receiving canal. Paracetamol eliminated rates by the AS process were about 61-66% of which 56.6-58.7% by biodegradation and 4.5-8.4% by adsorption. In addition, batch sorption studies indicate that the sludge had high potentiality in Paracetamol adsorption in the AS process in which 15% of the adsorbed mass could be desorbed out into a clean environment. According to Freundlich equation, K_F were 0.35 and 0.2 with n of 1.255 and 1.00 for adsorption by the sludge of 2-10 µg Paracetamol/L and for desorption out from the sludge into clean water, respectively.

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Student's signature Thesis Advisor's signature

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Siriporn Poltam

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LIST OF ABBREVIATIONS

WWTP	=	Wastewater treatment plant
AS	=	Activated sludge
PPCP	=	Pharmaceuticals and personal care products
MSTFA	=	N-methyl-N-trimethylsilyltrifloroacetamide
rpm	=	round per minute
MLSS	=	Mixed liquor suspended solids
MLVSS	=	Mixed liquor volatile suspended solids
SV_{30}	=	Sludge volume at 30 minute
SVI	=	Sludge volume index
r^2	=	Correlation coefficient
LC_{50}	=	Lethal Concentration, 50%
EC_{10}	=	Concentration of a compound where 10% of its maximal effect is observed
EC_{50}	=	Concentration of a compound where 50% of its maximal effect is observed
LOEC	=	Lowest Observed Effect Concentration
NOEC	=	No Observed Effect Concentration
LOD	=	Limit of detection
LOQ	=	Limit of quantification

TREATMENT OF PARACETAMOL IN BANGKOK'S SEWAGE BY ACTIVATED SLUDGE PROCESS AND ITS ATTENUATION IN RECEIVING CANAL

INTRODUCTION

Pharmaceuticals are a set of compounds which have obtained increasing attention over the past decade. There are many different compound classes which are intended to affect a specific area of a disease. Recently, it has become clear that the elimination of certain pharmaceutical compounds during wastewater treatment processes is rather low and as a result, they are found in surface, ground and drinking waters (Jones *et al.,* 2005; Yu *et al.,* 2006; Fram and Belitz, 2011).

Many pharmaceuticals, upon administration, are degraded in the body and may even become inactive, but others, often those applied externally, excreted or not absorbed fully, can leave the body in their active forms. Previous studies indicate that, as a result, an array of pharmaceuticals, metabolites and their conjugates are being discharged into the wastewater system (Ternes, 2000; Miao *et al.,* 2002; Heberer, 2002).

Many commonly used drug groups (e.g. antibiotics) are used in amounts similar to those of many pesticides and other organic micro-pollutants but they are not required to undergo the same rigorous testing for environmental fate and effects. Drugs and their metabolites have thus been subject to many years of uncontrolled emission into the environment as complex mixtures via a number of pathways; primarily from wastewater treatment works (WTW) effluents or the land application of sewage sludge. Most drugs are designed so that they retain their chemical structure long enough to do their therapeutic work and this property, combined with their continuous input, may enable them to remain in the environment for extended periods of time (Jones *et al.,* 2003; Kasprzyk *et al.,* 2009).

Research has shown that many pharmaceuticals are not completely removed during wastewater treatment and as a result this has led to their occurrence being reported in WTW effluents, rivers and lakes, and more rarely in groundwater (Jones-Lepp *et al.,* 2004; Stackelberg *et al.,* 2004; Joss, *et al.,* 2006; Zhou *et al.,* 2008; Kosma *et al.,* 2010).

Analgesics that are widely used today and very often used as acetaminophen or paracetamol. The fact that paracetamol is qualified as both drugs to relieve pain (Analgesic drug) and drug fever (Antipyretic drug). The main reasons that led to a widely used paracetamol because it is easy to buy without a prescription from a doctor. Therefore the usage of this drug is rapidly increasing. As paracetamol as a drug that likes medicine residents at least have been always available in house. Thus, the general publics are not aware of this drug because not know too much toxicity (Bessems *et al.,* 1995; Denizar *et al.,* 2006; Jose *et al.,* 2009).

Paracetamol toxicity is caused by excessive use or overdose of the analgesic drug paracetamol (called acetaminophen in North America). Mainly causing liver injury, paracetamol toxicity is one of the most common causes of poisoning worldwide. In the United States and the United Kingdom it is the most common cause of acute liver failure (Myers *et al.,* 2008; Lee, 2004). The toxic dose of paracetamol is highly variable. In general the recommended maximum daily dose for healthy adults is 4g. Higher doses lead to increasing risk of toxicity. In adults, single doses above 10 grams or 200 mg/kg of bodyweight, whichever is lower, have a reasonable likelihood of causing toxicity (Daly *et al.,* 2008).

Paracetamol will be highlighted, either because the concentrations found in water are high and because of their (increasing) high volume usage or because of the persistence of this compound (Bound and Voulvoulis, 2006 ; Kasprzyk *et al.,* 2009; Thomas *et al.,* 2007). For this reason, paracetamol may be able to cause the same harmful exposure potential as persistent pollutants, since their transformation and removal rates can be compensated by their continuous input into the environment.

In this study we aimed to determine the contamination of wastewater and sludge with paracetamol compound in order to obtain more information on its fate during sewage wastewater treatment. In addition, this study suggests that more needs to be known about the environmental fate of paracetamol so that we are able to provide a comprehensive risk assessment.

OBJECTIVES

The main objectives of this research study are:

1. To determine the occurrence of Paracetamol in sewage and its removal by activated sludge process in Bangkok City.
2. To assess natural potential removal of Paracetamol in the receiving canal.

Scope of study

1. Investigation Paracetamol in sewage treatment plant (Din Daeng Water Environment Control Plant) and the receiving canal.
2. Adsorption and desorption isotherm of Paracetamol on activated sludge.

LITERATURE REVIEW

1. Pharmaceutical Effects in Environment

Reports of occurrence of a wide variety of both human and veterinary medicines aquatic environment have been increasing steadily in recent years. Despite their likely continuous discharge, little is known about the ultimate fate and transport of many drug substances after their intended application. This has lead to pharmaceuticals, attracting increasing attention as water pollutants due to their possible environmental effects. While the production of pharmaceutical compounds is a potential route for drugs to the environment, human pharmaceuticals are thought to be more likely to come from point sources such as sewage treatment works (STW) (Jones *et al.,* 2003; Boyd *et al.,* 2003; Waterston, *et al.,* 2005).

Thousands of tons of pharmacologically active substances are used annually around the world to alter a vast array of structures, functions and metabolic processes within the body for the benefit of the patient. Surprisingly little is known about the ultimate fate of most drugs after their intended use but, with the development of more sensitive analytical techniques in recent years, evidence of the presence of human pharmaceutical compounds in aquatic systems around the world has been mounting. Consequently, these compounds have been attracting increasing attention as potential water pollutants (Jones *et al.,* 2005; Trovo *et al.,* 2008; Mompelat *et al.,* 2008).

Pharmaceuticals and personal care products (PPCPs), endocrine disruptors and illicit drugs are regarded as emerging environmental contaminants as many PPCPs are ubiquitous, persistent and biologically active compounds with recognized endocrine disruption functions. There are several direct and indirect pathways through which PPCPs can be introduced into the aqueous environment. Insufficiently treated municipal wastewater discharge is identified as the major route responsible for surface water contamination with PPCPs (Kasprzyk *et al.,* 2009; Zhou *et al.,* 2008; Marcel *et al.,* 2009).

The relatively new issue of pharmaceutical contamination of the environment offers the opportunity to explore the application of values to the construction, communication and management of risk (Enick and Moore, 2007). The still developing regulatory policies regarding environmental contamination with pharmaceuticals provide fertile ground for the introduction of values into the definition and management of risk. Summary of the current knowledge regarding pharmaceutical contamination of the environment and discuss specific attributes of pharmaceuticals that require special consideration (Table 1 and Table 2). The present analysis showing that if values are incorporated into assessing, characterizing and managing risk, the results of risk assessments will more accurately reflect the needs of various stakeholders.

In Thailand, paracetamol usage increased during 2000-2009 especially in tablet form, both in term production and import (Table 3), while the other drug was also increased but its controlled by prescription from a doctor (Food and Drug Administration, 2009) . By this reason, paracetamol may be able to cause the same harmful exposure potential as persistent pollutants, since its transformation and removal rates can be compensated by its continuous input into the environment. Therefore it suggests that more needs to be known about the environmental fate of paracetamol so that we are able to provide a comprehensive risk assessment aqua environmental around Thailand were tended to risk from toxicity of paracetamol.

Table 1 Acute effects of selected pharmaceutical compounds on aquatic organisms**.**

Chemical name	Species	Endpoint measured	Concentration (experimental) (µg/L)
Antimicrobials	*Microcystis aeruginosa* (cyanobacteria)	Growth EC_{50}	3.7
Penicillin–	*Oncorhynchus mykiss* (rainbow trout)	Hepatocyte cytotoxicity, 24 h EC_{50}	> 182,700
Amoxicillin	*Lemna gibba* (duckweed)	Wet weight, chlorophyll 7d LOEC	> 1000
Bacitracin	*Daphnia magna* (water fiea)	48 h LC_{50}	30,500
Chlorotetracycline	*Selenastrum capricornutum* (cyanobacteria)	72 h EC_{50}	3,100
	Microcystis aeryginosa (cyanobacteria)	7 d EC_{50}	50
Ciprofloxacen	Activated sludge Bacteria	EC_{50}	610
	Daphnia magna (water flea)	48 h NOEC	60,000
	Lemna gibba (duckweed)	Wet weight 7d EC_{50}	698
Erythromycin	*Salvelinus namaycush* (lake trout)	96 h LC_{50}	410,000
	Lemna gibba (duckweed)	Wet weight 7d LOEC	> 1000
Streptomycin	*Microcystis aeruginosa* (cyanobacteria)	MIC	300
	Microcystis aeruginosa (cyanobacteria)	7d EC_{50}	7

Table 1 (Continued)

Chemical name	Species	Endpoint measured	Concentration (experimental) (µg/L)
Metronidazole	*Daphnia magna* (water flea)	48 h LOEC	> 1000 mg/L
	Selenastrum capricornutum	72 h EC_{10}	19,900
	Daphnia magna (water flea)	Reproduction 21d NOEC	250,000
Psycho-active drugs			
Carbamazepine	*Brachionus calyciflorus* (rotifer)	Reproduction 48 h NOEC	377
(antiepileptic)	*Daphnia magna* (water flea)	48 h LC_{50}	> 1,380
	Oncorhynchus mykiss (rainbow trout)	Cell function 48 h EC_{50}	111,790
	Synechococcus leopolensis (cyanobacteria)	Growth 96 h EC_{50}	33,600
	Ceriodaphnia dubia (water flea)	Reproduction 7d NOEC	25
	Danio rerio – embryo (zebrafish)	Mortality 10d NOEC	25,000
Mianserin	*Danio rerio* (zebrafish)	Genome-wide oligo arrays (induction of VTG and zona pellucid proteins) 2 d nd 15 d exposure	25

Table 1 (Continued)

Chemical name	Species	Endpoint measured	Concentration (experimental) (µg/L)
Fluoxetine (SSRI)	*Ceriodaphnia dubia* (water flea)	48 h LC_{50}	234
	Oncorhynchus mykiss (rainbow trout)	Hepatocyte cytotoxicity, 24 h EC_{50}	1545
	Pimephales promelas- eggs (fathead minnow)	48 h LC_{50}	705
	Sphaerium striatinum (fingernail clam)	4 h LOEC	1550
	Gammarus pulex (crustacean)	1.5 h LOEC (nidaria)	100
Analgesic and non-steroidal anti-inflammatory drugs			
Acetaminophen (Paracetamol)	*Daphnia magna* (water flea)	Swimming ability 48 h EC_{50}	9200
	Streptocephalus probiscideus (fairy shrimp)	24 h LC_{50}	29,600
Acetylsalicylic acid	*Desmodesmus subspicatus* (green algae)	NOEC	3200
Diclofenac	*Oncorhynchus mykiss* (rainbow trout)	Hepatocyte cytotoxicity, 24 h EC_{50}	6042
	Daphnia magna (water flea)	Immobility 48 h EC_{50}	68,000

Table 1 (Continued)

Chemical name	Species	Endpoint measured	Concentration (experimental) (µg/L)
Ibuprofen	*Lepomis macrochirus* (bluegill sunfish)	96 h LC_{50}	7100
	Gammarus pulex (crustacean)	1.5 h LOEC (behavior)	0.001
Estrogens and hormone regulators			
17α-ethinylestradiol	*Cyprinodon variegatua* (sheephead minnow)	NOEC and LOEC fibrosis of the testis	0.0002 and 0.002
	Cyprinodon variegatua (sheephead minnow)	NOEC- hatching success	0.02
	Marisa cornuarietis (prosobranch snail)	NOEC and LOEC Superfemales	0.001 and 0.01
	Marisa cornuarietis (prosobranch snail)	LOEC Reduced fecundity	0.001
Estradiol	*Oryzias latipes Medaka* (post-hatch stage)	LOEC-all female fish 30d exposure	0.01
Estradiol	*Oryzias latipes Medaka* (reproducing adults)	LOEC- males with testis-ova, reduce male GSI, reduced egg production 21d exposure	0.0293

Table 1 (Continued)

Chemical name	Species	Endpoint measured	Concentration (experimental) (µg/L)
Ethinylestradiol	*Pimephales promelas* Fathead minnow (egg to adult)	LOEC all fish with female gonads (50% fertile) and LOEC severe physical deformities 305d exposure	0.004 0.016
	Pimephales promelas Fathead minnow (developing females)	LOEC increased egg production	0.0001
Estriol	*Oryzias latipes Medaka* (post-hatch)	LOEC altered sex ratio	0.01

Note: LC_{50}; Lethal Concentration, 50%, EC_{10}; concentration of a compound where 10% of its maximal effect is observed, EC_{50}; the concentration of a compound where 50% of its maximal effect is observed, LOEC; Lowest Observed Effect Concentration, NOEC; No Observed Effect Concentration, Vitellogenin (VTG); a type of protein

Source: Enick and Moor (2007)

Table 2 Chronic toxicity data for aquatic organisms exposed to human pharmaceuticals

Substance	Mode of action in humans/target pathogens	Taxonomic group	Species	Long-term exposure result (mg/L)	Acute to chronic ratio (if available)
Androgen (steroidal)					
Methyltestosterone	Transcriptional activation of androgen response elements in different target gene	Fish Fish Fish Invertebrate (snail) Invertebrate (snail)	*Carassius carassius* *Oryzias latipes* *Pimephales promelas* *Lymnaea stagnalis* *Marisa cornuarietis*	0.00001 <10.0 ng/l 0.01 1.0 ng/l <100 ng/l	>1,000,000
Anti-androgen (non-steroidal)					
Bicalutamide	Blocking and preventing testosterone from attaching (binding) to the receptors on the surface of the prostate cancer cells Inhibition of androgen-induced gene activation	Alga (Cyanobacteria) Alga (green)	Unspecified Unspecified	1 1	
Flutamide		Fish	*Oryzias latipes*	1.0	3.6

Table 2 (Continued)

Substance	Mode of action in humans/target pathogens	Taxonomic group	Species	Long-term exposure result (mg/L)	Acute to chronic ratio (if available)
Anti-bacterial					
Trimethoprim	Interference with folate synthesis in susceptible bacteria by binding to and reversibly inhibiting the enzyme dihydrofolate reductase	Plant (duckweed)	*Lemna gibba*	>1.0 (EC_{10})	
Anti-bacterial (aminoglycoside)					
Streptomycin	Irreversible binding to the bacterial 30S ribosome, freezing the 30S initiation complex (30S-mRNAtRNA) so that no further initiation can occur; also slows down protein synthesis that has already initiated and induces misreading of the mRNA	Plant (duckweed)	*Lemna gibba*	>1.0 (EC_{10})	

Table 2 (Continued)

Substance	Mode of action in humans/target pathogens	Taxonomic group	Species	Long-term exposure result (mg/L)	Acute to chronic ratio (if available)
Anti-bacterial (penicillin)					
Amoxicillin	Inhibition of cross-linkage between linear peptidoglycan polymer chains that make up a major component of the cell wall of Gram-positive bacteria	Invertebrate (nidarians)	*Hydra vulgaris*	>0.01	
		Plant (duckweed)	*Lemna gibba*	>1.0 (EC_{10})	
Anti-bacterial (sulfonamide)					
Sulfadimethoxine	Folic acid synthesis inhibitor	Plant (duckweed)	*Lemna gibba*	0.044(EC_{10})	
Sulfamethazine		Plant (duckweed)	*Lemna gibba*	>1.0 (EC_{10})	
Sulfamethoxazole		Alga (Cyanobacteria)	*Synechococcus leopolensis*	0.0059	
		Alga (diatom)	*Cyclotella meneghiniana*	1.25	
		Alga (green)	*Pseudokirchneriella subcapitata*	0.09	
		Invertebrate (rotifer)	*Brachionus calyciflorus*	25.0	
		Invertebrate (waterflea)	*Ceriodaphnia dubia*	0.25	

Table 2 (Continued)

Substance	Mode of action in humans/target pathogens	Taxonomic group	Species	Long-term exposure result (mg/L)	Acute to chronic ratio (if available)
Anti-bacterial (tetracycline)					
Chlortetracycline	Inhibition of bacterial protein	Plant (duckweed)	*Lemna gibba*	0.036 (EC_{10})	
Doxycycline	synthesis by preventing the	Plant (duckweed)	*Lemna gibba*	0.055 (EC_{10})	
Oxytetracycline	association of aminoacyl-tRNA	Plant (duckweed)	*Lemna gibba*	0.788 (EC_{10})	
	with the bacterial ribosome	Plant (duckweed)	*Lemna minor*	4.92 (EC_{50})	
Anti-epileptic					
Carbamazepine	Blockade of voltage-sensitive	Alga (Cyanobacteria)	*Synechococcus leopolensis*	17.0	
	sodium channels	Alga (diatom)	*Cyclotella meneghiniana*	10.0	
		Alga (green)	*Desmodesmus subspicatus*	74.0 (EC_{50})	
		Alga (green)	*Pseudokirchneriella*	>100.0	
		Fish	*Danio rerio*	25	
		Invertebrate (midge larva)	*Chironomus riparius*	0.625 mg/kg	
		Invertebrate (oligochaete worm)	*Lumbriculus variegatus*	>10 mg/kg	

Table 2 (Continued)

Substance	Mode of action in humans/target pathogens	Taxonomic group	Species	Long-term exposure result (mg/L)	Acute to chronic ratio (if available)
Non-steroid anti-inflammatory drug					
Acetaminophen (Paracetamol)	Believed to be due to the inhibition of prostaglandin synthesis	Plant (duckweed)	*Lemna gibba*	>1.0 (EC_{10})	
		Invertebrate (nidarians)	*Hydra vulgaris*	>0.01	
		Invertebrate (nidarians)	*Hydra vulgaris*	>0.01	
Acetylsalicylic		Alga (Cyanobacteria)	*Synechococcus leopolensis*	10.0	
acid (aspirin)		Alga (diatom)	*Cyclotella meneghiniana*	10.0	
Diclofenac		Alga (green)	*Desmodesmus subspicatus*	72.0 (EC_{50})	
		Alga (green)	*Pseudokirchneriella s.*	10.0	
		Fish	*Danio rerio*	4	
		Invertebrate (rotifer)	*Brachionus calyciflorus*	12.5	
		Invertebrate (waterflea)	*Ceriodaphnia dubia*	1.0	22.7
Ibuprofen		Plant (duckweed)	*Lemna minor*	7.5 (EC_{50})	
		Alga(green)	*Desmodesmus subspicatus*	315.0 (EC_{50})	

Table 2 (Continued)

Substance	Mode of action in humans/target pathogens	Taxonomic group	Species	Long-term exposure result (mg/L)	Acute to chronic ratio (if available)
Ibuprofen		Invertebrate (nidarians)	*Hydra vulgaris*	>0.01	1.68
		Invertebrate (snail)	*Planorbis carinatus*	1.02	
		Plant (duckweed)	*Lemna gibba*	>1.0 (EC_{10})	
		Plant (duckweed)	*Lemna minor*	22.0 (EC_{50})	
Oestrogen					
17β-oestradiol	Binding to oestrogen receptor; in	Fish	*Oryzias latipes*	10 ng/l	390,000
Diethylstilbestrol	contraception, inhibition of	Fish	*Oryzias latipes*	10 ng/l	140,000
(non-steroidal)	ovulation by suppression of mid-	Invertebrate (copepod)	*Nitocra spinepes*	0.003	97
	cycle surge of luteinizing	Invertebrate (copepod)	*Tisbe battagliai*	0.01	<10
	hormone, the inspissations of	Invertebrate (waterflea)	*Daphnia magna*	0.062	17.6
Ethinylestradiol	cervical mucus so as to constitute	Alga	*Unspecified*	0.054 (EC_{10})	
	a barrier to sperm, and the	Fish	*Oncorhynchus mykiss*	<0.1 ng/l	
	rendering of the endometrium	Fish	*Oryzias latipes*	10 ng/l	150,000
	unreceptive to implantation	Invertebrate (copepod)	*Nitocra spinepes*	0.05	

Table 2 (Continued)

Substance	Mode of action in humans/target pathogens	Taxonomic group	Species	Long-term exposure result (mg/L)	Acute to chronic ratio (if available)
β-adrenergic receptor blocker					
Metoprolol	Competitively blocks beta-adrenergic receptors in the heart and juxtoglomerular apparatus, but much less β2-antagonistic than propranolol	Alga (green)	*Desmodesmus subspicatus*	7.3 (EC_{50})	0.094
		Plant (duckweed)	*Lemna minor*	>320.0 (EC_{50})	
Propranolol	Prototype β-blocker; antagonizes β1 and β2 AR	Alga (Cyanobacteria)	*Synechococcus leopolensis*	0.35	
		Alga (diatom)	*Cyclotella meneghiniana*	0.094	
		Alga (green)	*Desmodesmus subspicatus*	5.8 (EC_{50})	
		Fish	*Oryzias latipes*	<0.0005	
		Invertebrate (amphipod)	*Hyalella azteca*	0.001	>48,600
		Invertebrate (waterflea)	*Ceriodaphnia dubia*	0.009	
		Plant (duckweed)	*Lemna minor*	114.0 (EC_{50})	

Source: Crane, et al. (2006)

Table 3 The information of production and import of paracetamol in Thailand, since years 2000-2009.

Years	Production	Unit*	Import	Unit
2000	220.56	kg	0.80	kg
	3,739,829,014.00	T	19,145,230.00	T
	22,258,730.07	L	11,877.41	L
	20,850,500.00	C	-	
2001	124.56	kg	0.80	kg
	3,334,078,106.80	T	28,170,800.00	T
	1,831,402.16	L	0.11	L
	163,624,780.00	C	-	
	10,000.00	b	-	
2002	147.28	kg	-	
	3,801,513,290.00	T	33,604,940.00	T
	1,952,400.2	L	-	
	202,452,000.00	C	-	
2003	49.265	kg	-	
	4,202,577,731.00	T	62,126,680.00	T
	2,628,446.952	L	0.843	L
	223,434,850.00	C	-	
	500.00	en	-	
2004	122.500	kg	-	
	2,143,182.516	L	9,552.960	L
	4,392,409,077.00	T	55,605,160.00	T
	412,391,620.00	C	24,608.00	C
	500.00	s	-	

Table 3 (Continued)

Years	Production	Unit*	Import	Unit
2005	0.450	kg	-	
	2,356,654.838	L	30,477.905	L
	5,783,415,237.00	T	67,198,130.00	T
	321,145,580.00	C	112,064.00	C
2006	1.45	kg	-	
	2,433,621.13	L	18,769.910	L
	5,764,347,952.00	T	70,254,398.00	T
	39,341,100.00	C	-	
2007	0.45	kg	-	
	2,148,762.983	L	24,163.490	L
	45,166,955,414.00	T	97,551,650.00	T
	183,790,634.00	C	-	
2008	2.00	kg	-	
	2,397,098.668	L	18,874.190	L
	6,840,705,008.00	T	101,242,510.00	T
	26,282,700.00	C	-	
	123,600.00	sp	248,000.00	sp
2009	3.00	kg	-	
	2,566,644.923	L	7,550,863.86	L
	7,056,246,017.00	T	112,884,030.00	T
	53,998,800.00	C	-	
	172,920.00	sc	256,151.00	b

Note: T; tablet, C; capsule, en; envelope, s; sachet, Sp; suppository, b; bottle, Sc; stick

Source: Food and Drug Administration (2009)

2. Paracetamol

2.1 Structure and activity

Paracetamol consists of a benzene ring core, substituted by one hydroxyl group and the nitrogen atom of an amide group in the para (1,4) pattern (Fig. 1) **(**Bales *et al.,* 1985). The amide group is acetamide (ethanamide). It is an extensively conjugated system, as the lone pair on the hydroxyl oxygen, the benzene pi cloud, the nitrogen lone pair, the p orbital on the carbonyl carbon, and the lone pair on the carbonyl oxygen are all conjugated. The presence of two activating groups also make the benzene ring highly reactive toward electrophilic aromatic substitution. As the substituents are ortho,para-directing and para with respect to each other, all positions on the ring are more or less equally activated. The conjugation also greatly reduces the basicity of the oxygens and the nitrogen, while making the hydroxyl acidic through delocalisation of charge developed on the phenoxide anion.

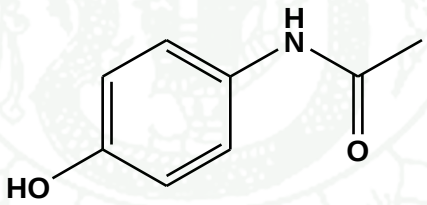


Figure 1 Chemical structure of paracetamol

Source: Bales *et al.* (1985)； Stanislav (2005)

2.2 Physical and chemical property

In some publications, it is described as 4-hydroxyacetanilide or N-acetyl-p-aminophenol and in the US pharmacopoeia it is known as acetaminophen.
Paracetamol is a white, odourless crystalline powder with a bitter taste (Fachaux *et al.,* 1995) and the physico-chemical property of paracetamol shown in Table 4

Table 4 Physico-chemical property of paracetamol

Property	
Systematic (IUPAC) name	N-(4-hydroxyphenyl) acetamide
Formula	$C_8H_9NO_2$
Molecule mass	151.17 g/mol
Density	1.263 g/cm³
Melting point	168 °C (334 °F)
Solubility in water	12.78 mg/mL (20 °C)
pH	6

Source: Granberg and Rasmuson (1999**)**

2.3 Paracetamol in use

Paracetamol relieves pain and fever in adults and children, and it is the most widely accepted medicine for this purpose. It is used mainly for its pain relief properties either as a medicine prescribed by a doctor or it can be purchased as an over-the-counter medicine both in retail pharmacies or grocers shops. Its pain relief (analgesic) and fever relief (antipyretic) effects are similar to those of aspirin and it works in a similar, though not identical, way. Unlike aspirin, however, increasing the dose does not result in clinically useful anti-inflammatory activity. Paracetamol is therefore not of value for reducing inflammation in the treatment of chronic rheumatic diseases as are the non-steroidal anti-inflammatory drugs like aspirin. Nevertheless, paracetamol does provide useful pain relief and is considered the first line treatment in osteoarthritis (Bessems *et al.,* 1995; Denizar *et al.,* 2006; Jose *et al.,* 2009).

2.3.1 Dosage

The recommended adult dose of paracetamol is two 500 mg tablets, with four hours between doses, and no more than eight tablets in 24 hours. If this recommended dose is adhered to, there will be no toxic effects, even in prolonged or habitual use. For children's dosages vary with the age of the child and the type of product, therefore the instructions on the pack should always be followed. In general, children's dosages are based on a single dose of 10 mg paracetamol per kilogram bodyweight, which can be repeated 4-6 hourly, not exceeding four doses per 24 hours (Kumar and Letha, 1997).

2.3.2 Overdose

The overdose threshold may be lowered in a person taking certain prescription medicines, or a person who is an alcoholic or is seriously undernourished. If the overdose is spread over a period of time the threshold may be higher, as the initial paracetamol dose is effectively metabolised. There are often no symptoms in the first 24 hours following overdose, although there may be mild nausea and vomiting. In a large overdose liver function deteriorates leading to jaundice, confusion, and loss of consciousness (Mitry *et al,* 2005; Morgan, 2005).

In adults, acetaminophen may induce hepatotoxicity after ingestion of 7.5 to 10 grams in a period of 8 hours or less (Clark *et al.,* 2001). The recommended maximum dose in a 24 hour period is 4grams or 8 tablets, single doses above 10 grams or 200 mg/kg of bodyweight, whichever is lower, have a reasonable likelihood of causing toxicity (Lee, 2004).. Toxicity can also occur when multiple smaller doses within 24 hours exceeds these levels. In adults, a dose of 6 grams a day over the preceding 48 hours could potentially lead to toxicity, while in children acute doses above 200 mg/kg could potentially cause toxicity (Stern *et al.,* 2004). Research shows that the common threshold for liver damage to occur from a single paracetamol overdose is 15 grams (30 tablets) although standard hospital guidelines allow an extra safety margin and assume liver damage could occur at a single overdose of 24

standard tablets or 150 mg/kg body weight, whichever is the smaller (Vale and Proudfoot, 1995). About 70% of patients allegedly ingested more than 140 mg/kg, a dose considered to be potentially toxic (Mohd *et al.*, 2006). Significant toxicity is unlikely to follow doses of up to 150 mg/kg of bodyweight but liver damage will probably ensue if the dose exceeds 250 mg/kg of bodyweight. Therefore 12 g or more is considered potentially life-threatening and treated accordingly (MacConnachie, 1998).

In children, single dose of 150 mg/kg can cause hepatocellular damage (Aripin and Choonara, 2009). A hepatotoxic event may occur in children with more than 140 mg/kg ingested. Common reasons for consuming large doses of acetaminophen include accidental or intentional overdose, alcohol-acetaminophen syndrome (chronic moderate to heavy alcohol use potentiates the toxic effects of acetaminophen on the liver; severe hepatotoxicity may occur after ingestion of as little as 4 grams in 24 hours) (Clark *et al.*, 2001).

In substantial overdose liver damage is likely to occur assuming the patient does not receive treatment. There is an antidote (a substance that controls the effects of a poison or disease) to paracetamol overdose and provided it is given within 12 hours, a complete recovery can be made. The antidote is often useful beyond 12 hours, showing benefit up to 48 hours after overdosing. Most medicines other than paracetamol, when taken in fatal overdose, bring about death in 12-18 hours (Clark *et al.*, 2001; MacConnachie, 1998).

2.4 Metabolism in human body

Paracetamol is readily absorbed after administration and widely distributed throughout most body fluids. Its metabolic pathway comprises conjugation to form glucuronide and sulphate derivatives. About 90% of the therapeutic dose is excreted in the urine in 24 h as conjugated derivatives, 1–4% of the excreted material being unchanged drug (Bosch *et al.*, 2006). Paracetamol is metabolised primarily in the liver, into non-toxic products. When taken in normal therapeutic doses, paracetamol

has been shown to be safe. Following a therapeutic dose, it is mostly converted to nontoxic metabolites by conjugation with sulfate, sulfation (sulfate conjugation) may account for 20–40% and glucuronide, glucuronidation is believed to account for 40% to two-thirds of the metabolism of paracetamol, with a small portion being oxidized via the cytochrome P450 enzyme system. Cytochromes P450 2E1 and 3A4 convert approximately 5% of paracetamol to a highly-reactive intermediary metabolite, *N*-acetyl-*p*-benzoquinoneimine (NAPQI). Under normal conditions, NAPQI is detoxified by conjugation with glutathione (GSH), accounts for less than 15% to form cysteine and mercapturic acid conjugates (Fig. 2). In cases of paracetamol overdose, the sulfate and glucuronide pathways become saturated, and more paracetamol is shunted to the cytochrome P450 system to produce NAPQI. As a result, hepatocellular supplies of glutathione become depleted, as the demand for glutathione is higher than its regeneration. NAPQI therefore remains in its toxic form in the liver and reacts with cellular membrane molecules, resulting in widespread hepatocyte damage and death, leading to acute hepatic necrosis (Bessems and Vermeulen, 2001; Fazlul, 2007; Copple et al., 2008). In animal studies, hepatic glutathione must be depleted to less than 70% of normal levels before hepatotoxicity occurs (Bessems *et al.*, 1997; Nicholls *et al.*, 1997; Evdokimova, 2001)**.**

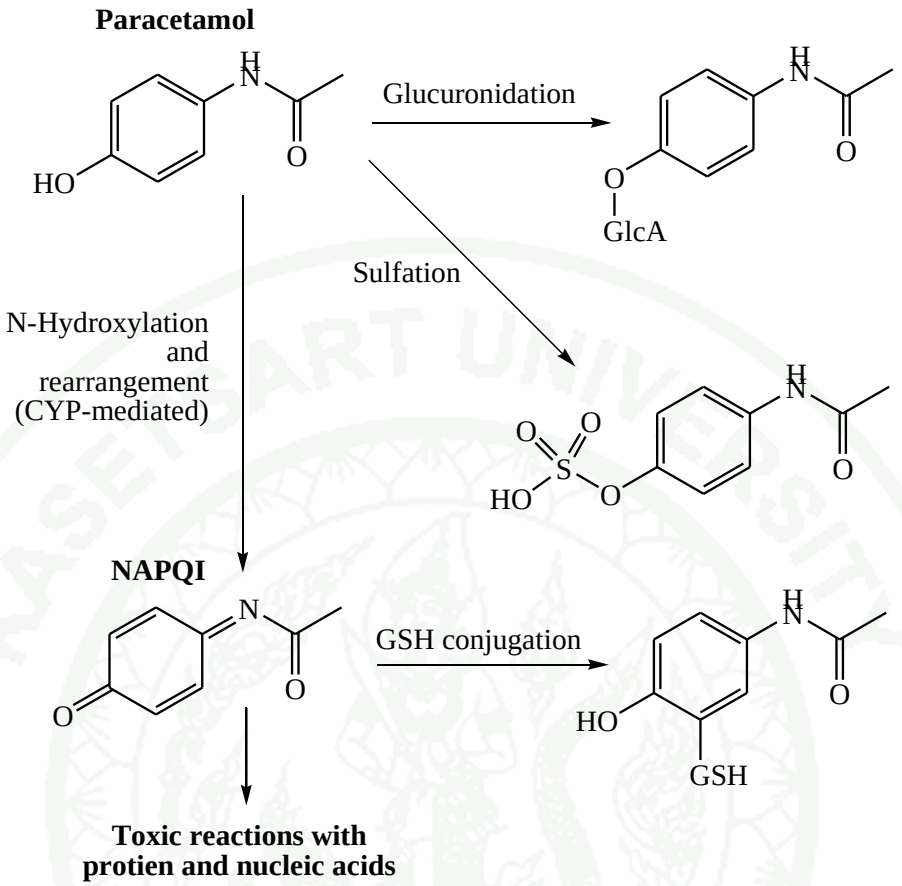


Figure 2 Metabolism of Paracetamol in human

Source: Nicholls *et al.* (1997); Fazlul (2007)

2.5 Toxicity

Paracetamol hepatotoxicity is, by far, the most common cause of acute liver failure in both the United States and the United Kingdom (Polson et al., 2008; Williams et al., 2011). Paracetamol overdose results in more calls to poison control centers in the US than overdose of any other pharmacological substance. Signs and symptoms of paracetamol toxicity may initially be absent or vague. Untreated, overdose can lead to liver failure and death within days (Lee, 2004; Myers *et al.*, 2008). The toxic dose of paracetamol is highly variable, higher doses lead to increasing risk of toxicity. Paracetamol is considered in overdose situation, it

produces hepatic necrosis and renal failure in both humans and experimental animals (Denizar *et al.*, 2006). Acute paracetamol overdose in children rarely causes illness or death, and it is very uncommon for children to have levels that require treatment, with chronic larger-than-normal doses being the major cause of toxicity in children (Stern *et al.*, 2004; Daly *et al.*, 2008).

3. Pharmaceuticals Occurrence and Removal by Activated Sludge Process

The ubiquitous occurrence of various pharmaceuticals as environmental contaminants is demonstrated by reports of their presence in WWTP influents and effluents at concentrations ranging from a few ng/L to the high ng/L (Table 5). The efficiency of the removal of pharmaceuticals was found to be strongly dependent on the technology implemented in the wastewater treatment plant (WWTP). In general, activated process gave a much highly removal efficiency of over 85% removal of all pharmaceutical studied (e.g. ibuprofen, amoxicillin, diclofenac, and paracetamol). The monitoring program revealed that the treated wastewater effluents were the main contributors to pharmaceutical concentrations (up to 3 kg of pharmaceuticals day^{-1}) in the rivers studied (Kasprzyk-Hordern *et al.*, 2009; Jones *et al.*, 2003; Jones, *et al.*, 2005). Different compounds were removed to different extent in the WWTP**,** varying from 43 to 92%, with the highest performance obtained by the WWTP with tertiary treatment (sand filtration) (Zhou, *et al.*, 2008). Removal efficiencies ranged between 13% and 97% and between 9% and 87% for municipal and hospital WWTP, respectively (Adriano, *et al.*, 2006; Kosma, *et al.*, 2010). As the Table 5, all drugs are removed in the range of 0 to 100%, paracetamol was removed most efficiently, at over 90% on mean whereas ibuprofen had 85% and diclofenac had 70% on mean. In addition, other drug had removal efficiencies in the range of, with large variability (25 to 95%). The negative values of removal rates refer to an increase in the concentration of an analyzed parent compound during treatment. This phenomenon of "negative removal" for some compounds was already reported in the literature (Bound and Voulvoulis, 2006).

Table 5 The occurrence and removal of pharmaceuticals by activated sludge process

Concentration of Pharmaceuticals (ng/L)				
Pharmaceuti-cals	**Influent**	**Effluent**	**%Removal**	**Reference**
Paracetamol	281	218	22.42	Bound and Voulvoulis, 2006
	20,600	900	95.63	Kosma et al., 2010
	6924	<20*	100	Roberts and Thomas, 2006
	211,380	11,733	94.45	Kasprzyk-Hordern et al., 2009
	12,424	785	93.68	Thomas et al., 2007
	2,262	187	91.73	Jones et al., 2005
Ibuprofen	385	391	-1.56	Bound and Voulvoulis, 2006
	12,500	1,500	88	Kosma et al., 2010
	27,979	2,972	89.38	Roberts and Thomas, 2006
	1,681	263	84.35	Kasprzyk-Hordern et al., 2009
	503	178	64.61	Thomas et al., 2007
	4,047	568	85.96	Jones et al., 2005
Salbutamol	141	170	-20.57	Bound and Voulvoulis, 2006
	3,571	193	94.60	Jones et al., 2005
Mefenamic â	193	195	-1.04	Bound and Voulvoulis, 2006
	363	340	6.34	Roberts and Thomas, 2006
	205	61	70.24	Kasprzyk-Hordern et al., 2009
	4,359	369	91.53	Jones et al., 2005
Clotrimazole	31	10	67.74	Roberts and Thomas, 2006

Table 5 (Continued)

Concentration of Pharmaceuticals (ng/L)				
Pharmaceuticals	**Influent**	**Effluent**	**%Removal**	**Reference**
Diclofenac	2,000	1,300	35	Kosma et al., 2010
	1,036	289	72.10	Roberts and Thomas, 2006
	690	98	85.80	Kasprzyk-Hordern et al., 2009
	362	256	29.28	Thomas et al., 2007
	397	119	70.03	Zhou et al., 2009
Trimethoprim	835	622	25.51	Thomas et al., 2007
Propranolol	334	62	81.4	Zhou et al., 2009
Carbamazepine	1,662	950	42.8	Zhou et al., 2009
Triclosan	-	21	-	Boyd et al., 2003
Naproxen	-	106	-	Boyd et al., 2003
17β-Estradiol	20	<3	100	Thomas et al., 2007
Estriol	128	<3	100	Thomas et al., 2007

Note: * The following pharmaceutical compounds <limit of detection

Most of the studies on the fate of pharmaceuticals in WWTP focused only on the aqueous phase, and concentrations of the compounds in sludge were rarely determined mainly due to the demanding efforts required in the analysis in this difficult matrix. However, various types of pharmaceuticals were also found in the sludge (Chenxi *et al.*, 2008; Jelic *et al.*, 2009; Azzouz and Ballesteros, 2012; Yu and Wu, 2012) as shown in Table 6. It is reported that paracetamol contents in the sludgeswere in ranges of 0.08-119 ng/g dry sludge.

Table 6 The occurrence and sorption removal of pharmaceuticals by the sludge in the activated sludge

Concentration of Pharmaceuticals (ng/g dry sludge)		
Pharmaceuticals	**Sludge (ng/g)**	**Reference**
Paracetamol	0.08	Azzouz and Ballesteros, 2012
,,	41-119	Yu and Wu, 2012
,,	42-103	Jelic et al., 2009
Ibuprofen	0.09-0.12	Azzouz and Ballesteros, 2012
,,	27-208	Yu and Wu, 2012
,,	43-117	Jelic et al., 2009
Diclofenac	0.095-0.77	Azzouz and Ballesteros, 2012
,,	86-421	Yu and Wu, 2012
,,	27-75	Jelic et al., 2009
Carbamazepine	0.052-0.19	Azzouz and Ballesteros, 2012
,,	60-371	Yu and Wu, 2012
,,	34.5	Chenxi et al., 2008
,,	10-13	Jelic et al., 2009
Triclosan	0.26-3.1	Azzouz and Ballesteros, 2012
,,	271-1965	Yu and Wu, 2012
,,	320	Chenxi et al., 2008
Naproxen	0.28-0.85	Azzouz and Ballesteros, 2012
,,	11-35	Yu and Wu, 2012
,,	5-4.3	Jelic et al., 2009
Niflumic acid	0.37	Azzouz and Ballesteros, 2012
Metoprolol	0.18-0.34	Azzouz and Ballesteros, 2012
Choramphenicol	0.31	Azzouz and Ballesteros, 2012
,,	1.2	Jelic et al., 2009

Table 6 (Continued)

Concentration of Pharmaceuticals (ng/g dry sludge)		
Pharmaceuticals	**Sludge (ng/g)**	**Reference**
Pyrimethamine	0.13-2.3	Azzouz and Ballesteros, 2012
Florfenicol	0.03	Azzouz and Ballesteros, 2012
17α-ethinylestradiol	0.25-0.45	Azzouz and Ballesteros, 2012
Clofibric acid	24-155	Yu and Wu, 2012
Estrone	23-31	Yu and Wu, 2012
Ciprofloxacin	778	Chenxi et al., 2008
Doxycycline	296	Chenxi et al., 2008
Tetracycline	180	Chenxi et al., 2008
Clarithromycin	5.2	Chenxi et al., 2008
,,	27-47	Jelic et al., 2009

4. Determination of Pharmaceuticals in Wastewater

The occurrence of pharmaceuticals in the aquatic environment is of increasing research interest, as modern sensitive techniques are used worldwide for their determination (Table 7). Pharmaceuticals and their metabolites are among the most important classes of chemicals currently being investigated in environmental matrices at trace levels that accurate quantification of pharmaceuticals in environmental matrices is difficult. Several years ago, it was impossible because appropriate analytical techniques did not exist. Nowadays, the techniques such as gas chromatography-mass spectrometry (GC-MS), gas chromatography- electron ionization mass spectrometry (GC-EI-MS) and liquid chromatography- mass spectrometry (LC-MS) in combination with modern extraction, derivatization and clean-up methods provide the opportunity to quantify many pharmaceutical compounds down to ng/L levels (Kostopoulou and Nikolaou, 2008).

Table 7 The analytical methods applied to the determination of pharmaceuticals in aqueous samples

Pharmaceuticals studied	Sample preparation	Column and temperature program used	LOD (ng/L)	Reference
GC-MS methods				
Ibuprofen, **Paracetamol**, Phenazone, Carbamazepine	SPME with fiber coating polyacrylate, Carbowax-DVB	HP5-MS (70°C for 2 min, 10 °C /min to 250 °C, 5 min, increased to280 °C and held for 10 min)	200–50,000	Kostopoulou and Nikolaou, 2008
Paracetamol, Ibuprofen Salbutamol, Mefenamic acid, Prapranolol	SPE with LiChrolut ENV+, derivatization with MSTFA, elution with methanol	DB5MS (50 °C for 7.5 min, 30 °C /min to 270 °C, held for 10 min)	2-4	Kostopoulou and Nikolaou, 2008
Salycilic acid, Ibuprofen, **Paracetamol**, Caffeine, Phenazone, Gemfibrozil, Naproxen, Triclosan, Fenofibrate, Diclofenac,	SPE with HR-P, elute with ethyl acetate	DB-5-MS (70 ◦C (2min) to 250 ◦C (5min) at 10 ◦C/min and finally from 250 to 280 ◦C (10 min) at 6 ◦C/min)	14.5-184.1	Kosma, et al., 2010

Table 7 (Continued)

Pharmaceuticals studied	Sample preparation	Column and temperature program used	LOD (ng/L)	Reference
Ibuprofen, **Acetaminophen**, Dipyrone, Diclofenac, Carbamazepine, Codeine Caffeine, Metabolites: 1,7-dimethylxanthine, carbamazepine 10,11- poxide	SPE with Oasis HLB, elution with ethyl acetate	ZB-5MS (105 °C for 1 min, 17 °C /min to 200 °C, for 1 min, 2 °C /min to 220 °C for 2 min, 5 °C /min to 290 °C, for 1 min)	1-1000	Kostopoulou and Nikolaou, 2008
Aspirin, Ibuprofen, Ketoprofen Naproxen, **Paracetamol**, Gemfibrozil, Salbutanol, Clenbuterol, Terbutalin, Diclofenac, Diazepam, Caffeine, Carbamazepine, mitryptiline,	SPE with Oasis MCX, derivatization with MSTFA, elution with ethyl acetate/acetone	HP-5MS (70 °C for 2 min, 10 °C /min to 250 °C, for 5 min)	0.1–2.6 for surface water, 3.2–28.6 for waste-water	Kostopoulou and Nikolaou, 2008

Table 7 (Continued)

Pharmaceuticals studied	Sample preparation	Column and temperature program used	LOD (ng/L)	Reference
Clofibric acid, Ibuprofen, **Acetaminophen**, Caffeine, Fluoxetine, Chlorophene, Naproxen, Triclosan, Bisphenol, Estrone, 17b-Estradiol	SPE with SDB-XC, elute with methanol, derivatization with BSTFA	DB-5MS (5 ºC/min to 165 ºC (5-min hold), then at 2 ºC/min to 175 ºC (0-min hold) and 10 ºC/min to 320 ºC (5-min hold)	0.6-178	Boyd et al., 2003
Ibuprofen, Paracetamol, Salbutamol, PropranololeHCl, Mefenamic acid	SPE with LiChrolut ENV+, derivatization with MSTFA, elution with methanol	BPX5 (50 °C for 7.5 min, 30 °C /min to 270 °C, held for 10 min)	0.82-1.56	Jones et al., 2003, Jones et al., 2005, and Bound and Voulvoulis, 2006

Table 7 (Continued)

Pharmaceuticals studied	Sample preparation	Column and temperature program used	LOD (ng/L)	Reference
LC-MS				
Paracetamol , Metoprolol , Diclofenac, Ibuprofen, 17b-Estradiol, 17a-Ethinylestradiol, Estriol, Estrone, Oxytetracycline, Tetracycline, Demeclocycline , Chlorotetracycline, Doxycycline, Meclocycline Trimethoprim, Ciprofloxacin, Sulfamethoxazole, Cefuroxime, clophosphamide, Ifosfamide	SPE with Strata X, elute with MeOH , MeOH (2% acetic acid) and finally MeOH (2% Ammonium hydroxide) (4 mL)	C18 (mobile phases for positive mode: modified water and modified methanol (20 mM ammonium acetate), and negative mode: water and methanol	1-20	Thomas et al., 2007

Table 7 (Continued)

Pharmaceuticals studied	Sample preparation	Column and temperature program used	LOD (ng/L)	Reference
Sulfamethoxazole, Acetyl-sulfamethoxazole, Trimethoprim, Erythromycin, **Paracetamol,** Ibuprofen, Mefenamic acid, Diclofenac, Clofibric acid, Propranolol, Lofepramine, Tamoxifen Carisoprodol, Phenazone, Ketoprofen B-blockers, Atenolol, Propranolol, Tamoxifen, Carbamazepine, Paroxetine, Sertraline, Clotrimazole, Simvastatin , Atorvastatin	SPE with Strata X, elution with methanol	Luna C18 (mobile phase of water, methanol and 40 mM ammonium acetate in water, adjusted to pH 5.5 by the addition of formic acid)	10-50	Kostopoulou and Nikolaou, 2008
	SPE with Strata X, Elution with MeOH , MeOH (2% acetic acid) and finally MeOH (2% ammonium hydroxide)	C18 (The mobile phases for positive mode: modified water (5 mM ammonium acetate, A) and modified methanol (5mM Ammonium acetate, B), and in negative mode: water (0.1% formic acid, A) and methanol (0.1% formic acid, B).	10	Langford and Thomas, 2009

Table 7 (Continued)

Pharmaceuticals studied	Sample preparation	Column and temperature program used	LOD (ng/L)	Reference
Phenazone, Dimethylaminophenazone, Propyphenazone, Metoprolol, Propranolol, Atenolo l, Bisoprolo,l Sotalol, Pindolol, Betaxolol, Salbutamol, Clenbuterol, Terbutaline	SPE with Oasis HLB, elution with methanol	C8 ZB-5MS (Positive-ion mode: Solvent A: acetonitrile Solvent B: formic acid 0.1% in Milli-Q water) (Negative-ion mode: Solvent A:acetonitrile Solvent B: Milli-Q water)	3.8-4.7	Kostopoulou and Nikolaou, 2008
HPLC-ESI-MS/MS				
Clofibric acid, Clotrimazole Dextropropoxyphene, Diclofenac, Erythromycin, Ibuprofen, Mefenamic acid, **Paracetamol,** Propranolol	SPE with StrataX , elute with methanol	C18 (mobile phase of water, methanol and 40 mM ammonium acetate in water, adjusted to pH 5.5 by the addition of formic acid.)	20	Roberts and Thomas, 2006

Table 7 (Continued)

Pharmaceuticals studied	Sample preparation	Column and temperature program used	LOD (ng/L)	Reference
Propranolol, Sulfamethoxazole, Carbamazepine, Indomethacine, Diclofenac,	SPE with Oasis HLB, elute with MeOH	C18 (mobile phase: eluent A (0.1% formic acid in ultrapure water), solvent B (acetonitrile) and eluent C (Methanol)	0.05- 5	Zhou et al., 2009
Quatro Micro triple–quadrupole –MS				
55 pharmaceuticals (e.g. ibuprofen, paracetamol. sulfamethoxazole, diclofenac, and aspirin)	SPE with Oasis MCX, elute with MeOH and 5% NH4OH in MeOH	C18 (Separated using a gradient method and the following mobile phase composition: water, methanol and acetic acid (0.5%))	5-10	Kasprzyk-Hordern et al., 2009

Note: LOD; Limit of detection

5. Determination of Pharmaceuticals in Sludge

During the course of wastewater treatment process, the PPCPs and EDCs (Endocrine disrupting compounds) may be adsorbed by the suspended solids and subsequently removed from water stream by sedimentation. Municipal sewage sludge, the solid fractions separated from the wastewater stream, therefore is potentially a sink of the wastewater-borne PPCPs. To track the fate and transport of sludge-borne PPCPs and EDCs in terrestrial and aquatic ecosystems, it is imperative to develop reliable and accurate analytical methods for detection of these compounds in municipal sewage sludge that has complex organic matrices that would bond with these compounds by surface adsorption. Currently analytical methods emphasized detection of the compounds in aqueous matrices, such as surface water and wastewater (Azzouz and Ballesteros, 2012). A studies were on measuring PPCPs and EDCs including Paracetamol present in solid matrices, such as sewage sludge, soil and sediment from which the targeted chemicals must be extracted, Microwave-assisted extraction (Azzouz and Ballesteros, 2012), Ultrasonication (Chenxi *et al.*, 2008 and Yu and Wu, 2012), Pressurized liquid extraction (Jelic *et al.*, 2009) and Accelerated solvent extraction (Jelic *et al.*, 2011) as shown in Table 8.

Table 8 The analytical methods applied to the determination of pharmaceuticals in sludge samples

Pharmaceuticals studied	Sample preparation	Column and temperature program used	LOD (ng/g)	Reference
GC-MS				
Acetylsalicylic acid, Diclofenac, Flunixin, Ibuprofen, Ketoprofen, Naproxen, Mefenamic acid, **Paracetamol**, Carbamazepine, Niflumic acid, Clofibric acid, Triclosan, Metoprolol, Florfenicol, Pyrimethamine, Thiamphenicol, Estrone, 17β-estradiol, 17α-ethinylestradiol	Microwave-assisted extraction, clean up with SPE (Oasis HLB), elution with ethyl acetate	DB-5 (70 °C for 1min, ramp to 150 °C at 14 °C /min, and ramp to 290 °C at 6 °C /min)	0.0008-0.0051	Azzouz and Ballesteros, 2012

Table 8 (Continued)

Pharmaceuticals studied	Sample preparation	Column and temperature program used	LOQ (ng/g)	Reference
LC–MS/MS				
Ciprofloxacin, Tetracycline Doxycycline, Clindamycin Clarithromycin, Erythromycin-H2O, Carbamazepine	Ultrasonication ; methanol, 0.1 M acetic acid and 5% Na2-EDTA (2:1:1), clean up with SPE (Strata-X)	Analytes were separated on a 100 × 4.6 mm (3 µm, 100Å end capped) Luna C8(2) Silica-based Column with 4×2.0 mm	0.5-57	Chenxi et al., 2008
LC–ESI-(QqLIT)-MS^2				
Paracetamol and 42 pharmaceutical compounds	Pressurized liquid extraction : ethanol/water, 1/2 (v/v), at 100°C clean up with SPE (Oasis HLB), elute with methanol	RP-18 (negative ionization; acetonitrile-methanol (1:1, v/v) as solvent A, water as solvent B, positive ionization; acetonitrile and water as eluent A and 0.1% formic acid as eluent B.	0.03-10.5	Jelic et al., 2009

Table 8 (Continued)

Pharmaceuticals studied	Sample preparation	Column and temperature program used	LOQ (ng/g)	Reference
HPLC-QLIT-MS/MS				
Hydrochlorthiazide, furosemide, atorvastatine, clarithormycin, carbamazepine and diclofenac	Accelerated solvent extraction (ASE), methanol-water (1:2), at 1500 psi and 100° C, clean up with SPE (Oasis HLB), elute with methanol	RP-18 (mobile phase for negative ionization; acetonitrile-methanol (1:1, v/v), for positive ionization; acetonitrile as eluent A and 0.1% formic acid as eluent B.	0.5-7.1	Jelic et al., 2011
GC-MS				
Acetylsalicylic acid, Diclofenac, Ibuprofen, Ketoprofen, Naproxen, Clofibric acid **Paracetamol**, Triclosan, Carbamazepine, Estrone	Ultrasonic extraction method, clean up with SPE (HLB) , elute with methanol	HP-5MS (70°C (held for 1 min) to 120°C at 20°C /min, raised to 250 °C at 10 °C /min and then to 280°C at 5°C /min and held for 3 min)	4.7-39	Yu and Wu, 2012

Note: LOQ; Limit of Quantification

6. Activated Sludge Process

The activated sludge process utilizes a fluidized, mixed growth of microorganisms under aerobic conditions to use the organic materials in the wastewater as substrates, thus removing them by microbial respiration and synthesis. The main units of the system, consist of a biological reactor basin with its oxygen supply (the aeration tank), a solid-liquid separator (the final clarifier), and the recycled sludge pumps.

The feed wastewater flow, mixes with the recycled activated sludge flow, immediately prior to entering the biological reactor is termed the mixed liquor, and the mixed liquor suspended solids (MLSS) usually range from 2000 to 4000 mg/L by dry weight. Upon entering the reactor, the activated sludge rapidly adsorbs the suspended organic solids in the wastewater, this period lasting from about 20 to 45 minutes. After adsorption, the adsorbed organic solids are solubilized and oxidized by biological oxidation as the mixed liquor moves through the aeration tank. The rate of sorption gradually decreases as the mixed liquor passes through the tank. The sorbed soluble organic materials are oxidized by biological oxidation with a reaction time usually less than that required for the adsorbed suspended organic substances. The oxygen supply for the aeration tank is usually furnished by diffused compressed air or mechanical surface aeration, however, pure oxygen has been used in some instances. Aeration by diffused compressed air or mechanical means has a dual purpose, because it must supply the required oxygen for the aerobic bio-oxidation and provide sufficient mixing for adequate contact between the activated sludge and the organic substances in the wastewater. A simplified biochemical equation for the utilization of organic matter as a substrate for respiration and cell synthesis in the activated sludge process is

$$\text{Organic matter} + O_2 \xrightarrow[\text{microbes}]{\text{Aerobic}} \text{New cells} + \text{Energy for cells} + CO_2 + H_2O + \text{Other end product} \qquad (1)$$

Some of the other end products are NH_4^+, NO_2^-, NO_3^- and PO_4^{-3}. The empirical equation that has usually been found to represent activated sludge is $C_5H_7O_2N$, which has a molecular weight of 113. The net mass of cells produced daily represents the mass of cells that must disposed of daily as waste activated sludge (WAS). Part of the settled material, the sludge, is returned to the head of the aeration system to re-seed the new wastewater entering the tank. This fraction of the floc is called return activated sludge (RAS). Many sewage treatment plants use axial flow pumps to transfer nitrified mixed liquor from the aeration zone to the anoxic zone for denitrification. These pumps are often referred to as internal mixed liquor recycle pumps (IMLR pumps). The raw sewage, the RAS, and the nitrified mixed liquor are mixed by submersible mixers in the anoxic zones in order to achieve denitrification.

In a sewage (or industrial wastewater) treatment plant, the activated sludge process can be used for one or several of the following purposes:

- oxidizing carbonaceous matter: biological matter.
- oxidizing nitrogeneous matter: mainly ammonium and nitrogen in biological materials.
- removing phosphate.
- driving off entrained gases carbon dioxide, ammonia, nitrogen, etc.
- generating a biological floc that is easy to settle.
- generating a liquor that is low in dissolved or suspended material.

(Syed, 1994; Reynolds and Richards, 1982)

7. Biodegradation of Pharmaceuticals

Despite that many pharmaceuticals were persistent in environment, biodegradation of many pharmaceuticals has been observed in WWTP, which actually represents the most important removal mechanism in WWTP. The large number of different pharmaceuticals, with highly variable molecular structures complicates their efficient removal. Structure–biodegradability relationships obtained for a large data set of organic chemicals showed that compounds including esters, nitriles and aromatic alcohols have functional groups that may increase biodegradability, whereas aromatic amines, iodide, nitro and azo groups increases a compound's persistence. Jones et al., 2005 reported that long and highly branched side chains render a compound more persistent, whereas unsaturated aliphatic compounds are more biodegradable than saturated analogues or aromatic compounds with complicated aromatic ring structures and sulfate or halogen groups. Nevertheless, various investigators have reported on the absence of a relationship between (Sipma et al., 2010). Gusseme et al., 2011 also reported that *Delftia tsuruhatensis* and *Pseudomonas aeruginosa* were able to remove paracetamol in 48 h from 10.325±0.027 mg/L to 0.263±0.034 mg/L (97 %removal) and 6.152±0.083 mg/L (40 % removal), respectively.

8. Din Daeng Water Environment Control Plant

The Bangkok Wastewater Treatment Project was developed for more than 20 years and there have been numerous studies. The existing of the Water Environment Control Plant was shown in Table 9. The Din Daeng Water Environment Control Plant is the highest of the service area and population that also the capacity of treatment and there also usage the Activated Sludge system for treatment wastewater (Table 10). As the reason, that we are chooses this plant for this study.

Table 9 Bangkok Wastewater Treatment Plants

Water Environment Control Plant	Area (km^2)	Population	System	Capacity (m^3/day)
1. Si Phraya	2.7	120,000	Contact Stabilization A.S.	30,000
2. Rattanakosin	4.1	70,000	Two Stage A.S.	40,000
3. Din Daeng	37	1,080,000	Activated Sludge	350,000
4. Chong Non Si	28.5	580,000	Cyclic Activated Sludge System	200,000
5. Nong Khaem	44	520,000	Vertical Loop Reactor A.S.	157,000
6. Thung Khru	42	177,000	Vertical Loop Reactor A.S.	65,000
7. Cha Tu Chak	33.4	432,000	Cyclic Activated Sludge System	150,000

Source: Bangkok Metropolitan Administration, BMA (2011)

Din Daeng Water Environment Control Plant (Fig. 3 and 4) was located at Mitmaitree Road, Din daeng, Bangkok, Thailand. The scope of services are;

- To manage the quality of water and wastewater,
- To collect and treat wastewater to environmental standards,
- To provide the consult and advice customers,
- To outsourcing operations and maintenance in utility services.

The service area is about 37 Square Kilometres consists of Pom-Prap, Sumpanthawong, Pathumwan, Ratchthevi, and some part of Dusit, Phyathai, Din Daeng districts. The plant capacity is 350,000m^3/day and the management and infrastructure were shown in Table 8. This project is Turn-Key project including

construction and operation works. It was conducted by NOSS Consortium (Company). The construction cost for initial plan is 6,382 million Baht, under the supervision by Dorsch Consult & Associates, with consulting service of 199,998,500 baht. 75% of the total budget is subsidized by Government and the remaining 25% shared by Bangkok Metropolitan Administration (BMA). The contract was signed on 1 November 1993. The NOSS Consortium has stopped their construction work since 3 April 1998 resulting in the termination of the contract by BMA since 29 September 1999.

The remaining works are scheduled to be completed by new contractors. All those works were signed contracts on 30 March 2001 and are expected to be completed on 30 September 2004 except the first part. For remaining work, the budget is subsidized by Government 50% and the remaining 50% shared by BMA. The contract of the fifth part is responsible for one year operation and maintenance after the finish date of the construction. The plant was operated successfully on October 2005. The private company has operated the plant for BMA since then. In the recent, Utility Business Alliance (UBA), the wastewater treatment technology company is the private company that operated the plant.

Figure 3 Din Daeng Water Environment Control Plant

Source: Bangkok Metropolitan Administration, BMA (2011)

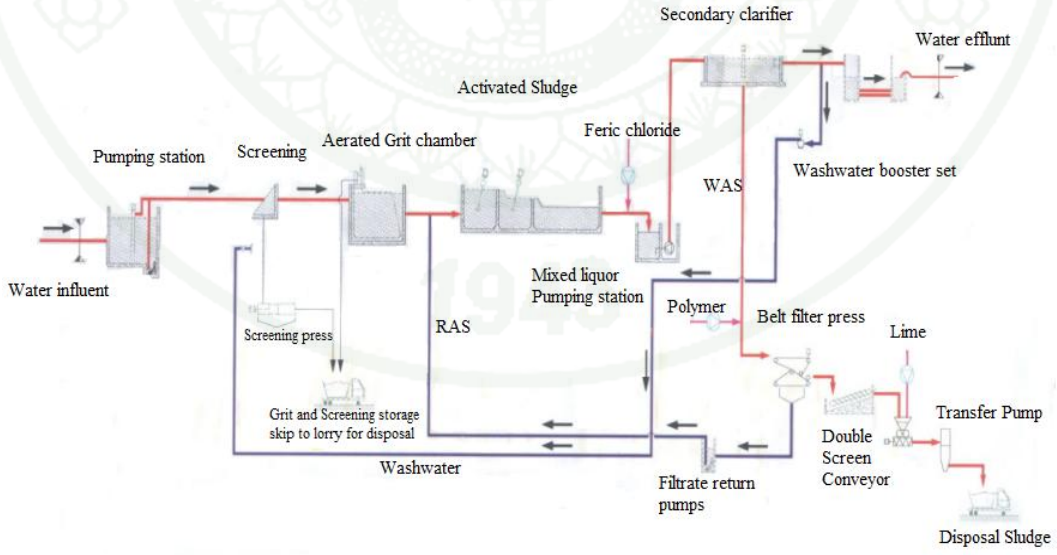


Figure 4 Flow diagram of Din Daeng Water Environment Control Plant

Source: Din Daeng Water Environment Control Plant (2011)

Table 10 Management infrastructure of Din Daeng plant

Description	**Operation**	**Unit**
Service area	37	Km^2
Treat Water Capacity	150,000	m^3 / day
Wastewater Treatment Capacity	350,000	m^3 / day
Population	1,080,000	people
Wastewater collection pipeline	Combined System	
Wastewater collection pipe diameter	0.15 to 3.2	M
Wastewater collection pipe length	66,449	Km
No. of MH (Manhole)	964	
Pumping	7	Station
Process	Activated Sludge	
Point of discharge the treated water	Buangmagkason	

Source: Din Daeng Water Environment Control Plant (2011)

8.1 Details of Wastewater Treatment Process

8.1.1 The first treatment are includes pumping wastewater to the physical separation (Screening) to remove large object such as rags, paper, plastics, metals, and something like this and then wastewater were pumped to the aerated grits chambers to separate the grit includes sand, dust, cinder, seeds, bone chips, and other materials in wastewater that are heavier than organic matters.

8.1.2 The biological treatment (activated sludge process), using microbes to remove those pollutants that can settle or float and the soluble organics. Microorganisms are mixed thoroughly with the organics so that they can grow and stabilize the organics. As the microorganisms grow and are mixed by the agitation of

the air, the individual organisms clump together (flocculate) to form an active mass of microbial floc called “activated sludge”. The mixture of the activated sludge and wastewater in the aeration basin is called “mixed liquor”. The combination of wastewater and biological mass is commonly known as mixed liquor. In all activated sludge plants, once the wastewater has received sufficient treatment, an excess mixed liquor is discharged into settling tanks and the treated supernatant is run off to undergo further treatment before discharge. Part of the settled material, the sludge, is returned to the head of the aeration system to re-seed the new wastewater entering the tank. This fraction of the floc is called return activated sludge (RAS). Excess sludge is called surplus activated sludge (SAS.) or waste activated sludge (WAS).

8.1.3 Removal of sludge (Sludge treatment). As a result of the biological treatment and chemical additions within the secondary treatment stage, sludge will be generated. This sludge will be a mixture of waste biomass and chemical sludge. Treatment of the combined sludge will comprise thickening and dewatering by combined gravity belt filter press units followed by the addition of Hydrated Lime (Up to 30% by weight) to assist in the prevention of odor. The final sludge cake will comply with the minimum requirement of 20% dry solids and will be transported off site or turn it into fertilizer pellets or disposed of to landfill.

8.1.4 Deodorizing (Odour control), odors caused by wastewater pumping station, grid gravel trap, and waste storage tank that the odors were treated with carbon reactors before released into the atmosphere (Din Daeng Water Environment Control, 2009).

8.2 Treatment Performance

Bangkok is the capital city which is the economic center of Thailand. Its activities include commercial, industrial and service have caused the expansion of the city and its population, resulting in accumulation of environmental pollution to the point that nature cannot cope with the pollution loadings, especially for water

pollution. This is evident in the rivers, canals and other water bodies which show signs of deterioration such as black color and offending odors due to lack of dissolved oxygen, therefore which requires special treatment process if for consumption.

Because most of the sites are small, the STPs will be housed in a multi storey or at least two storey's building. The process design for every STP is Activated Sludge with nutrients removal process. The discharge effluent should meet the following requirements:

- Dissolved Oxygen (DO) ≥ 5 mg/L
- Biochemical Oxygen Demand (BOD) ≤ 20 mg/L
- Total Suspended Solid (TSS) ≤ 30 mg/L
- Total Kjeldahl Nitrogen (TKN) ≤ 10 mg/L
- Total Phosphorus (TP) ≤ 2 mg/L

.

The operating parameters and flow rate data of Din Daeng Water Environment Control Plant were shown in Table 11. The detection frequencies of wastewater (in all the wastewater influent and effluent samples) and the concentration of activated sludge presents as the average value of each month, from January to April, 2011. As the results, the water quality of the effluent shows that its quality was under the effluent standard of, which the DO is more than 5 mg/L; BOD is less than 20 mg/L; TSS is less than 30 mg/L; TN is less than 10 mg/L, and TP is less than 2 mg/L.

The concentrations of MLSS in the aeration tank (3 aeration tanks) are shown in Table 10. The term of MLSS were usually controlled in ranges from 3000 to 7000 mg/L, SVI range is from 60 to 90 mg/L, SV_{30} range is from 250 to 500 mg/L, that means these system are efficiently working to treated the wastewater to be the higher qualities water before discharge to environment.

Table 11 The results of wastewater analysis in 2011

Month	Flow rate (m^3/d)	Parameters													
		pH		COD (mg/L)		DO (mg/L)		BOD (mg/L)		TSS (mg/L)		TN (mg/L)		TP (mg/L)	
		In	Out	In	Out	In	Out	In	Out	In	Out	In	Out	In	Out
Jan.	244,031	7.30	7.37	89.01	24.09	-	7.11	31.20	3.99	25.61	10.55	17.98	8.62	1.5	0.97
Feb.	226,822	7.38	7.52	101.60	24.54	-	6.46	40.08	4.90	38.06	11.50	19.89	7.89	1.35	0.96
Mar.	192,943	7.26	7.28	99.48	21.39	-	6.71	40.52	3.76	35.94	9.31	19.96	7.70	1.29	0.77
Apr.	184,701	7.25	7.33	91.21	24.35	-	6.78	35.14	3.94	43.61	11.55	21.31	7.78	1.19	0.84

Source: Din Daeng Water Environment Control Plant, UBA (2011)

Table 12 The concentration of MLSS in the aeration tanks in 2011

Month	Aeration tank 2					Aeration tank 3					Aeration tank 4					RAS/WAS
	MLSS (mg/L)	MVLSS (mg/g)	Ratio (%)	SV_{30} (ml/L)	SVI (ml/mg)	MLSS (mg/L)	MVLSS (mg/g)	Ratio (%)	SV_{30} (ml/L)	SVI (ml/mg)	MLSS (mg/L)	MVLSS (mg/g)	Ratio (%)	SV_{30} (ml/L)	SVI (ml/mg)	(mg TS/L)
Jan.																
Ave	3124	1824	58	248	82	3175	1924	56	266	85	2102	1188	59	196	109	19014
Mean	2940	1840	58	240	79	3000	2120	55	260	85	1920	1160	59	190	92	17480
SD	835	434	3.2	89	31	885	309	3.6	91	25	1450	160	3.3	94	59	4675
Feb.																
Ave	4576	2640	58	413	90	4233	2455	61	357	85	2914	1610	61	252	88	18110
Mean	4590	2510	60	413	86	4100	2370	60	342	85	2720	1560	62	235	89	17300
SD	649	387	5.5	106	21	686	326	3.4	84	16	686	227	5.8	63	16.6	4845
Mar.																
Ave	6845	4080	58	491	75	7182	4132	55	514	76	5031	2514	54	396	85	17532
Mean	6560	3680	57	483	69	6780	3940	57	493	72	5010	2200	58	400	80	18020
SD	1423	800	10.7	73	21	1635	1043	10	75	22	1318	790	15	64	29	4712
Apr.																
Ave	6651	4065	56	418	68	6633	4025	56	443	71	5927	3380	57	378	71	14892
Mean	6470	4020	56	410	64	6020	4030	56	434	73	5300	3700	57	371	69	13510
SD	1985	1082	3	59	20	2035	1500	3.5	50	17	2029	1332	3.9	48	28	4457

Note: RAS; Return Activated Sludge, WAS; Waste Activated Sludge, Aeration tank 1 is not work

Source: Din Daeng Water Environment Control Plant, UBA (2011)

9. Environmental Factors Effecting on Adsorption and Desorption of Paracetamol by Adsorbents

As the previous reports, more than 95% Paracetamol and other pharmaceuticals could be adsorbed on various types of adsorbents but neglected for activated sludge (Table 13). The removal rates of adsorption capacity were according to the environmental conditions such as contract time, sorbent concentration, pH, temperature or type of adsorbent. Paracetamol adsorption tended to increase with temperature (Terzyk and Rychlicki, 2000 and Villaescusa *et al.,* 2011), Paracetamol sorption was not pH dependent. Ion exchange was not a mechanism responsible for paracetamol sorption (Villaescusa *et al.,* 2011). At neutral pH, Paracetamol showed no significant sorption to any of the media, silica, alumina, and hydrophobic medium (Lorphensri *et al.,* 2006). The increasing tendency of adsorption was observed in the lower pH condition (Urase and Kikuta, 2005 and Bui and Choi, 2009). The circumstances that result in experimental artifacts yielding apparent desorption can be grouped into three principal categories. One is failure to allow the adsorption and desorption processes to reach their true equilibrium conditions. It is commonly acknowledged that most solute-sorbent systems require several weeks or months to approach true adsorption/desorption equilibrium. The second one is failure to properly account for losses of solution to reactor components and compartments. The third one is the so-called solid effect, often attributed to the partitioning of solute into dissolved macromolecular or colloidal organic matter not removed during the post-adsorption solid separating procedure (Hong-Jian *et al.,* 2010).

Table 13 Comparisons of paracetamol and other pharmaceuticals adsorption and desorption previously found in some adsorbent (batch study)

Compounds	Adsorbents	Isotherm equations	Batch study				Reference
			Adsorption		Desorption		
			Isotherm	Rate	Rate	Isotherm	
Paracetamol	Vegetable wastes (grape stalk, yohimbe bark and cork bark)	Pseudo-first order model	K=0.0041 (min^{-1})	0.77-1.74 mg g^{-1}	-	-	Villaescusa et al., 2011
	Activated carbon	Pseudo-second order	k_2=540-1000 (g $mg^{-1}min^{-1}$)	87-171 mg g^{-1}	-	-	Ruiz et al., 2010

Table 13 (Continued)

Compounds	Adsorbents	Isotherm equations	Batch study				Reference
			Adsorption		Desorption		
			Isotherm	Rate	Isotherm	Rate	
carbamazepine, clofibric acid, diclofenac, ibuprofen,and ketoprofen	SBA-15	Frandilch equation	K_F=0.5-1.10, n=1.04-1.34	49-94.3 %	K_F=0.5-1.10, n=1.04-1.34	20-40%	Bui and Choi, 2009
ciprofloxacin	Activated carbon, carbon nanotubes and carbon xerogel	Pseudo-first order model	60 to 300 mg g^{-1}				Carabineir et al., 2011

Table 13 (Continued)

Compounds	Adsorbents	Isotherm equations	Batch study				Reference
			Adsorption		Desorption		
			Isotherm	Rate	Isotherm	Rate	
17b-estradiol, estrone, 17a-ethynilestradiol , bisphenol A, benzophenone , clofibric acid, gemfibrozil, ibuprofen, fenoprofen, ketoprofen, naproxen, diclofenac, propyphenazone carbamazepine	Activated Sludge	Pseudo-first order model	K'/X=0.0002 -0.027 (L/h-gMLSS)	5-65%	-	-	Urase and Kikuta, 2005

10. Adsorption and Desorption Isotherm

The most popular adsorption model for a single solute system, the Freundlich model is an empirical equation based on the distribution of solute between the solid phase and aqueous phase at equilibrium. Although the Freundlich model is suitable used for heterogeneous surfaces but can describe adsorption phenomenon over the restricted range only. It is often found when the Freundlich equation is fitted to data at high and intermediate concentrations and may provide a poor fit to data at low concentrations, since the Freundlich equation does not approach Henry's Law of ideal dilute solutions (Ng *et al.,* 2002). The adsorption and desorption data were analyzed by using the Freundlich equation:

$$q_e = K_F C_e^{\,n} \qquad (2)$$

Where; q_e is equilibrium concentration of paracetamol adsorbed (ng/g), C_e is equilibrium concentration of paracetamol (ng/L), K_F is the Freundlich constant, and n is the Freundlich exponent (Hong-Jian *et al.,* 2010). Eq. (1) can be linearized by taking logarithms (Eq. 3) to find out the parameters K_F and n.

$$\log q_e = \log K_F + (n) \log Ce \qquad (3)$$

A linear form of the Freundlich isotherm can be obtained by taking the log of each sides of the Freundlich equation to give log Ce is plotted on the x-axis against log qe on the y-axis, log K_F becomes the of the line and n becomes the slope of the line. Investigators have tried to link the Freundlich parameters K_F and n to mechanisms of adsorption. The Freundlich isotherm is linear if n=1 and, as n decreases, the isotherm becomes more nonlinear (Hong-Jian *et al.,* 2010, Cynthia and Raymond, 2006). A larger value for n indicates a larger change in effectiveness over different equilibrium concentrations. Also, when n is >1.0, the change in adsorbed concentration is greater than the change in the solute concentration (Ng *et al.,* 2002).

The mass of Paracetamol adsorbed onto the activated sludge was detected by measuring the mass of paracetamol that disappeared from the solution phase at the end of adsorption experiment. The fraction of paracetamol adsorbed on the activated sludge was calculated by the equation:

$$q_a = (C_i - C_{eq})V/M \quad (4)$$

Where q_a is the amount of paracetamol adsorbed onto the activated sludge (g/g, dry activated sludge), C_i is the initial concentration of paracetamol (ng/L), C_{eq} is the equilibrium concentration of paracetamol at the end of the adsorption experiment (ng/L), V is the volume of solution (L), and M is the mass of the dried activated sludge (g) (Osman, *et al.,* 2004; Wang *et al.*, 2006; Ruiz, *et al.,* 2010; Hong-Jian *et al.,* 2010). The fraction of paracetamol desorbed from the activated sludge was calculated using the equation:

$$q_{des} = (C_2 - C_1)V/M \quad (5)$$

Where q_{des} is the amount of paracetamol desorbed from activated sludge (g/g, dry activated sludge), C_1 is the solution phase paracetamol concentration of distillate water equilibrium experiment (0 ng/L), C_2 is the solution phase paracetamol concentration of the current equilibrium experiment (ng/L).

MATERIALS AND METHODS

Materials

1. Chemicals and Equipment

1.1 Paracetamol (Acetaminophen, *N*-Acetyl-*p*-aminophenol, Standard grade (Purity 99.98%), Sigma Aldrich, UK)

1.2 N-methyl-N-trimethylsilyltrifloroacetamide (MSTFA, Derivaization grade, Sigma Aldrich, UK)

1.3 Methanol (Analytical grade (99.99%), J.T.Baker)

1.4 Hexane (Analytical grade (99.99%), J.T.Baker)

1.5 Nitrogen (High Purity grade, Purity 99.99%, TIG)

1.6 Helium (High Purity grade, Purity 99.99%, TIG)

1.7 SPE cartridge (filled with HCP-SA 100 mg Polyamide-Divinylbenzene Copolymer Trimethylaminopropyl, PA-DVBT, Vertical)

1.8 Vacuum manifold (4012, 12 Position Vacuum manifold Set-Complete, Athena Technologies)

1.9 Vacuum pump (Model, N035.3AN.18), Scientific Promotion Co.,LTD)

1.10 Gas chromatography –mass spectrophotometry (GC-MS, Shimudzu QP 2010 Plus)

1.11 Autoclave (High Pressure Stream Sterilizer, Tomy SX-500)

1.12 Homogenizer (Glas-COl)

1.13 Centrifuge (Model Z383, Hermle)

1.14 Gas Chromatography (Agilent GC 6890 Series (Plus), Column CTR I)

2. Wastewater and Disposal Sludge Samples

2.1 Din Daeng Water Environment Control Plant, the locations of sampling point are shown in Fig. 5

Sampling point 1: wastewater influent

Sampling point 2: settled sewage

Sampling point 3: disposal sludge (Sludge treatment)

Sampling point 4: effluent

Wastewater sampling at each point (in each times) were performed in the same day in January (1 time), February (1 time), March (2 times) and April (2 times).

2.2 Receiving canal, the location where receives effluent from Din Daeng Water Environment Control Plant. The locations of sampling point were three points, approximately far from the discharge point 1, 2, 3 kilometers (Fig. 6). Samples were collected in same day as the samples from the treatment plant.

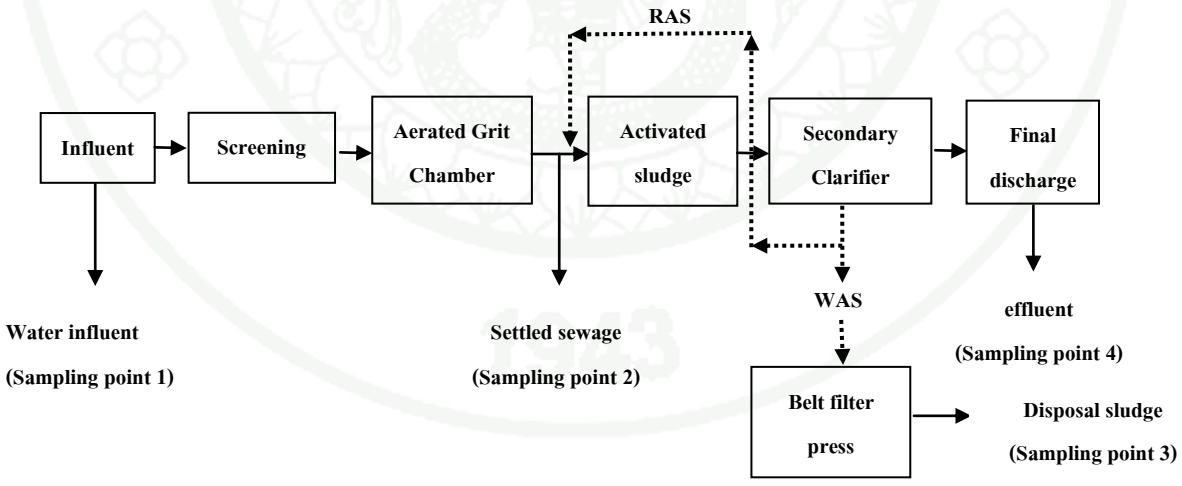
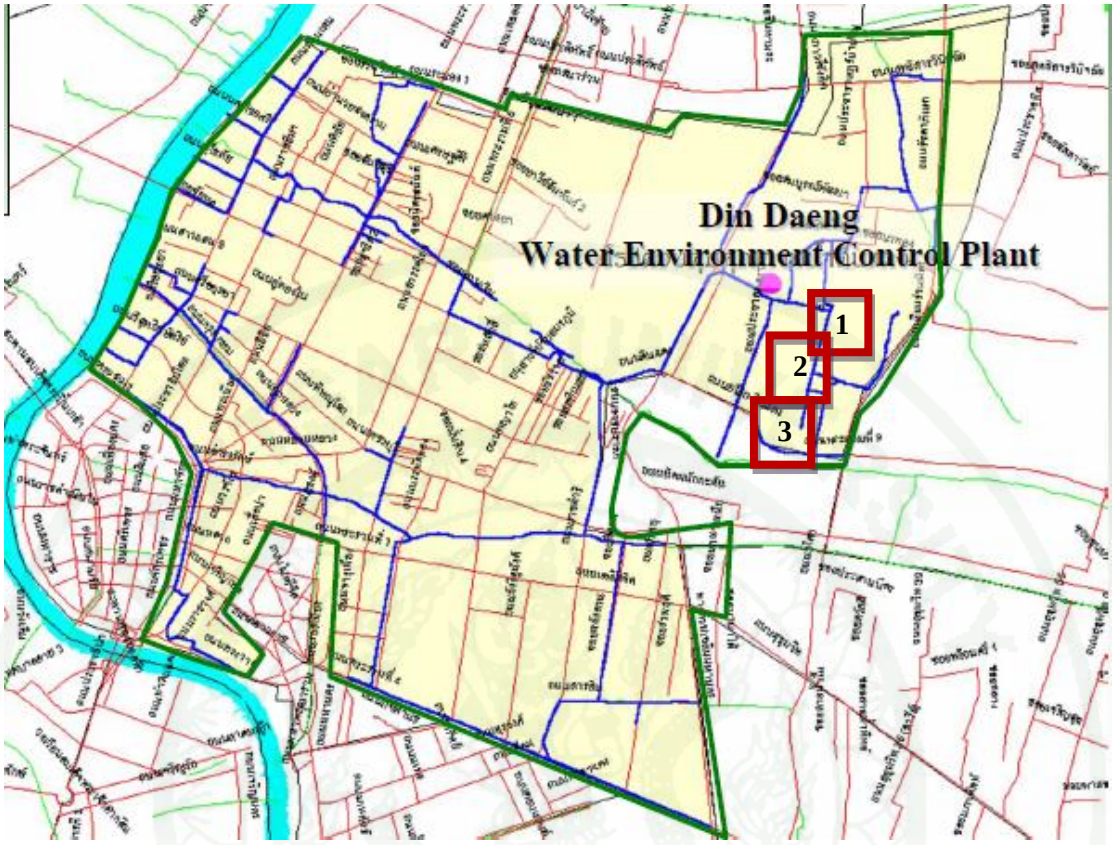


Figure 5 Flow diagram of the unit treatment process of the Activated Sludge



Note: 1, 2, and 3 are the location of receiving canal sampling

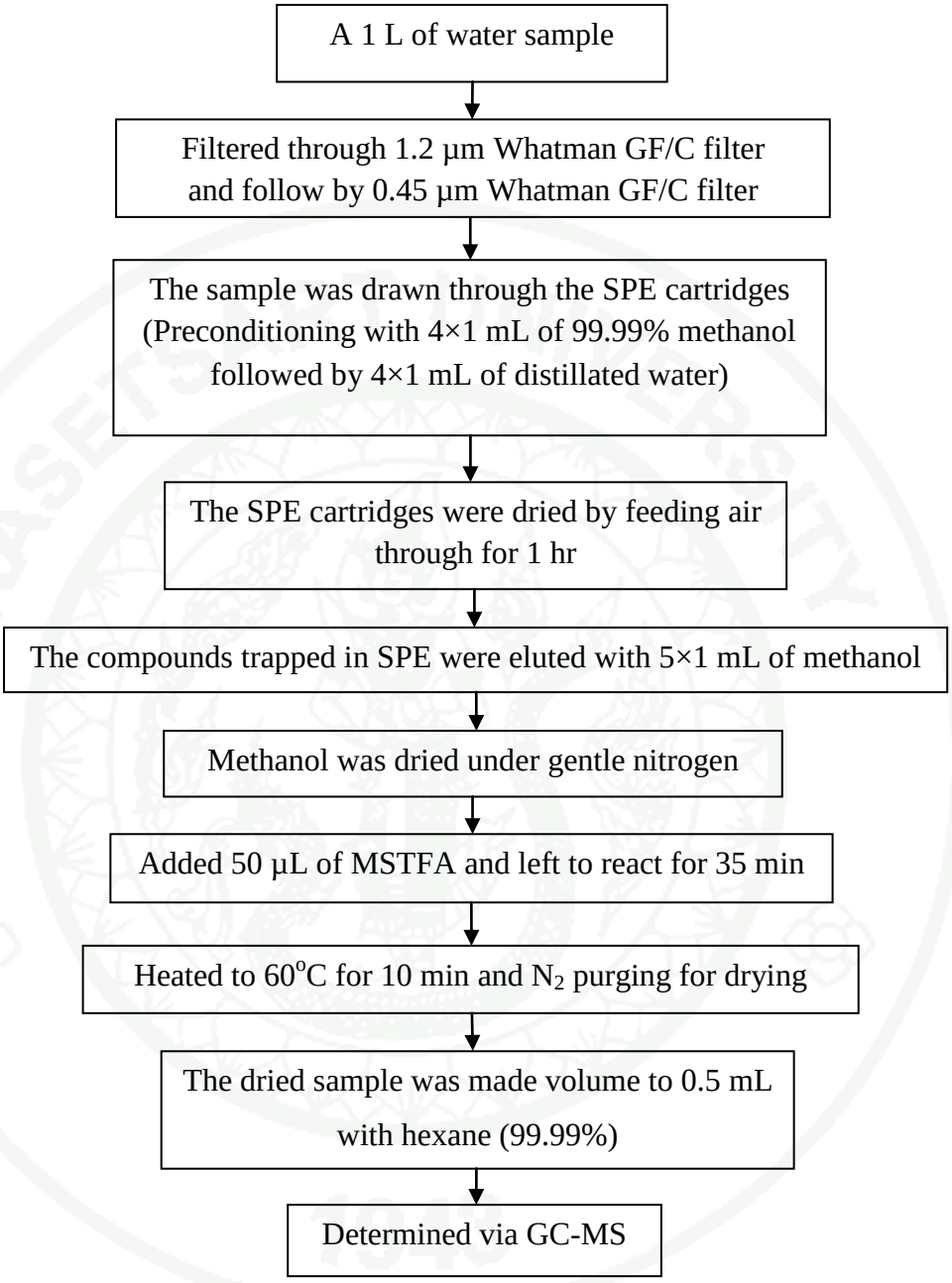
Figure 6 Location of water sample collection points along the receiving canal

Methods

1. Paracetamol Extraction and Determination

1.1 Water sample

One litre of the raw wastewater sample was filtered through a ceramic 90 mm filter, with a 1.2 µm Whatman GF/C filter and followed by a ceramic 45 mm filter, with a 0.45 µm Whatman GF/C filter. The SPE cartridge, filled with 100 mg (no end capped) of HCP-SA (Polyamide-Divinylbenzene Copolymer Trimethylaminopropyl, PA-DVBT, Ligand) was preconditioned with 4×1 mL of methanol (99.99%) followed by 4×1 mL of distillate water and the liquid phase was drawn through a SPE cartridge at a flow rate of approximately 5 mL a minute. When the sample had passed through, 4 mL of distilled water was used to rinse the solid phase, the cartridge was then dried by drawing air through it for 1 hr. The compounds trapped in SPE were eluted from the cartridges using 5×1 mL of methanol (99.99%) which was subsequently evaporated by using a gentle nitrogen stream. A 50 µL volume of the derivatisation compound (N-methyl-N-trimethylsilyltrifloroacetamide, MSTFA) was added and the vials sealed. The mixture was left for 35 min after which it was heated to 60 $^{\circ}$C for a further 10 min. The samples were again blown to dryness under the nitrogen stream, before being made up to a volume of 0.5 ml with hexane (99.99%) (Jones *et al.*, 2003) and analyzed via GC-MS. All samples were analyzed within 24 hr of derivatisation. The overall extract process is shown in Fig. 7.



Note: 4×1mL, Elute with 1 mL of methanol (4 times)

Figure 7 Extraction of paracetamol from wastewater sample

1.2 Sludge sample

A 100 g of the fresh sludge sample (22%TS) were added into 250 ml of distilled water, stirred at 150 rpm for 1 hr, under 50°C. Then, the 500 ml Teflon bottles were used to centrifuge samples for 15 min at 3500 rpm. The liquid phase was then collected (this process were carried out for 2 times), filtered and extracted as described above for the extraction of aqueous phase samples. Solid phase was added with 200 ml of methanol (99.99%) and carried out to homogenizing at 100 rpm. The mixer was centrifuged for 15 min at 3500 rpm, liquid phase (methanol) was evaporated (dryness) and the derivatives reagent (N-methyl-N-trimethylsilyltrifloroacetamide, MSTFA) were added. The samples were again purged to dryness under the nitrogen stream before being made up to a volume of 0.5 ml with hexane and analyzed via GC-MS. The overall extract process is shown in Fig. 8. Calculation of Paracetamol in the sludge is presented in the appendix B. It was noted that almost paracetamol more than 99.9% was eluted from the sludge in to the distilled water at 50°C (first step), therefore it is recommended for future study that further extraction with methanol in next step can be neglected in this sludge protocol.

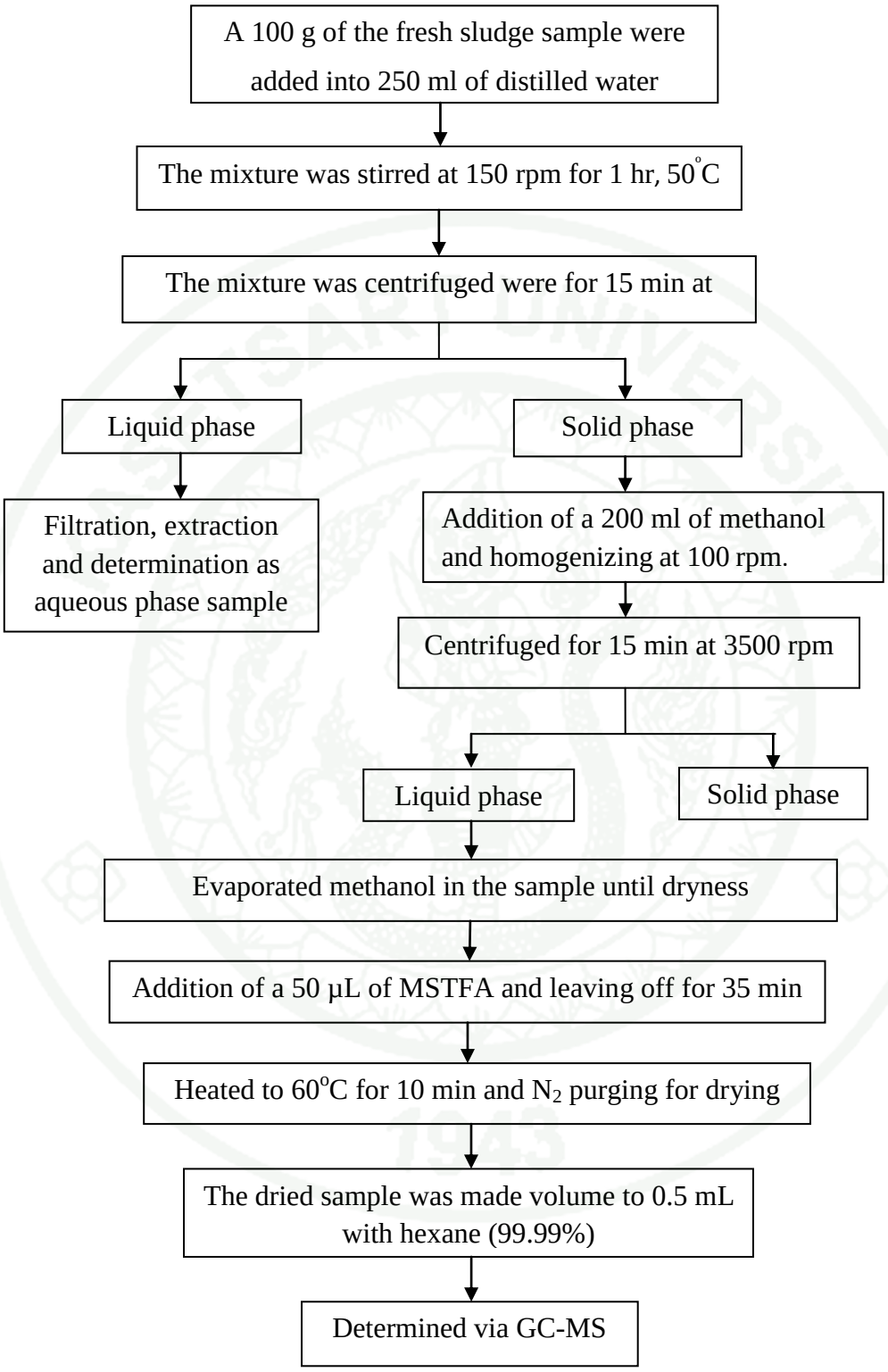


Figure 8 Extraction process of paracetamol in sludge sample

2. Adsorption/Desorption Experiment

2.1 Preparation of disposal sludge

The fresh sludge sample was sterilized at 121^{o}C for 15 minutes in triplicate. The microbial activity testing of each sterilized sample was performed prior to be used in the experiment in order to confirm that microorganism has not activity during the adsorption and desorption procedure. The determination of the amount of CO_2 released from the activated sludge was investigated. The sample of 10 g was placed into the serum vial 50 mL thereafter sealed and left for two days at 4^{o}C. The headspace gas in the vial was taken and determined for CO_2 concentration through GC, then it was determined again when it was left at 25 $^{\circ}$C for 2 h and at 30 $^{\circ}$C for 5 days.

2.2 Adsorption-desorption experiment

Equilibrium batch experiments were conducted to determine adsorption and desorption isotherms of paracetamol on the activated sludge. The 22.7 gram of sterile sludge was added in a 100 mL of normal saline (0.85%NaCl) at 50°C for 5 min in order to wash out the excess paracetamol in the sludge, and then the sample were centrifuged at 25°C for 15 min at 3500 rpm in order to take the normal saline out. The sludge was mixed with varied concentrations (C_0) of paracetamol (2, 4, 6, 8, or 10 µg/L) in 1 L in the glass bottom and covered under aerobic conditions and then the mixtures were stirred at 150 rpm for 1 h (the end of the adsorption equilibrium time), the mixtures were subsequently centrifuged at 25°C for 15 min at 3500 rpm. An aliquot of supernatant solution were filtered, extracted and analyzed by the GCMS system (as described above for the extraction of wastewater samples). The solid phase were then desorption experiment, 1 L of water were added in to the sludge and the mixtures were stirred at 50°C for 1 hr. (the end of the desorption equilibrium time), the mixtures were subsequently centrifuged, an aliquot of supernatant solution were filtered and extracted as described above. The overall experiment is shown in Fig. 9.

Adsorption experiment

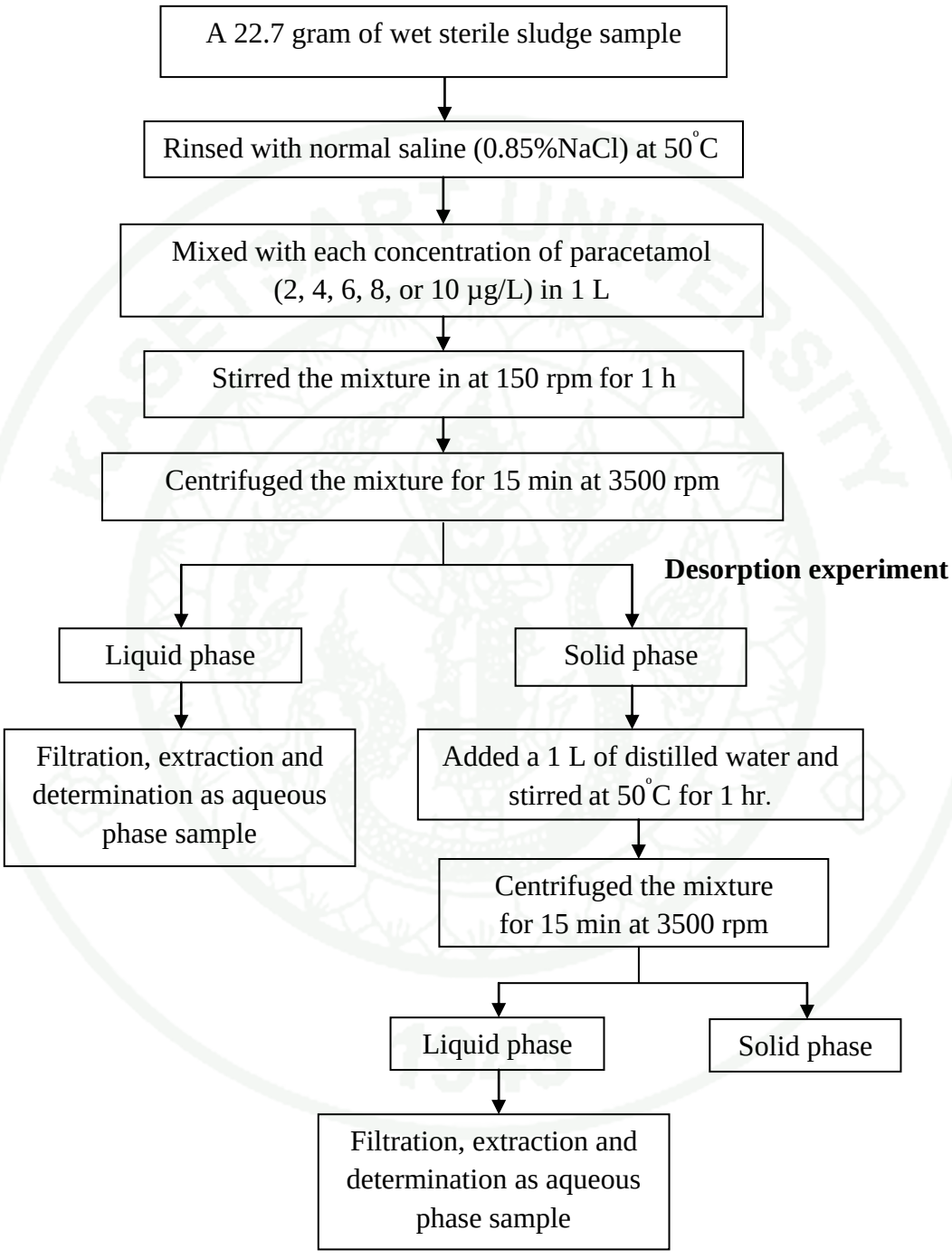


Figure 9 Determination of Adsorption-desorption of paracetamol

RESULTS AND DISCUSSION

1. Concentrations of Paracetamol in Sewage, Settled Sewage and Effluent

The concentrations of Paracetamol in sewage, settled sewage and effluent varied insignificantly during investigation period with in ranges of 500-800 ng/L, 440-750 ng/L, and 170-288 ng/L respectively (Figure 10). Although the concentrations of Paracetamol in the effluent existed in nano levels, however the large volumes of the discharge treated water were about 200,000-300,000 cu.m/d, therefore the daily discharged Paracetamol into the receiving canal was 40.67 g/d on average.

The occurrence of paracetamol as environmental contaminants is demonstrated by reports of their presence around the world in WWTP influents and effluents in ranges of 281-211,380 ng/L and <20-11,730 ng/L, respectively as shown in Table 14. Similarly, the concentrations of Paracetamol compound in this study were found in those ranges. The variation may be due to the different density in population in the area or regional variations in drug use or possibly due to the high density of pharmaceutical industries or local hospital output. According to the usage of paracetamol is on the rise with an estimated increase during 2000 to 2009 in Thailand (Food and Drug Administration, 2009). Paracetamol enters into the environment through individual human activities and as residues from manufacturing, agribusiness, hospital and community usage. Individuals may lead paracetamol into the environment through waste excretion and bathing as well as by directly disposing of unused medications to septic tanks, sewers, or trashes.

Because paracetamol tends to dissolve relatively easily and does not evaporate at normal temperatures, it often ends up in soil and water contents. While the full effects of paracetamol on the environment are not understood, there is concern about the potential for hazard because of its unpredictable performance when mixed with other chemicals from the environment or concentrate in the food chain that is a reason to concerning the chronic effect of this chemical. Therefore, it is more necessary to be

known about its persistence in the environment for further risk evaluation. It is likely that other pharmaceuticals with appropriate physio-chemical properties were not analyzed for this study that may also present and contaminate in the aquatic environment.

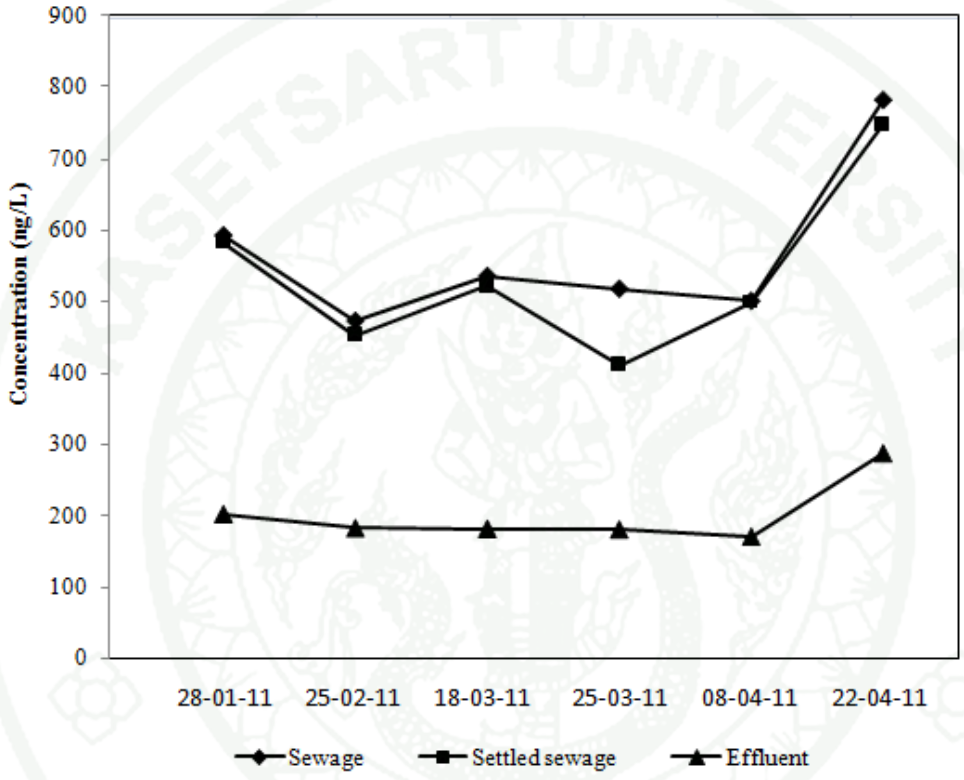


Figure 10 Distribution of Paracetamol in the activated sludge process

Table 14 Comparisons of paracetamol concentrations previously found in some sewage treatment plant (AS) of the other countries

Country	Concentration (ng/L)			$\%R_{aq}$	Techniques	Reference
	Influent	Effluent	Receiving canal			
UK	281	218	165	22.42	GC-MS	Bound and Voulvoulis et al., 2006
	211,380	11,730	650	94.45	Quatro Micro triple-	Kasprzyk-Hordern et al., 2009
	178,120	353	305	99.80	quadrupole-MS	
	6924	<20*	0	100	HPLC-ESI-MS/MS	Roberts and Thomas, 2006
Norway	12,424	785	-	93.68	LC-MS	Thomas et al., 2007
Greece	20,600	900	-	95.63	GC-MS	Kosma et al., 2010
	9,300	3,600		61.29		
England	2,262	187	-	91.73	GC-MS	Jones et al., 2005
Thailand	**566**	**201**	**170**	**64.66**	**GC-MS**	**This study**

Note: * The following pharmaceutical compounds <limit of detection

2. Concentrations of Paracetamol in Disposal Sludge

The concentrations of Paracetamol in disposal sludge varied insignificantly during investigation period with in ranges 14.5-18.2 ng/g dried sludge (Table 15).

Table 15 The concentrations of Paracetamol in disposal sludge

Sample times	Concentration (ng/g dry sludge)
18-3-54	16.8
25-3-54	18.2
8-4-54	16.9
22-4-54	14.5

According to the analysis of Paracetamol in the sludge (section 1.2, Methods), it suggests that at 50°C all of the amount of Paracetamol can dissolve out from the solid phase to water phase. Therefore, leaching of Paracetamol from the disposal sludge in landfill may be easily occurring due to common high temperature in landfill matrix.

The occurrence of paracetamol was found in the sludge in AS process fluctuate in ranges of 0.08-119 ng/g dry as shown in Table 6. The concentrations of Paracetamol compound, in this study were found in those ranges. The variation may be due to the methodology of extraction paracetamol from the sludge matter. Beside, this may be due to different characteristics of biomass in the sludge such as sludge age, microbial species, etc.

Sorption of paracetamol contributed to the elimination from the aqueous phase with more than 20% related to the amount of this compound at the influent. This finding clearly indicates the importance of the analysis of sludge when studying wastewater treatment performances. Since many of the analyzed compounds were found in the sludge samples, the overall removal rate was the parameter used to

compare the removal performances of the studied treatment plants (Yu and Wu, 2012). The amount found in effluent or sludge depended on the removal efficiency of plant and/or the physicochemical properties of the compounds. As the influent concentrations can give us information about the consumption of pharmaceuticals, the effluent and the sludge concentrations are important from the environmental point of view, since the pharmaceuticals find their way to the environment through discharges of treated waters to rivers, or disposal of sludge to agricultural and forest land (Jelic *et al.,* 2011). Sludge generated in waste water treatment process can be a major sink for some pharmaceutical and personal care products (PPCPs). The land application of sewage sludge can therefore potentially introduce PPCPs into the environment (Chenxi *et al.,* 2008).

3. Concentrations of Paracetamol in Receiving Canal

The concentrations of Paracetamol in the receiving canal at 1, 2, and 3 km from the discharge point were 114-231 ng/L, 95-216 ng/L and 135-230 ng/L respectively. They were found proximate levels to those in the effluents (170-288 ng/L) as shown in Figure 11, which indicates that slight degradation of Paracetamol was found in the receiving canal during 3 kilometers from the discharged point. The occurrence of Paracetamol in the receiving canals and rivers in the other countries were in ranges of 0-650 ng/L as shown in Table 14. The concentrations of Paracetamol compound, in this study were found in those ranges. These variations are dependent on the processes involved and weather conditions in the region. It is also possible that human metabolites, such as glucuronide conjugates, may be hydrolysed back to the parent compound during wastewater treatment or even in the environment. This may lead to greater than expected concentrations in rivers. In some cases the products of the metabolic and treatment processes may exhibit similar or even greater toxic effects than the parent compound (Roberts and Thomas, 2006).

Bound and Voulvoulis, 2006 also reported that the improper disposal of unused medicines, in household waste or via the toilet instead of returning to a pharmacist may be a factor. Any medicines flushed down the toilet bypass the metabolic processes within the body where, in the case of paracetamol, for example, 96% of the parent compound is modified. These compounds, which in the case of household waste disposal also avoid removal in the WWTW, could be making a disproportionate contribution to the overall environmental load.

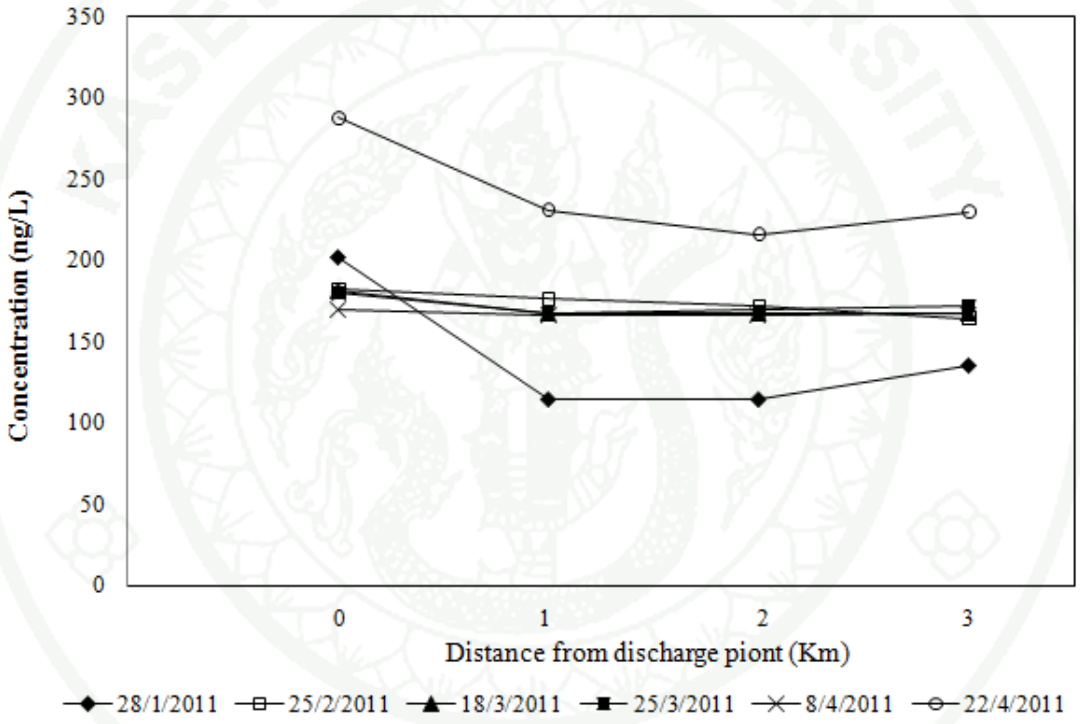


Figure 11 Concentrations of Paracetamol in the receiving canal compared to the effluent

4. The Removal rate of Paracetamol during the Activated Sludge Process

Mass balance of the flow of paracetamol through the activated sludge process was performed by using the results from the concentration analysis multiplied by daily flow rate of the wastewater. The aqueous-phase removal, R_{aq} (%) is obtained from Eq. 6. For the adsorption removal, R_{ad} (%), paracetamol content in the sludge and MLSS concentration in aeration tank are used in absorbed mass calculation (M_{ad}), as shown in Eq. 7. The calculated biodegradation removal, $R_{cal\ biodeg}$ (%), of the target compound was calculated from subtraction between influent mass, effluent mass and adsorbed mass, M_{bio} as shown in Eq. 8.

$$\%R_{aq} = 100 \times \frac{M_{in} - M_{eff}}{M_{in}} \quad (6)$$

$$\%R_{ad} = 100 \times \frac{\text{Adsorbed Mass in Sludge } (M_{ad})}{M_{in}} \quad (7)$$

$$\%R_{cal\ biodeg} = 100 \times \frac{M_{in} - (M_{ad} + M_{eff})}{M_{in}} \quad (8)$$

Where; $M_{in} = Q_{in}C_{in}$

$M_{out} = Q_{eff}C_{eff}$

$M_{ad} = C_{MLSS}C_{ds}$

$M_{bio} = M_{in} - M_{ad}$

$Q_{influent} = Q_{effluent}$ = Flow rate of water (m^3/d)

$C_{in} = C_{influent}$ = Concentration of Paracetamol in influent (ng/L)

$C_{eff} = C_{effluent}$ = Concentration of Paracetamol in effluent (ng/L)

MLSS = The amount of MLSS (ton/d)

C_{ds} = Concentration of Paracetamol in disposal sludge (ng/g dry sludge)

R_{aq} is the total mass removed by the activated sludge treatment. M_{in} was the total mass of entering paracetamol from the process. M_{eff} is the total mass leaving the process in the effluent (Jelic *et al.*, 2011). M_{ad} is the total adsorbed mass in the MLSS

and M_{bio} was calculated from subtraction between influent mass, effluent mass and adsorbed mass. The removal rate (%) of Paracetamol during the activated sludge process is shown in Table 16. As the result, paracetamol removal from aerated grit chamber ($\%R_{ag}$) was varied insignificant and very low (0-3.74%), these may be due to paracetamol was much soluble in water more than adsorption on grits or other settleable solids. However, the significant difference was observed for paracetamol removal on 25th Mar, 2011, showed higher removal (21%). This may be due to variation contents of organic settleable solids of incoming wastewater, which might be high on that day.

It was found that the removal from aqueous-phase ($R_{aq\text{-}phase}$) was 64.69% on average. By calculation of a missing part in mass balance equation as shown in Eq. 9, the biodegraded Paracetamol in the activated sludge process was 58.01% on average. This result is different from many researchers (Roberts and Thomas, 2006 and Kasprzyk-Hordern *et al.,* 2009) who reported that over 99% removal of Paracetamol in AS process is by biodegradation. However, in this study we found that the removal of Paracetamol in the AS was much lower than this from some other countries (Table 14). This could be due to regional variations in usage or differences in WWTP capabilities. The efficiency of the removal of PPCPs strongly depended on the wastewater technology implemented in WWTP (Kasprzyk-Hordern *et al.,* 2009). Besides, in this study, we also found that not only biodegradation, adsorption of Paracetamol in the AS process were 4.5-8.4 %, by calculation from the mass of Paracetamol in the disposal sludge. As the result, indicated that adsorption of Paracetamol in the AS process is one of the removal mechanisms in Bangkok's sewage Treatment Plant.

$$M_{in} = M_{ad} + M_{bio} + M_{eff} \quad (9)$$

Table 16 Fates of Paracetamol in the activated sludge process

Sample	Mass of Paracetamol (g/d)						avg	sd
	28-1-11	25-2-11	18-3-11	25-3-11	8-4-11	22-4-11		
1. Sewage	144	107	103	100	92	144	115.0	23.3
2. Settled sewage	143	103	101	79	92	139	109.5	25.86
$\%R_{ag}$ (1-2)	0.99	3.74	1.94	21.00	0.00	3.47	5.19	7.88
3. Effluent	49	41	35	35	31	53	40.67	9.85
$\%R_{aq}$ (1-3)	65.97	61.68	66.02	65.00	66.30	63.19	64.69	3.88
4. Disposal sludge	nd	nd	0.024	0.026	0.020	0.017	0.022	0.004
5. M_{ad} ($MLSS_{ad}$)	-	-	7.74	8.36	7.45	6.42	7.50	0.81
% R_{ad}	-	-	7.52	8.36	8.14	4.46	7.12	1.81
$\%R_{cal\ biodeg.}$	-	-	58.50	56.64	58.17	58.74	58.01	0.95

Note: nd: not determined; aq: aqueous phase; ad: adsorption; cal biodeg: calculated biodegradation, avg: average, sd: standard deviation; %R: removal percentage; $MLSS_{cal}$: calculated adsorbed paracetamol in MLSS; ag: aerated grit chamber

5. Adsorption-Desorption Isotherm

5.1 Microbial activity examination

As shown in Figure 12 it can be seen that CO_2 had been produced when the temperature was increased from 4°C to 30 -40°C. At 4°C, the rate of CO_2 production remained steady of about 0.5 µgCO_2/g dry sludge-h for 2 days (48 h). After left the sample at 25°C for 2 h, the rate of CO_2 production was not changed indicating that the microbial activities remained unchanged during this period. Finally, after left at room temperature (30-40°C) for 5 days (120 h), the average production activity of CO_2 increased to 87.14 µgCO_2/g dry sludge-h. The microorganisms have grown under aerobic conditions in the fermentative metabolic pathways resulted the increases of the CO_2 production rate and O_2 uptake rate with time (Fig. 13). According to increasing CO_2 production at the room temperature, it suggests that the future experiment must be aware about microbial activity at room temperature (30-40°C) for a long term study. This study showed that triplicate sterilization of the sludge could not complete degermination since carbon dioxide production indicated the re-growth of some heat tolerable microorganisms. Because the adsorption-desorption experiment had been run for 1-3 h, therefore there might be less biological degradation of Paracetamol by the activated sludge during the adsorption-desorption studied.

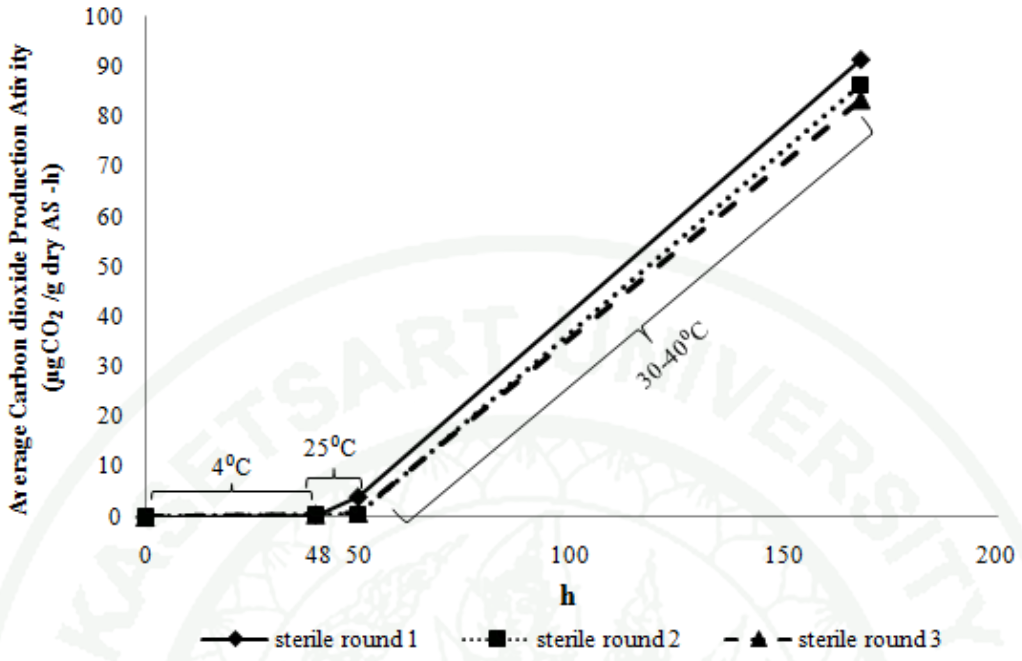


Figure 12 Average rate of carbon dioxide production of the sterile activated sludge in different temperature

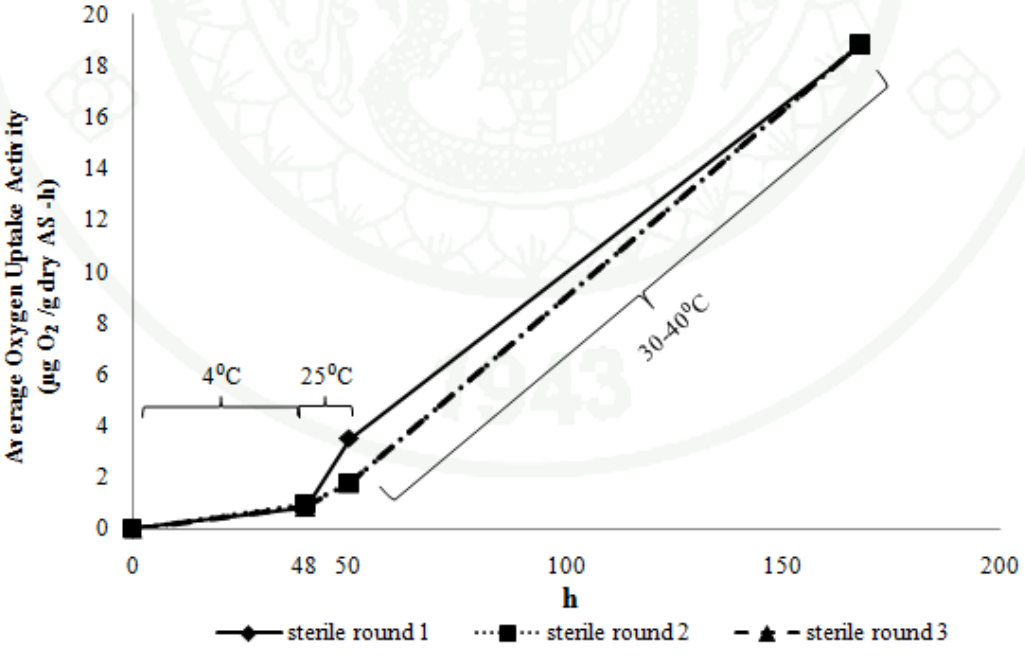


Figure 13 Average rate of oxygen uptake of the sterile activated sludge in different temperature

5.2 Adsorption and desorption isotherm of paracetamol on activated sludge

The data of adsorption and desorption were analyzed using the Freundlich equation that can be linear by taking logarithms to find out the parameters K and n. The results of log of Paracetamol dosages/remaining in water were plotted in linear form as shown in Fig.14 and 15, the adsorption and desorption equations are obtained as follows:

Adsorption: $\log q_{ad} = 1.255 \log C_e - 0.456$ (10)

Desorption: $\log q_{des} = 1.000 \log C_e - 0.699$ (11)

As the result, summarized of adsorption and desorption isotherms are shown in Table 17. K_F value of adsorption in activated sludge was higher than that in the desorption process, which suggests that some fractions of Paracetamol is reversibly bound to the activated sludge. The n value of adsorption and desorption was equal 1.255 and 1.00 respectively which is indicative of linear adsorption and desorption isotherms respectively. Moreover, the differences between paracetamol adsorption and desorption isotherms were found as increase in initial concentration (C_i) as shown in Fig. 16. The initial concentration of Paracetamol is higher, the discrepancy of adsorption and desorption mass of paracetamol on sludge will be larger. As the correlation coefficient (r^2) measures the strength of the linear relationship, it is used to determine how well the Freundlich model represents the data. It showed with 98% for adsorption and 100% for desorption, the level of significance that the Freundlich model adequately represents the data.

Besides, these isotherms were used to calculate the adsorption potential of Paracetamol on the studied activated sludge. By assumption of the amount of Paracetamol adsorbed/desorbed at the equilibrium when of effluent equal 201 ng/L. It indicates that the activated sludge can adsorbed Paracetamol of 272 ng/g,dry. In this study, Paracetamol adsorption on the activated sludge in batch was higher than the real plant (14.5-18.2 ng/g,dry), this might be due to the high concentrations of

Paracetamol in the experiment, which is much larger than that in the real situation. As according to Freundlich equation, adsorption capacity is enhanced by initial concentration of the solute. Besides, desorption of the absorbed Paracetamol possibly occurs in clean environment of 40.2 ng/g,dry or 15 % of the total absorbed mass (Table 17), it suggests that the sludge should be carefully handled/treated further to avoid fate of Paracetamol into the environment. As the desorption experiment which increasing the temperature to 50°C that in order to estimate the probability of desorption of paracetamol in the landfill where the place had high temperature which may be concern about desorption of paracetamol in the leachate landfill and may be contain in the environment.

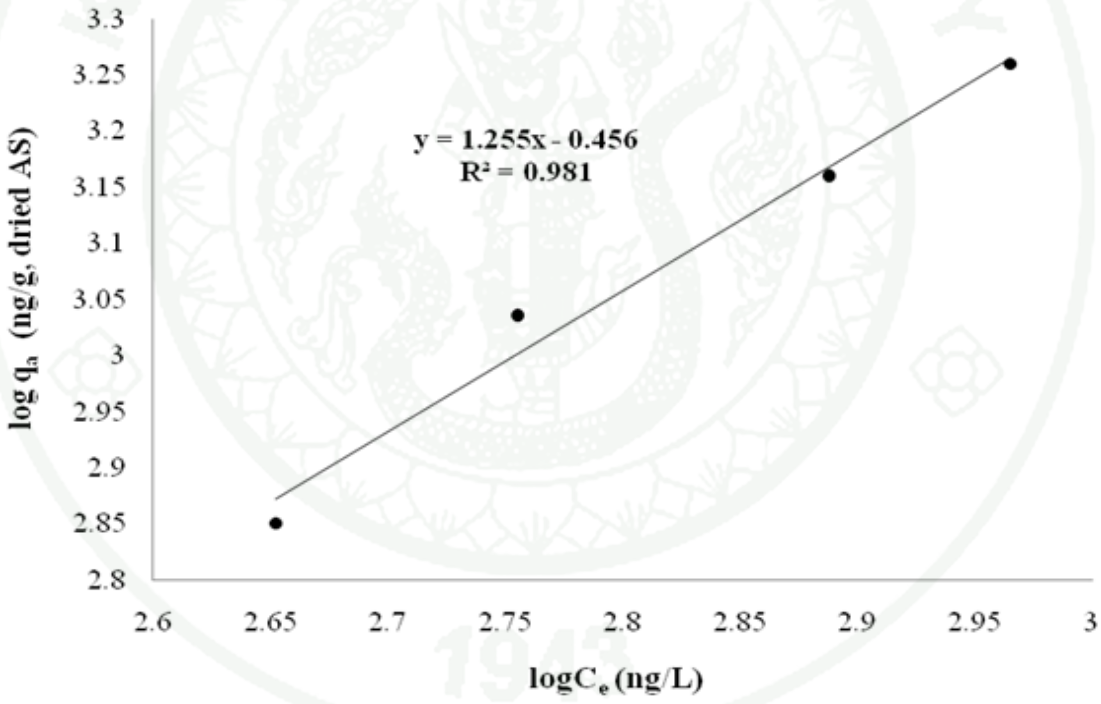


Figure 14 Adsorption isotherm of Paracetamol on activated sludge

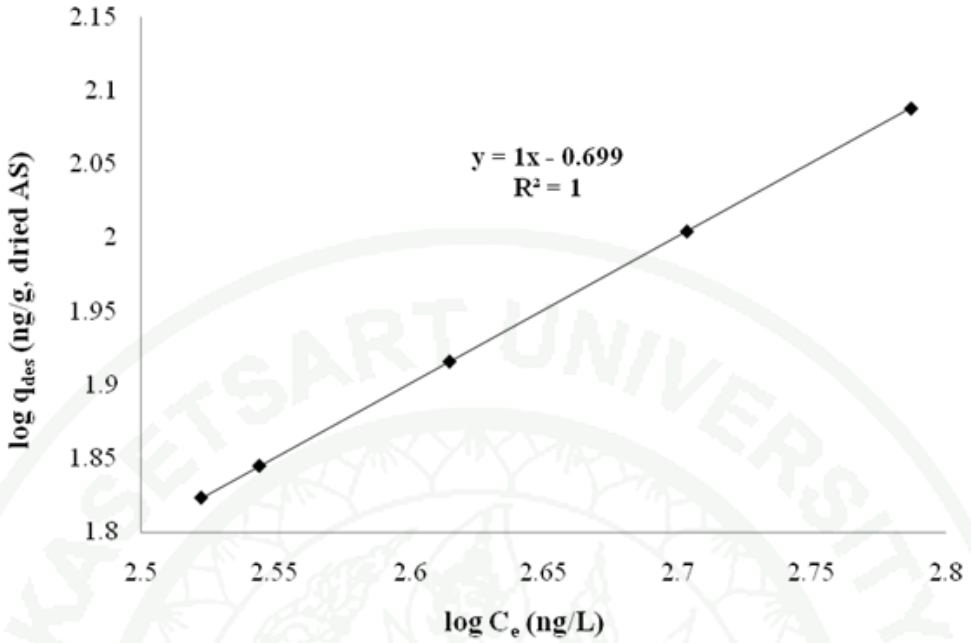


Figure 15 Desorption isotherm of Paracetamol on activated sludge

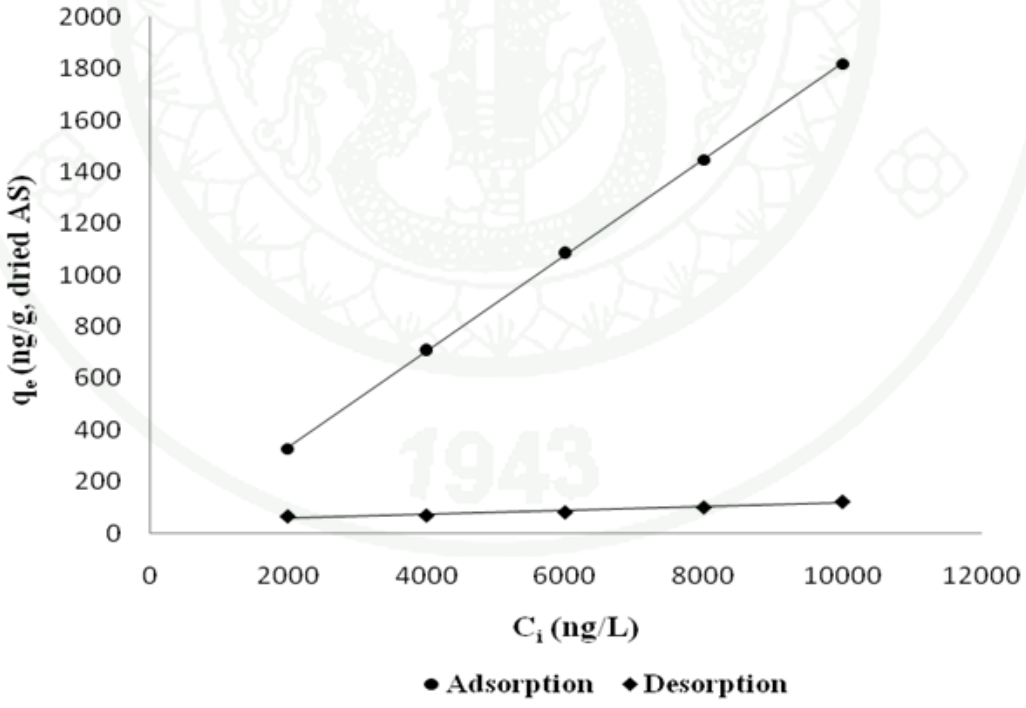


Figure 16 Adsorption and desorption of paracetamol on activated sludge with different initial paracetamol concentration (C_i)

Table 17 Freundlich isotherms of adsorption and desorption of Paracetamol on the sludge

Regress equation	**log K_F**	**K_F**	**n**	***R^2***	**q_e (ng/g) at C_e=201 ng/L**
Adsorption	- 0.456	0.35	1.255	0.98	272
Desorption	- 0.699	0.2	1.000	1.00	40.20

CONCLUSION

The concentrations of Paracetamol in sewage, settled sewage, effluent and disposal sludge varied insignificantly during investigation period with in ranges of 500-800 ng/L, 440-750 ng/L, and 170-288 ng/L and 14.5-18.2 ng/g dried sludge, respectively. Determinations of Paracetamol in the AS discharge water/sludge and receiving canal samples indicate high persistence in biodegradation by exhibiting several hundred nanograms of concentrations. The existing AS process is moderate efficient to remove Paracetamol from Bangkok's sewage by only 61-66% in which 56.6-58.7% by biodegradation and 4.5-8.4%. The concentrations of Paracetamol in the receiving canal were found proximate levels to those in the effluents which indicate that slight degradation of Paracetamol was found in the receiving canal during 3 kilometers from the discharged points. As the result, the concentrations of Paracetamol several hundred nanograms per litre (170 ng/L) were still present in the effluent when it was discharged. In addition, in batch adsorption-desorption studies indicates the activated sludge can adsorbed Paracetamol of 272 ng/g,dry and desorption of Paracetamol from the sludge into clean water was 15% of the total adsorbed one. Adsorption and desorption isotherms of Paracetamol were measured by using freundlich equation indicated the Freundlich constant, K_F is 0.35 and 0.2 respectively, and the Freundlich exponent, n is 1.255 and 1.00 respectively. The data showed that the differences between Paracetamol adsorption and desorption isotherms were larger when the Paracetamol concentration increased. Therefore, these would seem to indicate that adsorption of Paracetamol in the AS process is a significant removal mechanism.

RECOMMENDATION

1. As the results, paracetamol were not completely removal by activated sludge process. In future study should investigate the environmental factors influence on paracetamol removal by the activated sludge such as temperature, pH and sludge ages.

2. In the determination of Paracetamol process, after extracting the compound with SPE cartridge, should be eluting with methanol rapidly, if not it should be kept in freezer at temperature < 0°C. Besides, all samples should be analyzed within 24 h of derivatisation.

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APPENDICES

Appendix A

Determination of Paracetamol by GCMS

1. Condition of GC/MS

1.1 Instrumentation

Gas Chromatograph acquisition parameters: Shimaszu QP 2010 with a auto-sampler, a programmable temperature, splitless capillary column injector fitted with a RTx 35 column (length 30 m, internal diameter 0.25 mm, and trickiness 0.5 µm) with Helium as the carrier gas, a total flow of 50 ml/min, a column flow 0f 1 ml/min and a purge flow of 3 ml/min. The GC oven temperature program was 50°C, held for 7.5 min, then increased at 30°C min^{-1} to a final temperature of 270°C which was held for 10 min.

1.2 Mass Spectrometric Acquisition Parameters

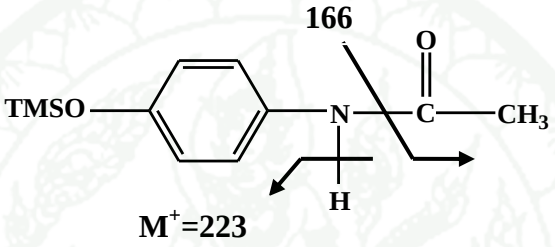
Mass spectrometric electron impact source conditions were as follows: Ion source, 200°C; ionizatio voltage 70 V; emission current 150 uA. Identification and quantification was performed by selected ion monitoring using the most abundant and diagnostic ions of each compound. Matches for poor quality mass spectra can lead to mis-identification of compounds, peak identities were therefore confirmed by the use of a secondary ion. The characteristic ion for quantification of compound and the secondary ion for peak confirmation were 223 and 166 respectively. The dwell time for each channel was 0.1s and the ion groups used for identification in the SIM mode.

2. Preparation of Calibration curves

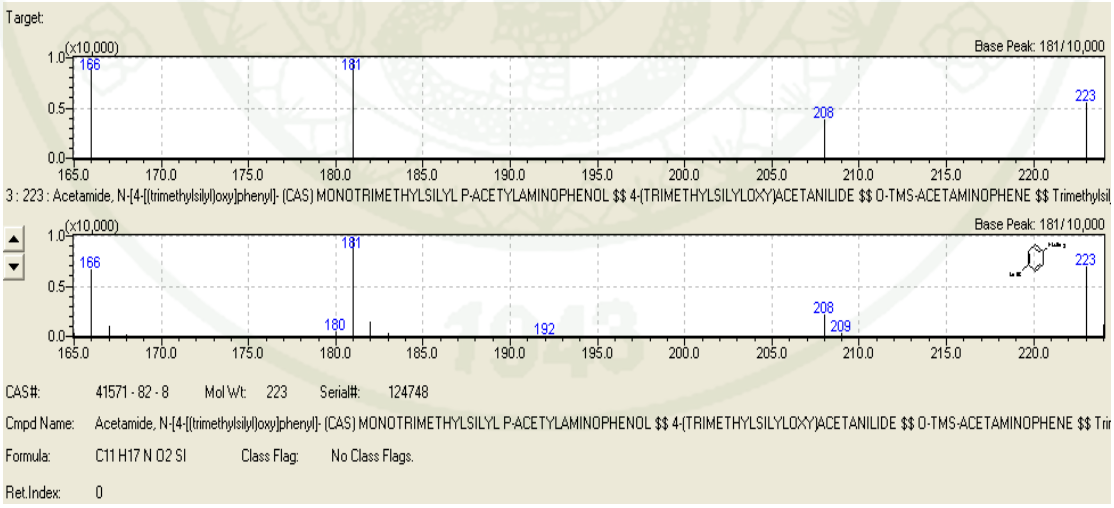
The 100 mg of paracetamol standard (Standard grade (Purity 99.98%), Sigma Aldrich, UK) was dissolved in 100 mL of methanol (Analytical grade, Purity 99.99%, J.T.Baker) to give a 1000 mg L^{-1} stock solution. This was then diluted again to a 100 ppm solution. From this a series of standards were developed containing the paracetamol, in methanol, in the range of 0.5 to 10 ppm (0.5, 2, 4, 6, 8 and 10 ppm).

A 50 µl volume of the derivatisation compound, MSTFA (N-methyl-N-trimethylsilyltrifloroacetamide, Derivaization grade, Sigma Aldrich, UK), was added

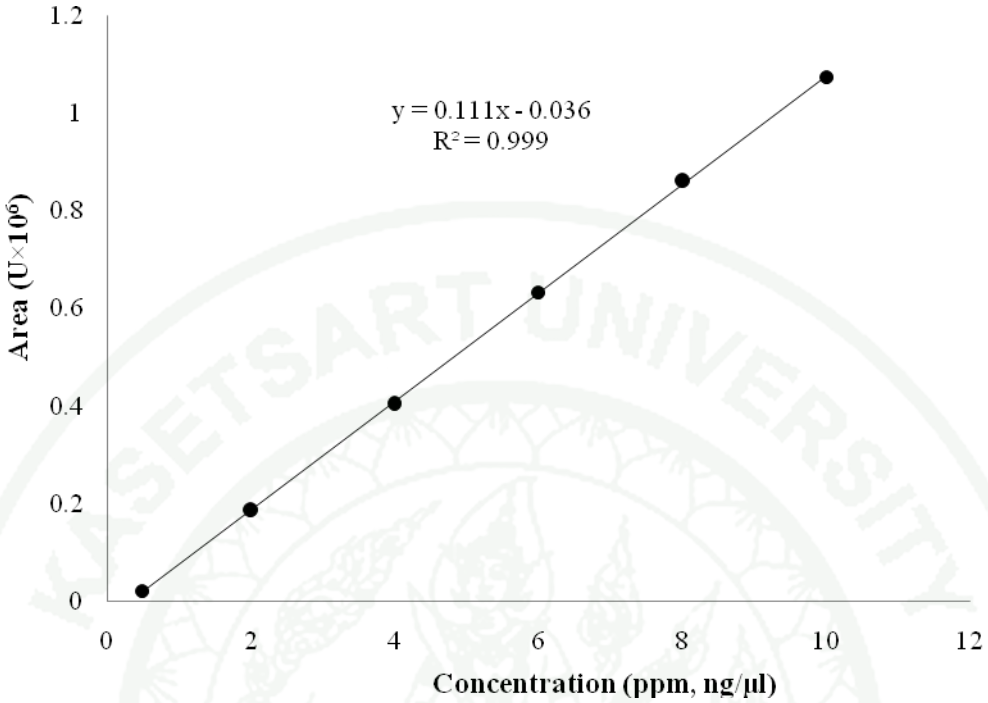
and the vials sealed. The mixture was left chemical reaction for 35 min after which it was heated to 60°C for a further 10 min. The samples were again blown to dryness under the nitrogen stream (HP grade, Purity 99.99%, TIG), before being made up to a volume of 1 mL with hexane (Analytical grade, Purity 99.99%, J.T.Baker) and analyzed via GC-MS, Calibration curve in each run, preferably in triplicate . Standard solutions were used to identify peak retention times (15.8-15.9 min) to subsequently calibrate the instrument (Appendix Figure A3), the resulting calibration curves were linear within the concentration range and correlation coefficients were 0.9998.



Appendix Figure A1 The chemical structures of the TMS derivatives of the paracetamol (Acetamide, N-[(trimethylsilyl)oxy]phenyl]



Appendix Figure A2 The typical mass chromatographs of the TMS derivatives of the paracetamol (Standard)



Appendix Figure A 3 The calibration curve of the TMS derivatives of the paracetamol

3. Validation

3.1 Calculation of Limit of detection (LOD) and Limit of quantitative (LOQ)

The limit of detection and the limit of quantification were calculated for this method using the calibration data (as shown in Appendix Figure A3), the resulting calibration curves were linear within the concentration range and correlation coefficients were 0.9998.

$$LOD = Y_b + 3S_b$$

$$LOQ = Y_b + 10S_b$$

The equation; $y = 0.111x - 0.036$ (1)

Where, Y_b is intercept Y (-0.036)

S_b is standard deviation of intercept Y (0.00365)

$$Y_b+3S_b = -0.036 + (3\times0.00365)$$

$$Y = - 0.02$$

Substitute, Y = -0.02 in equation (1) to find x

$$-0.02 = 0.111x - 0.036$$

$$X = 0.144$$

Therefore**,** LOD is 0.144 ppm (ng/µl) and the LOQ is 0.32 ppm (ng/µl).

3.2 Recovery studies

A distillated water were spiked with the drug standards and recovery studies were performed at fortification levels of 0.5 and 1.2 µg L^{-1}. The percentage recovery was calculated by dividing the concentration found, by the concentration expected from the standard solution (using the previously established calibration curves) and multiplying by 100 as shown in eq. 2. The results of the recovery experiments in distillation waters (Average recovery (%) ±S.D, n = 3) at the concentration of 0.5 µg/L and 1.2 µg/L were 82±0.006% and 89±0.01% respectively (Appendix Table A1).

% Recovery = 100*(Estimated Concentration)/True Concentration (2)

Appendix Table A1 The result of %Recovery of distillation water

Level (µg/L)	**Concentration (µg/L)**				**%Recovery**	**S.D**
	(1)	(2)	(3)	Ave		
0.5	0.414	0.419	0.407	0.41	82	0.006
1.2	1.061	1.082	1.065	1.07	89	0.01

Appendix B

Experimental Data

Appendix Table B1 The moisture content (%) of disposal sludge

Wet weight of sample (g)	Dry weight of sample (g)	$W_w - W_d$	Moisture content (%)	Ave.
(1) 3.0074	0.6525	2.3549	78.30	
(2) 3.0146	0.6546	2.3600	78.29	78.28 %
(3) 3.0222	0.6567	2.3655	78.27	

Appendix Table B2 The concentration of paracetamol in wet disposal sludge sample

Sample times	Concentration (ng/100g, wet sludge)				
	(1)	(2)	(3)	Ave	SD
28-1-54	nd	nd	nd	-	-
25-2-54	nd	nd	nd	-	-
18-3-54	391	379	370	380	8.60
25-3-54	417	419	392	409.33	12.28
8-4-54	376	377	387	380	4.97
22-4-54	351	330	330	337	9.90

Note: nd: not determined

Appendix Table B3 The concentration of paracetamol at each sampling point over the sampling period

Sampling point	Concentration (ng/L) (Mean, n=3)											
	28-1-11				25-2-11				18-3-11			
	(1)	(2)	(3)	**Ave**	(1)	(2)	(3)	**Ave**	(1)	(2)	(3)	**Ave**
Influent	592	590	595	592	472	470	475	472	534	539	531	535
Settled sewage	586	580	585	584	450	450	455	454	519	524	522	522
Effluent	201	200	205	202	182	180	185	182	176.5	179.5	186.5	181
Canal. 1	117	115	110	114	177	175	177	176	166	166.5	168	167
Canal. 2	116	110	115	95	175	170	172	172	168	166.5	166	167
Canal. 3	139	135	130	135	166	160	165	164	168	166	167	167

Appendix Table B3 (Continued)

Sampling point	Concentration (ng/L) (Mean, n=3)											
	25-3-11				8-4-11				22-4-11			
	(1)	(2)	(3)	**Ave**	(1)	(2)	(3)	**Ave**	(1)	(2)	(3)	**Ave**
Influent	512	518	520	517	506	496	497	500	788	780	777	782
Settled sewage	449	444	430	441	466	500	499	499	743	756	750	750
Effluent	179.5	181	178.5	180	170.5	169.5	169	170	294	230	230.5	288
Canal. 1	171	166.5	162.5	167	167	167	164.5	166	234	230.5	230.5	231
Canal. 2	170.5	169	168.5	169	166	167.5	165	166	216.5	217.5	214.5	216
Canal. 3	172.5	171	171.5	172	168.5	167	166.5	167	231.5	229	230	230

Appendix Table B4 The CO_2 production from activated sludge (Assume initial day, CO_2 = 0.03%)

Sample sterile	CO_2 production (μgCO_2/g dry AS-h)								
	2 day at 4°C			2 h after left at 25°C			5 day after left at 30°C		
	$\%CO_2$ current	$\%CO_2$ current - $\%CO_2$ initial	CO_2 production	$\%CO_2$ current	$\%CO_2$ current - $\%CO_2$ initial	CO_2 production	$\%CO_2$ current	$\%CO_2$ current - $\%CO_2$ initial	CO_2 production
Sterile 1st	0.096	0.066	0.45	0.121	0.025	4.02	34.28	34.157	91.60
Sterile 2nd	0.111	0.081	0.54	0.113	0.002	0.32	32.32	32.207	86.37
Sterile 3th	0.108	0.078	0.52	0.113	0.005	0.80	31.24	31.127	83.47

Appendix Table B5 Oxygen uptake rate (Assume initial day, O_2 = 21%)

Sample sterile	O_2 uptake rate (μgO_2/g dry AS-h)								
	2 day at 4°C			2 h after left at 25°C			5 day after left at 30°C		
	$\%O_2$ current	$\%O_2$ initial - $\%O_2$ current	O_2 reduction	$\%O_2$ current	$\%O_2$ initial - $\%O_2$ current	O_2 reduction	$\%O_2$ current	$\%O_2$ initial - $\%O_2$ current	O_2 reduction
Sterile 1st	20.66	0.34	0.84	20.6	0.06	3.51	1.3	19.3	18.82
Sterile 2nd	20.6	0.4	0.98	20.57	0.03	1.76	1.26	19.31	18.83
Sterile 3th	20.65	0.35	0.83	20.62	0.03	1.76	1.29	19.33	18.85

Appendix Table B6 The concentration of paracetamol base on adsorption and desorption on activated sludge

Level of sample (ng/L)	The concentration of paracetamol (ng/L)							
	Adsorption				Desorption			
	(1)	(2)	(3)	Ave	(1)	(2)	(3)	Ave
2000	372	370	370	371	334	332	332	333
4000	451	450	449	450	354	346	350	350
6000	570	569	568	569	412	414	410	412
8000	775	772	770	772	506	505	503	505
10000	922	920	922	921	614	612	610	612

Appendix Table B7 The amount of Paracetamol base on adsorption and desorption on activated sludge

Adsorption					Desorption				
C_i (ng/L)	C_e (ng/L)	log C_e (ng/L)	q_a (ng/g, dry AS)	log q_a (ng/g,dry AS)	C_1 (ng/L)	C_2 (ng/L)	log C_e (ng/L)	q_{des}(ng/g, dryAS)	log q_{des} (ng/g,dry AS)
2000	371	2.57	326	2.51	0	333	2.52	66.6	1.82
4000	449	2.65	710	2.85	0	350	2.54	70.0	1.85
6000	569	2.76	1086	3.04	0	412	2.61	82.4	1.92
8000	772	2.89	1446	3.16	0	505	2.70	101	2.00
10000	922	2.96	1816	3.26	0	612	2.79	122.4	2.09

Appendix C

Data Calculation

1. Moisture content determination

The sterile fresh sludge sample were measured the moisture content (%) by 3 gram wet of the fresh sludge (disposal sludge) sample was dried in oven at 105°C for 24 hr., weigh the gram dry of sludge and calculated the moisture content as eq. 3 (Benke and Kearfott, 1999):

$$M_c = ((W_w - W_d)/W_w) \times 100 \quad (3)$$

Where: M_c is the moisture content (%) of material n

W_W is wet weight of the sample

W_d is weight of the sample after drying.

2. Calculation of removal percentage (%) of paracetamol in activated sludge process

2.1 Calculation of removal percentage from aqueous-phase (%$R_{\text{Aqueous phase}}$, %R_{aq})

$$R_{aq}(\%) = 100 \times \frac{M_{in} - M_{eff}}{M_{in}}$$

Where; M_{in} = $M_{influent} = Q_{in}C_{in}$

M_{out} = $M_{effluent} = Q_{eff}C_{eff}$

$Q_{influent}$ = $Q_{effluent}$ = Flow rate of water

C_{in} = $C_{influent}$ = Concentration of Paracetamol in influent

C_{eff} = $C_{effluent}$ = Concentration of Paracetamol in effluent

Calculate mass of paracetamol in sewage (influent), M_{in} and in the effluent, M_{eff} on 18-3-11, using the average concentration of paracetamol in influent and effluent , 535 ng/L and 181 ng/L respectively that shown in Appendix Table B3. The flow rate (Average in each month) of wastewater entering the process, 192,943 m^3/d was used from the data in Table 11.

The concentration of paracetamol in influent (C_{in}) = 535 ng/L

The concentration of paracetamol in effluent (C_{eff}) = 181 ng/L

The average flow rate of wastewater (Q_{in}) = 192,943 m^3/d

$$M_{in} = \frac{192{,}943\ m^3}{d} \times \frac{535\ ng}{L} \times \frac{1000\ L}{m^3} \times \frac{1\ \mu g}{1000\ ng} \times \frac{1\ mg}{1000\ \mu g} \times \frac{1\ g}{1000\ g}$$

$$= 103.22\ g/d$$

$$M_{eff} = \frac{192{,}943\ m^3}{d} \times \frac{181\ ng}{L} \times \frac{1000\ L}{m^3} \times \frac{1\ \mu g}{1000\ ng} \times \frac{1\ mg}{1000\ \mu g} \times \frac{1\ g}{1000\ g}$$

$$= 34.92\ g/d$$

Therefore, the mass of paracetamol in sewage (influent) and in the effluent were 103 g/d and 35 g/d respectively.

Thus;

$$\%R_{Aqueous\ phase} = 100 \times \frac{M_{in} - M_{eff}}{M_{in}}$$

$$= 100 \times \frac{103 - 35}{103}$$

$$= 66.02\ \%$$

Therefore, the removal rate from aqueous-phase were 68 g/d or 66.02%

2.2 Calculation of the adsorption of paracetamol in the activated sludge process, and the adsorption removal rate ($\%R_{adsorption}$) on 18-3-11

Where, the moisture content of disposal sludge = 78.28 %

Therefore, disposal sludge 100 g were contain water 78.28 g (ml) and dry solids 21.72 g

1) Calculate the mass of Paracetamol adsorbed on the disposal sludge (solid phase)

The concentration of Paracetamol in effluent, 181 ng/L
as shown in Appendix Table B3. So, it can be calculate the paracetamol in the water part of 100 g wet disposal sludge:

$$= 78.28 \text{ ml} \times \frac{181 \text{ ng}}{\text{L}} \times \frac{1 \text{ L}}{1000 \text{ ml}}$$

= 14.17 ng/100g, wet sludge (1)

As in the sludge analysis (Appendix Table B2); sludge 100 g were firstly added into 250 ml distilled water and stirred at 50°C (2 times, a total of 500 ml). The supernatant contained paracetamol of 380 ng/500 ml.

So, the concentration of paracetamol in the total sludge were;

= 380 ng/100 g, wet sludge (2)

The mass of paracetamol that was adsorbed in the dry solid of the sludge can be calculated

= (2) – (1)
= 380 – 14.17 (ng/100g, wet sludge)
= 365.83 ng/100g, wet sludge

Therefore, the mass of paracetamol adsorbed on the sludge were 365.83 ng/100 g wet sludge

2) Calculate the mass of Paracetamol in Waste Activated Sludge (WAS), due to the average flow rate of waste activated sludge (WAS) was 81 m^3/d (27 m^3/h, 3 h daily), the TSS of the WAS were 17,532 mg/L as shown in Table 12 and the moisture content of disposal sludge is 78.28 % (Appendix Table B1).
From 1), the mass of Paracetamol in 100 g wet sludge = 365.83 ng/100 g sludge
The total solids of wet sludge = 21.72 %

So, paracetamol content in dried sludge (C_{ds}) was ;

$$\frac{365.83\ ng}{21.72g} = 16.84 \quad ng/g,dry\ sludge$$

The average flow rate of WAS = 81 m^3/d

The TSS of the WAS = 17,532 mg/L

= 17.532 g/L

So, the paracetamol mass in dry sludge wasted per day

$$= \left[\frac{81\ m^3}{d} \times \frac{17.532\ g}{L} \times \frac{1000\ L}{m^3}\right] \times \frac{16.84\ ng}{g}$$

$$= 1{,}420{,}092 \quad g,\ dry/d$$

$$= 1{,}420{,}092\ g/d \times 16.84\ ng/g$$

$$= 2{,}392{,}195 \quad ng/d$$

Therefore, the mass of Paracetamol wasted by disposal sludge (M_{ds}) was 0.024 g/d

3) Calculate the amount paracetamol in MLSS in the aeration tanks per day, 3aeration tanks working

3.1) Working volume calculation

From, $HRT = \frac{\text{Volume of the aeration tank } (m^3)}{\text{Influent flow rate, Q } (m^3/h)}$

Where; HRT = 8-10 h = 9 h

Q = 192,943 m^3/d

Therefore, the working volume of the 3 aeration tanks (m^3)

$$= 9\ h \times \frac{192{,}943\ m^3}{d} \times \frac{1\ d}{24\ h}$$

$$= 72{,}353.6\ m^3/3\ tanks$$

$$= 24{,}118\ m^3/tank$$

The volume of aeration tank or working volume were 24,118 m^3/tank

3.2) Dried mass content in aeration tanks calculation

Aeration tank No. 2; MLSS = 6,845 mg/L•d (Table 12)

so, the MLSS in day $= \frac{6{,}845\ mg}{L•d} \times 24{,}118\ m^3 \times \frac{1000\ L}{m^3}$

$$= 1.65\times10^{11}\ mg/d$$

$$= 165\ ton/d$$

Aeration tank No. 3; MLSS = 7,182 mg/L•d

so, the MLSS usage in day $= \frac{7{,}182\ mg}{L•d} \times 24{,}118\ m^3 \times 1000\ \frac{L}{m^3}$

$$= 1.73\times10^{11}\ mg/d$$

$$= 173\ ton/d$$

Aeration tank No. 4; MLSS = 5,031 mg/L•d

so, the MLSS usage in day $= \frac{5{,}031\ mg}{L•d} \times 24{,}118\ m^3 \times 1000\ \frac{L}{m^3}$

$$= 1.21\times10^{11}\ mg/d$$

$$= 121\ ton/d$$

Therefore, the total MLSS in day = 165 + 173 +121 (ton/d)

= 459 (ton/d)

3.3) Calculate the adsorption of Paracetamol by MLSS in the aeration

Where, MLSS = 459 ton solids/d

C_{ds} = 16.84 ng/g, dry sludge

So, the mass of Paracetamol adsorbed by MLSS ($MLSS_{ad}$) per day

= 459 ton/d × 16.84 ng/g × 1000 kg/ton × 1000 g/kg

= 7,729,560,000 ng/d

$MLSS_{ad}$ = 7.73 g/d

Therefore, the adsorbed paracetamol on MLSS in aeration tanks was 7.73 g/d

3.4) Calculate the adsorption removal of Paracetamol by MLSS in aeration tanks Because the paracetamol content in MLSS and influent were:

$MLSS_{ad}$ = 7.73 g/d ; M_{in} = 103g/d

So, $\%R_{ad} = 100 \times \frac{M_{ad}}{M_{in}}$

$= 100 \times \frac{7.73}{103}$

= 7.52 %

Therefore, the adsorption removal of Paracetamol ($\%R_{ad}$) by MLSS was 7.52%

2.3 Calculation of the paracetamol by removal biodegradation ($\%R_{cal\ biodeg}$) on 18-3-11.

Where; $M_{in} = M_{ad} + M_{bio} + M_{eff}$

$M_{bio} = M_{in} - (M_{ad} + M_{eff})$

$= 103 – (35 + 7.73)$

$$= \quad 60.27 \text{ g/d}$$

$$\%R_{\text{cal biodeg}} = 100 \times \frac{M_{bio}}{M_{in}}$$

$$= 100 \times \frac{60.27}{103}$$

$$= 58.51\ \%$$

Therefore, the biodegradation of paracetamol in the activated sludge process was 60.27 g/d or 58.51%

3. Calculation of CO_2 production from activated sludge

Example sample sterile round 1

$$PV = nRT$$

$$n = \frac{PV}{RT}$$

$$\frac{g}{Mw} = \frac{PV}{RT}$$

$$g = \frac{PV \times Mw}{RT}$$

Where:

$$P = \frac{\%CO_2 \text{ atm}}{100}$$

$\%CO_2$ = $\%CO_2$ current - $\%CO_2$ initial (0.03%)

V = Volume of air in serum vial

= $V_{\text{serum vial}} - V_{\text{sludge sample}}$ (Density of fresh sludge is 1.04 g/mL)

= 50 – 9.62 ml

= 40.38 ml = 0.04 L

R = 0.08205 L-atm/mol-K

T = temp (303 K)

Mw = Molecular weight of CO_2 (44 g/mole)

Therefore;

$$g = \frac{\%CO_2}{100} \times \frac{V}{RT} \times Mw$$

$$g = \frac{(0.096 - 0.03)}{100} \times \frac{0.04}{(0.08205)(303)} \times 44 \times 1000 \frac{mg}{g} \times 1000 \frac{\mu g}{mg}$$

$$= 46.72\ \mu g/10\ g, \text{ wet sludge}$$

Where; the moisture content of disposal sludge were 78.28 %

Therefore, the CO_2 production from activated sludge were 21.51 µg/g, dry sludge

Where, 2 day (48 h) experiment, average respiration rate of the sludge (carbondioxide production rate)

$$= 21.51/48\ (\mu g\ CO_2/\ g, \text{ dry sludge-h})$$

$$= 0.45\ \mu g\ CO_2/\ g, \text{ dry sludge-h}$$

Therefore, CO_2 production from activated sludge was 0.45µg CO_2/ g, dry sludge-h

4. Calculation of Oxygen uptake rate

Example sample sterile round 1

$$PV = nRT$$

$$n = \frac{PV}{RT}$$

$$\frac{g}{Mw} = \frac{PV}{RT}$$

$$g = \frac{PV}{RT} \times Mw$$

Where:

$$P = \frac{\%O_2}{100}\ atm$$

$$\%CO_2 = \%O_2 \text{ initial} - \%O_2 \text{ current } (\%O_2 \text{ initial} = 21\%)$$

V = Volume of air in serum vial

= $V_{serum\ vial} - V_{sludge\ sample}$ (Density of fresh sludge is 1.04 g/mL)

= 50 – 9.62 ml

= 40.38 ml = 0.04 L

R = 0.08205 L-atm/mol-K

T = temp (303 K)

Mw = Molecular weight of O_2 (16 g/mole)

Therefore;

$$g = \frac{\%O_2}{100} \times \frac{V}{RT} \times Mw$$

$$g = \frac{(21 - 20.66)}{100} \times \frac{0.04}{(0.08205)(303)} \times 16 \times \frac{1000\ mg}{g} \times \frac{1000\ \mu g}{mg}$$

= 87.52 µg/10 g, wet sludge

Where; the moisture content of disposal sludge were 78.28 %

Therefore, the O_2 reduction from activated sludge were 40.3 µg/g, dry sludge

Where, 2 day (48 h) experiment, respiration rate of the sludge (oxygen uptake rate)

= 40.3 /48 (µg O_2/ g, dry sludge-h)

= 0.84 µg O_2/ g, dry sludge-h

Therefore, O_2 reduction from activated sludge was 0.84 µg O_2/ g, dry sludge-h

5. Calculation of amount of paracetamol base on adsorption and desorption on activated sludge

Adsorption

Example Paracetamol concentration in influent (C_{in}) 2,000 ng/L

The amount of adsorbed on the activated sludge was calculated by the equation:

$$q_a = (C_i - C_{eq})V/M$$

Where: C_i = 2000 ng/L

C_{eq} = 371 ng/L

V = 1 L

M = 5 g, dry

Therefore;

q_a = (2000 – 371) 1 L/5 g

q_a = 326 ng/g, dry activated sludge

Desorption

Example Paracetamol concentration in influent (C_{in}) 2,000 ng/L

The amount of paracetamol desorbed from the activated sludge to clean water was calculated using the equation:

$$q_{des} = (C_2 - C_1)V/M$$

where: C_2 = 333 ng/L

C_1 = 0 ng/L

V = 1 L

M = 5 g, dry

Therefore;

q_{des} = (333 – 0) 1L/5g

q_{des} = 66.6 ng/g, dry activated sludge

6. Using the Freundlich isotherm to calculate the adsorption and desorption potential of Paracetamol on studied activated sludge

Adsorption

$q_{ad} = K_F C_e^{n}$

Where; K_F = 0.35

n = 1.255

C_e = 201 ng/L (the average concentration of paracetamol in effluent, from Appendix Table B3)

Therefore;

$q_{ad} = 0.35\ (201)^{1.255}$

= 272 ng/g,dry sludge

Desorption

$q_{des} = K_F C_e^{n}$

Where; K_F = 0.2

n = 1

C_e = 201 ng/L (the concentration of paracetamol in effluent, from Appendix Table B3)

Therefore;

$q_{ad} = 0.2\ (201)^{1}$

= 40.2 ng/g,dry sludge

Therefore, the adsorption potential of Paracetamol on studied activated sludge were 272 ng/g, dry sludge and desorption of Paracetamol to distillated water were 40.2 ng/g,dry sludge

Appendix D
Samples location and Equipments

Appendix Figure D1 Influent of wastewater treatment plant (Sewage)

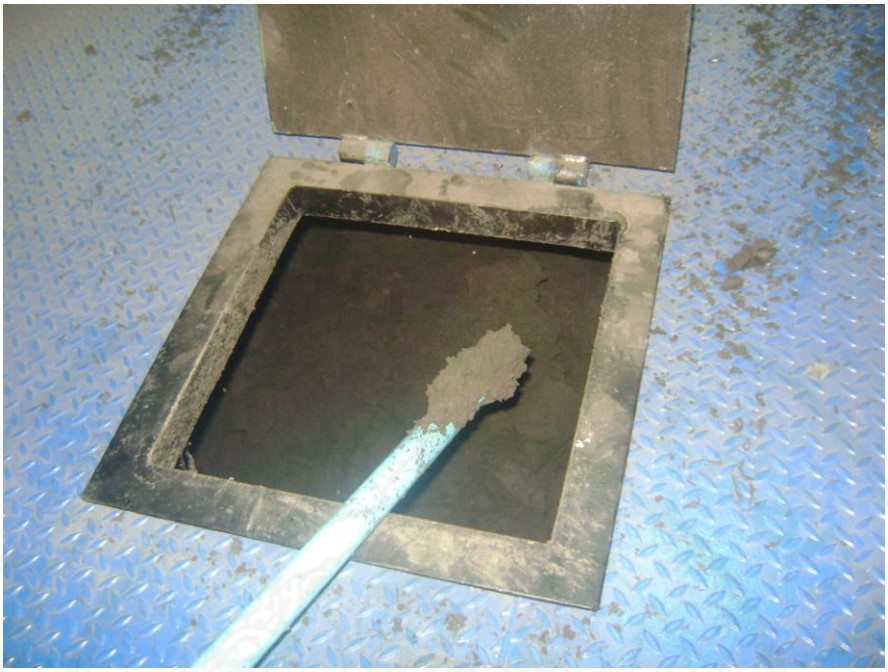
Appendix Figure D2 Screening

Appendix Figure D3 Aerated Grit Chambers

Appendix Figure D4 The influent before AS system (Settled sewage) of WWTP

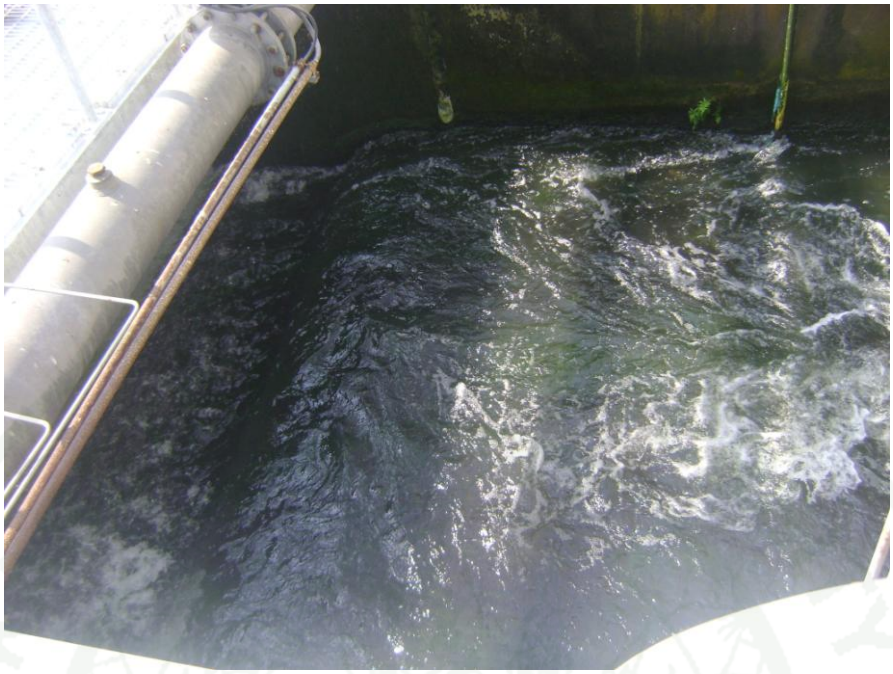
Appendix Figure D5 Aeration Chamber

Appendix Figure D6 Belt Filter Presses



Appendix Figure D7 The dispasal sludge

Appendix Figure D8 Final Clarifier

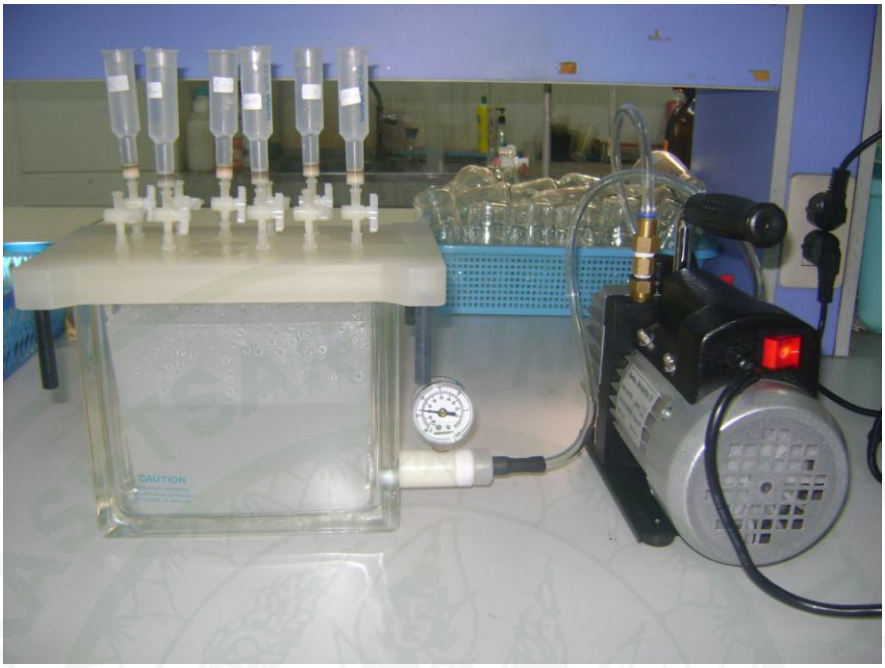


Appendix Figure D9 Effluent of wastewater treatment plant

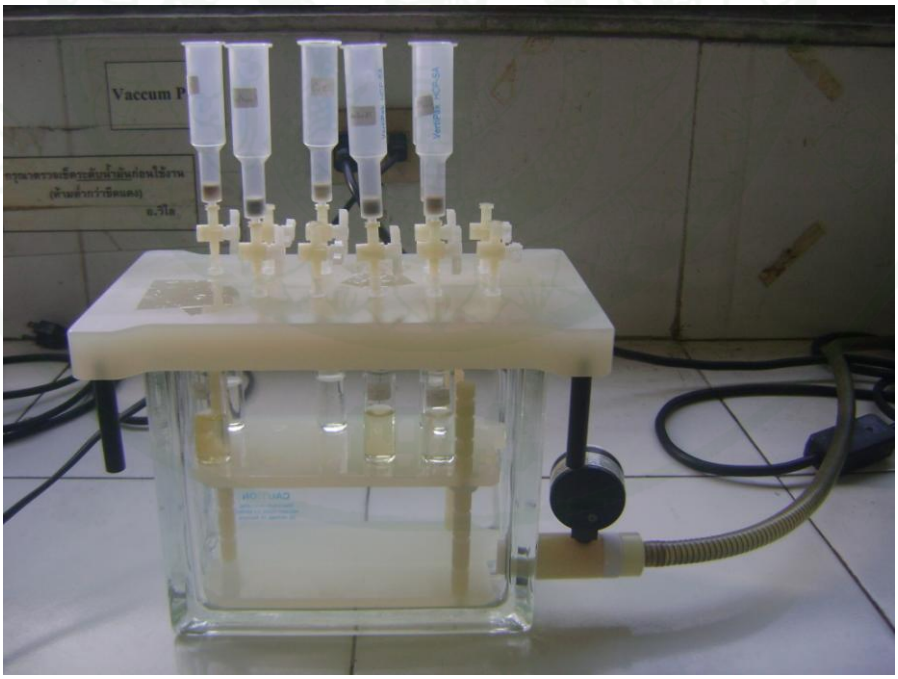
Appendix Figure D10 Receiving canal point 1

Appendix Figure D11 Receiving canal point 2

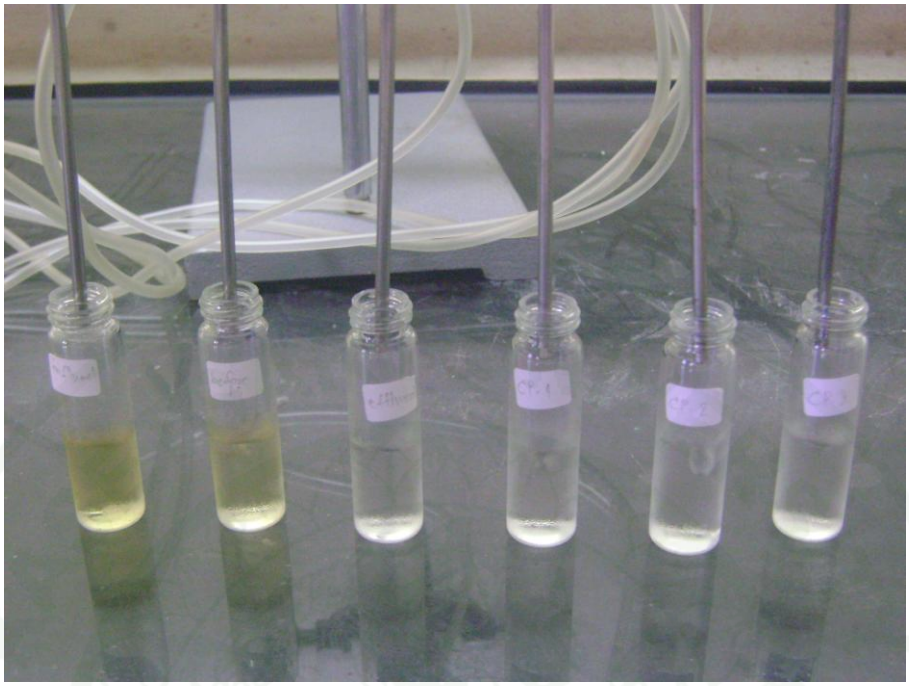
Appendix Figure D12 Receiving canal point 3



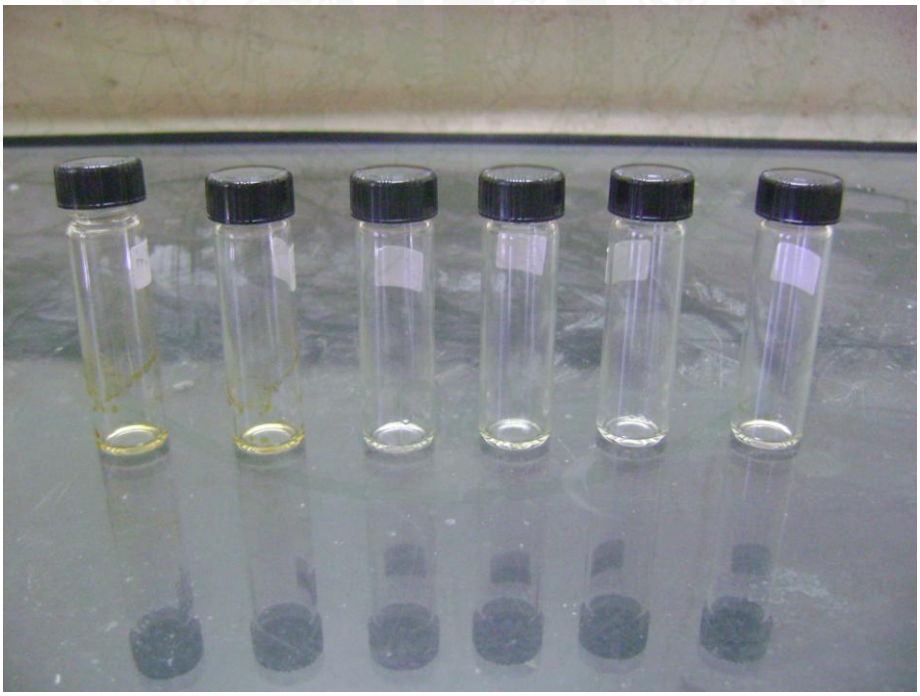
Appendix Figure D13 The set of solid phase extraction



Appendix Figure D14 Elution of the paracetamol with methanol



Appendix Figure D15 Dryness methanol under a gentle nitrogen



Appendix Figure D16 Addition of 50 µL of MSTFA and dryness

Appendix Figure D17 Heat the sample to 60^{o}C for 10 min

Appendix Figure D18 Determination of Paracetamol by GCMS

(a) **(b)**

(c) **(d)**

Appendix Figure D18 Homogenizer (a), Autoclave (b), Paracetamol-activated sludge mixers, before stirrer (c) and stirring (d)

Appendix Figure D19 Centrifuge (Model Z383, Hermle)

Appendix Figure D20 GC instrument (Agilent GC 6890 Series (Plus), Column CTR I) for determine %CO_2

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