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THESIS

PHOTODEGRADATION OF ORGANOTIN COMPOUNDS IN AQUEOUS TiO_2 SUSPENSION

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A Thesis Submitted in Partial Fulfillment of
the Requirements for the Degree of
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Natthapon Warapo 2011: Photodegradation of Organotin Compounds in Aqueous TiO_2 Suspension. Master of Science (Chemistry), Major Field: Chemistry, Department of Chemistry. Thesis Advisor: Associate Professor Apisit Songsasen, Ph.D. 135 pages.

The photodegradation of organotin compounds (TBT, DBT and MBT) in aqueous TiO_2 suspension was studied. First, a procedure for the determination of organotin compounds in water samples was optimized. The extraction efficiency of organotin compounds depends on amount of tropolone, NaCl and pH. The appropriate conditions of extraction were pH 1.66, concentration of tropolone was 0.05% in hexane and amount of NaCl were 60 mg. Moreover, the stoichiometries of complexes between MBT and DBT with tropolone were determined by continuous variation method. The stoichiometric of ratio DBT:tropolone and MBT:tropolone were 1:1 and 1:2, respectively. The N-doped TiO_2 photocatalyst was prepared via the sol-gel method using titanium(IV) tetraisopropoxide as a precursor. The results from photodegradation of TBT under UV-light irradiation, using N-doped TiO_2, P25-TiO_2 and undoped TiO_2 and without catalyst indicated that P25-TiO_2 was able to degrade TBT with the highest conversion efficiency. Under visible light and natural light illumination, N-doped TiO_2 provided the best catalytic efficiency for TBT, DBT and MBT. The rate constant of photodegradation of DBT and MBT were higher than TBT with the order of MBT > DBT > TBT. MBT was detected as intermediate product of the photodegradation of DBT under natural light illumination. The photodagradation of mix organotins solution under natural light illumination, after 2 h, the amount of TBT increased because the recombination process of MBT and DBT. N-doped TiO_2 effectively degraded TBT in sea water from Lam Chabang Harbour Gulf of Thailand which was contaminated by TBT.

Student's signature   Thesis Advisor's signature   ___ / ___ / ___

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Natthapon Warapo
February, 2011

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LIST OF ABBREVIATIONS

TeBT = Tetrabutyltin
TBT = Tributyltin
DBT = Dibutyltin
MBT = Monobutyltin
TBTCl = Tributyltin Chloride
DBTC = Dibutyltin Dichloride
MBTC = Monobutyltin Trichloride
TBTO = Tributyltin Oxide
TBTN = Tributyltin Naphthenate
TPTH = Triphenyltin Hydroxide
TCTH = Tricyclohexyltin Hydroxide
TCTT = Tricyclohexyltin Triazole
TNTO = Trineophenyltin Oxide
TPTA = Triphenyltin Acetate
TPrT = Tripropyltin
TEtT = Triethyltin
JCPDS = Joint Committee on Powder Diffraction Standard
SEM = Scanning Electron Microscopy
TEM = Transmission Electron Microscopy
UV-Vis = UV-Vis Spectrophotometry
EA = Elemental Analysis
GC/FPD = Gas Chromatography/Flame Photoemission Detector
GC/MS = Gas Chromatography/Mass Spectrometer
OTCs = Organotin Compounds
PVC = Polyvinyl Chloride
ORTEP = Organotin Environmental Programe
SPC = Self-Polishing Copolymer
IMO = International Maritime Organization
EDCs = Endocrine Disrupting Chemicals

LIST OF ABBREVIATIONS (Continued)

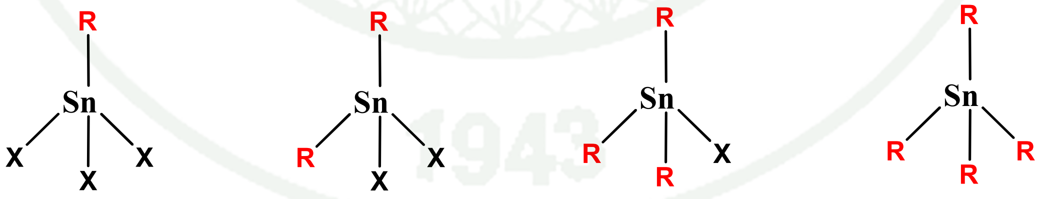
POP = Persistent Organic Pollutant
UNEP = United Nations Environment Programe
EQS = Environmental Quality Standard
SPEA = Scottish Environmental Protection Agency
SPC = Solid Phase Extraction
SPME = Solid-Phase Micro Extraction
SDME = Single Drop Micro Extraction
ICP-MS = Inductive Couple Plasma and Mass Spectrometer
QF-AAS = Quartz Furnace and Atomic Adsorption Spectrophotometer
MIP-AES = Microwave Induce Plasma and Atomic Emission Spectrophotometer
ICP-AES = Inductive Couple Plasma and Atomic Emission Spectrophotometer
AIST-Kansai = National Institute of Advanced Industrial Science and Technology

PHOTODEGRADATION OF ORGANOTIN COMPOUNDS IN AQUEOUS TiO_2 SUSPENSION

INTRODUCTION

1. Discovery and physico-chemical properties of organotin compounds

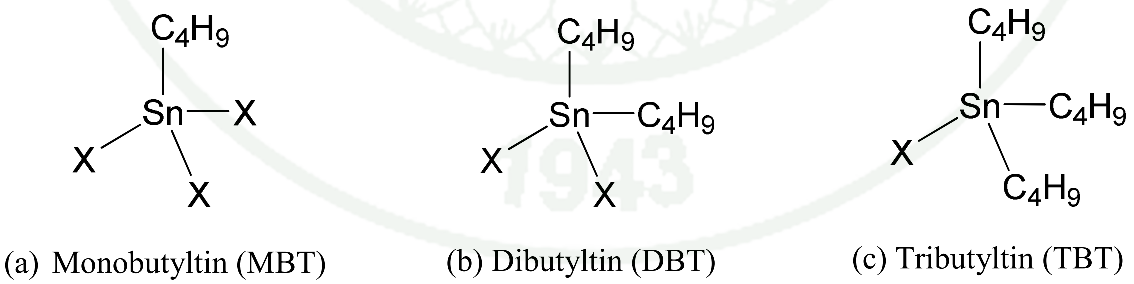
Organotin compounds (OTCs) were discovered 157 years ago in the first study of Sir Edward Frankland who successfully synthesized diethyltin-diiodide in 1853 (Kerk, 1975). Further investigations on the OTCs have lead to the discovery of more than 800 organotin compounds to date. All compounds in the organotin family are anthropogenic in origin, except methyltins which are the only compounds that can be produce by biomethylation. Organotins are not widely used due to the fact that no applications existed until they were found to have potential advantage in industrial production, i.e. production of plastic and polyvinyl chloride (PVC). During the development of OTCs, the biocide property of the trisubstituted organotin species was discovered 50 years ago in the Netherlands (Kamruddin *et al.*, 1995). Tributyltin compounds were then seen as important toxic ingredients in fungicides, molluscicides, repellant, wood preservatives and antifouling paint.



Monosubstituted   Disubstituted   Trisubstituted   Tetrasubstituted

Figure 1 Structure of monosubstituted organotin, disubstituted organotin, trisubstituted organotin and tetrasubstituted organotin where X is an ionic specie and R is alkyl or aryl group

Organotin compounds have a central Tin (Sn) atom, with sp^3 hybridization. They are organic derivatives of tetravalent tin which are characterized by the presence of covalent bonds between a tin atom and carbon atoms. The basic chemical formula for organotin compound is expressed as R_nSnX_{4-n}, in which R is an alkyl or aryl group and X is an inorganic substituent. Organotin compounds are divided to four types such as, Monosubstituted organotin ($RSnX_3$), Disubstituted organotin (R_2SnX_2), Trisubstituted organotin (R_3SnX) and Tetrasubstituted organotin (R_4Sn), the structure are shown in figure 1. The majority of organotin compounds, such as monobutyltin (MBT), dibutyltin (DBT) and tributyltin (TBT), are comprised of five major commercial applications: PVC Heat Stabilizers, Biocides, Catalysts, Agrochemicals, and Glass Coatings (Maguire *et al*., 1984). These uses account for approximately 20 kilotons of tin consumption per year. Monobutyltin (MBT) is employed in the glass industry. It forms thin film of Sn-Si bonds which offer stronger surface in glass containerware. The particular importance of these dibutyltin (DBT) lies in its outstanding ability to preserve the clarity and transparency of PVC, not only when being processed but also in subsequent service. Organotin-stabilized PVC is used in water pipes and in food packaging applications, as tin compounds used in these applications are known as nontoxic. Generally, trisubstituted organotins (TBT) are more toxic than di- (DBT) and monosubstituted (MBT) compounds (Mendo *et al.*, 2007).



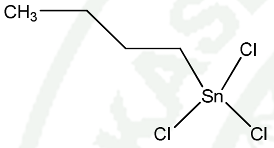
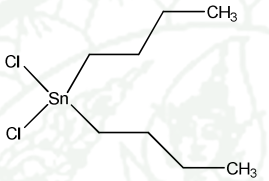
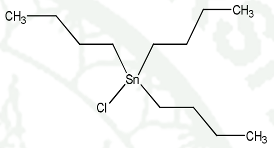
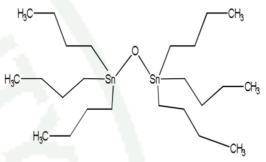
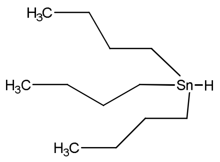
(a) Monobutyltin (MBT) (b) Dibutyltin (DBT) (c) Tributyltin (TBT)

Figure 2 Structure of monobutyltin (MBT), dibytyltin (DBT) and tributyltin (TBT) where X is an ionic specie

Tributyltin (TBT) is a sub group of the trialkyl organotin family containing 3 butyl groups. The structure of TBT is shown in figure 2c. TBT by itself is unstable and will break down in the environmental unless it is combined with anionic substituent, such as hydride (TBTH), halide (TBTF, TBTCl), acetate (TBTOAc) and oxide (TBTO). TBT can be liquid or solid at room temperature with characteristic odour. The phase of TBT depends on the species of anion. It is considered lipophilic and thus has poor water solubility, approximately 1 mg/L (Laughlin *et al*., 1986), but it is soluble in hexane and most organic solvents. The solubility of TBT compounds in water is influenced by such factors as the oxidation-reduction potential, pH, temperature, ionic strength and, the concentration and composition of dissolved organic matter (Hall *et al*., 2000). TBT compounds will become positively charged after the tin-anionic bond is broken down in solvent. In sea water, TBT exists mainly as a mixture of chloride, the hydroxide, the aqua complex, and the carbonate complex (Laughlin *et al*., 1986).

The physical properties of organotin compounds are varied and depend on the anionic group. Examples of the organotin compounds and their properties are shown in table 1.

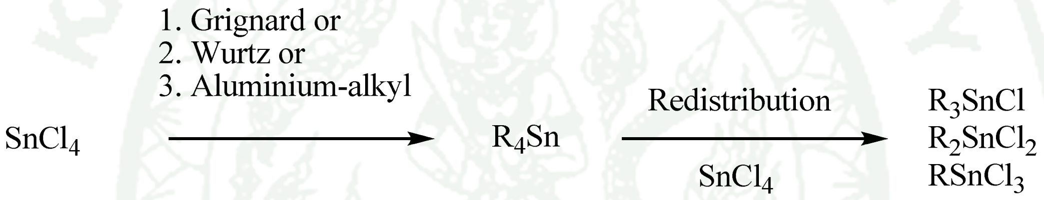
Table 1 The chemical identifier and physical properties of organotin compounds

structure					
IUPAC	Trichlorobutyl Stannane	Dichlorobutyl Stannane	Tributyltinchloride	Bis(tributyltin) Oxide	Tributyltin hydride
Chemical name	n-Butyltin trichloride	Dibutyltin dichloride	Tributyltin chloride	Tributyltin oxide	Tributyltin hydride
CAS Number	214-263-6	613-18-1	1461-22-9	56-35-9	688-73-3
Molecular formula	$C_4H_9SnCl_3$	$(C_4H_9)_2SnCl_2$	$(C_4H_9)_3SnCl$	$(C_4H_9)_3SnOSn(C_4H_9)_3$	$(C_4H_9)_3SnH$
Molecular weight	282.16	303.84	325.51	596.10	291.06
Boiling point (ºC)	> 200 ºC	135 °C 10 mmHg	171-173 ºC 25 mmHg	180 ºC 2 mmHg	80 ºC 0.4 mmHg
Melting point (ºC)	-63 °C	37-40 °C	-16 °C	< - 45 °C	-
Flashing point (ºF)	177.8	235.4	>230.0	-	104.0
Density (at 25 ºC)	1.650 - 1.750 g/mL	1.400 g/mL	1.200 g/mL	1.170 g/mL	1.082 g/mL

Source: Sigma-Aldrich (2009)

2. Synthesis pathways

Organotin is a man-made organometal. The preparation process has been successfully used since 1848. It can be prepared via a two steps reaction in which tin halides, for example tin tetrachloride ($SnCl_4$), is the initial substance reacted with suitable reagent to form tetra-alkyltin compounds. Routes of the first step synthesis can be by Grignard reaction, Wurtz reaction or reaction with organo aluminium compounds (AlR_3). Tetrabutyltin, the product from the initial reaction will then redistribute in subsequent reactions to form less alkylated organotin chlorides by tin tetrachloride. The two steps process is shown in figure 3.



$$SnCl_4 \xrightarrow{\begin{array}{l}\text{1. Grignard or}\\ \text{2. Wurtz or}\\ \text{3. Aluminium-alkyl}\end{array}} R_4Sn \xrightarrow[SnCl_4]{\text{Redistribution}} \begin{array}{l} R_3SnCl \\ R_2SnCl_2 \\ RSnCl_3 \end{array}$$

Figure 3 Two steps preparation of organotin.

Source: Blunden and Evans (1990)

TBT can also be prepared by direct synthesis via reaction of alkyl iodide. The product from the reaction is dialkyltin iodide.

3. Major application of organotin compounds

Organotin environmental program association (ORTEP) has given the information for major application of organotin compound (Batt, n.d.) Mono and Diorganotin compounds

3.1. mono- and diorganotin compounds

a) PVC heat stabilizers

Mono- and diorganotins are used extensively as heat stabilizers for processing polyvinyl chloride (PVC). The primary purpose of these tin stabilizers is to reduce the polymer backbone degradation of the PVC. They do this by scavenging the HCl lost during processing at high temperatures and stabilizing the unstable chloride sites in the PVC molecule. Tin mercaptide stabilizers are some of the most effective PVC stabilizers available. They contain both tin and sulfur. Tin, acting as a base, reacts with the HCl initially released during PVC processing. The strength of this base is critical so it will not extract HCl from the PVC, but only react with the HCl that is already released. Only a very few bases have the right balance of reactivity to allow this. The mercaptan, a weak sulfur-containing acid, reacts with the unstable chloride sites on PVC to heal the polymer and reduce further decomposition. The high molecular weights and ester function in the mercaptan ligands also promote solubility of the stabilizer in PVC and provide lubrication during polymer processing. There are three major types of tin stabilizers. They are distinguished by their respective alkyl groups: octyl, butyl, and methyl.

Octyltin stabilizers have the lowest tin content and are somewhat less efficient. However, they are approved for food contact applications by most regulatory authorities worldwide. Butyltin stabilizers have been the dominant types used until methyltins were introduced. Methyltin stabilizers have a higher tin content and lower raw material cost compared to the other two types. Some formulations (mercaptides) have also been approved for food contact applications.

The ligands (the chemical group attached to the tin atom) are used to differentiate the various tin stabilizers. The primary ligands are thioglycolic acid esters, reverse esters, and carboxylic acids. The main applications for tin stabilizers are building products, such as pipe and fittings, and siding and profiles (windows, etc.), packaging, and flexible PVC.

The substitutes for tin stabilizers are manufactured from lead or mixed metals such as Calcium/Zinc. Lead stabilizers have the benefit of low cost but are declining in use due to environmental concerns. Tin and mixed metal stabilizers, in fact, are replacing them. Mixed metal stabilizer technology is more expensive than tin, and less effective in stabilization. It is estimated that between 12 to 13K tons of tin are used annually in tin stabilizers worldwide. This market is expected to grow about 4% annually.

b) Catalysts

Catalysts are used to speed up chemical reactions, especially polymerization. The most common applications for mono-and diorganotin catalysts are in chemical synthesis and the curing of coatings. In chemical synthesis, the organotins are used for the esterification and transesterification of mono- and polyesters. These products are then used for plasticizers, synthetic lubricant manufacturing, and polyester polyol production, as well as some coating applications.

As curing catalysts, one of the largest uses of organotins is in electrocoat (E-coat) coatings. These electrocoating products are sold into a wide range of applications, with the largest being automotive, where they provide excellent rust resistance. The catalysts are also used in urethane coatings as well as polyurethane foam production. Other applications include curing silicones and silanes. Some of the more common organotins used as catalysts are:

- Hydrated Monobutyltin Oxide
- Butyl Chlorotin Dihydroxide
- Butyltin tris (2-ethylhexoate)
- Dibutyltin diacetate
- Dibutyltin oxide
- Dibutyltin dilaurate
- Butyl Stannoic Acid
- Dioctyltin dilaurate

Although not technically classified as organotins, since they do not have a tin- carbon bond, other tin chemicals such as stannous oxide, stannous oxalate, and stannous bis(2-ethylhexoate) are used extensively in chemical synthesis as catalysts.

Outside of tin-based chemistry, substitute products are limited in the area of urethane/E-coat catalysts. There are some Bismuth and Beryllium based catalysts, but none have been successful in penetrating the market to date due to a lack of cost/performance benefit.

For polyester production, again, the substitutes are few. There is limited non-tinsubstitution (particularly in the USA.), which is usually in the form of titanates when it exists. Plasticizers (monoesters) are typically produced at lower temperatures and lend themselves more readily to the use of acids and titanates as catalysts. Sulfuric and sulfonic acids are regularly used in these production schemes. The advantages of tin-based products are normally seen at higher temperatures.

Monoesters produced for synthetic lubricant applications are typically manufactured at higher temperatures and better lend themselves to the use of tin catalysts.

c) Glass coating

Monoorganotins are used on glass containers in Hot End Coatings (HEC). In HECs, a metallic oxide is deposited on the hot glass surface of bottles thereby preventing microfissures. The predominant chemical used is monobutyltin trichloride (MBTC) although some inorganic stannic chloride ($SnCl_4$, also known as tin tetrachloride) is used. In the various container markets, glass bottles are beginning to be displaced by ones produced from PET. This trend is expected to continue.

On flat glass, mono- and diorganotins, deposited by chemical vapor deposition (CVD), are used in the manufacture of Low E glass. They reduce the heat loss through the metallic oxide coating deposited on the glass surface. Here, MBTC as well as dimethyltin dichloride (DMTC), are the dominant products. As with containers, stannic chloride is also used in less sophisticated processes.

3.2. Triorganotin compounds

a) Biocide

Tributyltin (TBT) is unique among the organotins in that it is used as a biocide. The monobutyl- and dibutyltins do not exhibit these properties.

In the marine antifoulant (MAF) paint market, tributyltin is used as a biocide in paint formulations. These paints are then used to protect the underwater surface area of a ship’s hull against barnacles, algae, etc. in order to avoid increased fuel consumption and premature dry-docking. Triorganotins were introduced for this application since 1960s. Originally, tributyltin oxide (TBTO) was freely dispersed in what were called Free Association Paints (FAP). These paints had uncontrolled, rapid leaching rates of the biocide.

In response to the negative performance and environmental effects of FAPs, tributyltin methacrylate copolymer systems were developed which had selfolishing behavior. These revolutionary new systems, called Self-Polishing Copolymers (SPC) had controlled, uniform leach rates of the biocide by incorporating the tributyltin biocide into the polymeric binding system of the paint formulation.

Throughout the 1980s many countries worldwide began restricting the use of TBT paints because of their environmental impact resulting from the misuse of the product in pleasure craft and other small coastal vessels. In the late 1980s, the Organotin Antifoulant Paint Control Act was passed in the United States, which restricted the use of TBT paints to vessels greater than 25 meters in length. It also specified the allowable leach rates of MAF paints sold in the US as well as restrictions on applications and waste disposal. Presently, the International Maritime Organization (IMO) has proposed a worldwide ban on TBT MAF paints commencing with a ban on its application to vessels as of January 1, 2003 and a total ban on its presence on vessel hulls as of January 1, 2008.

TBTO and tributyltin naphthenate (TBTN) are also used for industrial wood treatment and preservatives. This use is declining and mainly concentrated in tropical areas.

TBTO is used in formulations in the USA for industrial cooling tower water treatment to control slime, algae, and fungi. This use is quite small and is declining as other biocides continually replace TBTO.

b) Agrochemical

There are five main triorganotin ingredients used as pesticides for crop protection:

- Triphenyltin Hydroxide (TPTH or Fentin Hydroxide)
- Tricyclohexyltin Hydroxide (TCTH or Cyhexatin)
- Tricyclohexyltin Triazole (TCTT or Azocyclotin)
- Trineophenyltin Oxide (TNTO or Fenbutatin Oxide)

- Triphenyltin Acetate (TPTA or Fentin Acetate)

These products are used primarily as fungicides and acaracides.

- Fungicides - pesticides which kill or inhibit the growth of fungi
- Acaracides - pesticides which kill mites and ticks (acarides)

As fungicides, TPTA and TPTH are used primarily for high value crops. Tin fungicides are used when the possibility of disease is very high, which justifies the added costs. They are used on potatoes, sugar beets, and pecans.

As acaracides, the efficiency of TCTH, TCTT, and TNTO is excellent. They are also not considered susceptible to resistance development. They are used on citrus, top fruit, vines, vegetables, and hops.

There are substitute products available, depending on the market segment. For example on potatoes, a substitute for TPTH is propamocarb hydrochloride /chlorothalonil and dimethomorph / mancozeb. On sugar beets, tetraconazole can be used. Substitutes for TCTH include dicofol, hexythiazox, propargite, pyribaden, and tebufenpyrad.

The organotin products typically have a cost advantage for growers when one considers the rate at which the product is applied, the cost of the product itself, and the number of days between sprayings. However, a single treatment method is not normally used. Growers typically rotate two or three treatment types in order to avoid the buildup of resistance to any one fungicide.

4. Toxicity of organotin compound

The toxicity of organotin compounds are strongly influenced by the length of the alkyl chains attached to the tin (Clarkson, 1991). Generrally, the toxicity of organotin compounds are influenced more by the alkyl substituents than the ionic substituents, which from the rest of the molecule (Kaloyanova and Batawi, 1991). Tributyltin compounds are moderately toxic via both ingestion and dermal absorption. TBT lead to acute and chronic effect in non-target organisms even at low concentration. When expose to TBT, effect on reproduction, organ toxicity, carcinogenicity and imposex may occur.

4.1 Effect on human

Although the effects of TBT on humans are not clear, several incidents of human exposure to the biocide have been reported. TBT is a skin, eye and mucous membrane irritant and rigid dermatitis has been reported after direct contact with the skin. The potential problem is made worse by the lack of an immediate skin response. Skin burns or severe injuries were the most commonly causes by contact of liquid tributyltin chloride. The irritancy was not immediately apparent, thus contact with TBT was frequency ignored. This compound causes an acute burn which healed relatively quickly, or a more diffuse dermatitis which persisted. Treatment of undiluted TBT compounds on human skin established that tributyltin chloride, acetate, laurate and oxide all produce acute burns. Reddening, inflammation of the hair follicles, minute pustules and faint erythema are the main symptoms after exposure to the compound. The burns were not reported to be painful but itching and adherence of clothes to skin was problematic (Goh, 1985).

The exposure to TBT results in severe dermatitis where the compound had been retained on the skin for long periods. Inhalation of TBT sufferer reported nausea and vomiting. Post exposure resulted in elevated urine tin levels for several days (IPCS, 1990). TBT expose sufferer also reported irritant effects by developing rashes, severe itching, redness, swelling and blistering. Moreover, hospital examination showed extensive vesiculobullous lesions, erythema and oedema (Goh, 1985). Without immediate sensation delay symptom of the exposed areas was noted later (Lewis and Emmett, 1987).

4.2 Effect on microorganisms

Tributyltin is toxic to microorganisms and has been used commercially as a bactericide and algaecide. The concentrations that produce toxic effects are very considerably according to the species. Tributyltin is more toxic to gram-positive bacteria than to gram-negative bacteria (Lascourreges *et al*., 2000). The concentration of tributyltin that is toxic to bacteria depends on the species of bacteria exposures to tributyltin and the surrounding conditions (Suehiro *et al*., 2006; Harino *et al*., 1997). Tributyltin presence in solid phase tends to have higher toxicity than the liquid (Wuertz *et al*., 1991). The tributltin acetate and tributyl oxide inhibit growth of fungi and of the green algae *Chlorella pyrenoidosa* (IPCS, 1990). The primary productivity of a natural community of freshwater algae was reduced by the presence of tributyltin oxide (Wong *et al*., 1982).

4.3 Effect on aquatic organisms

TBT is lipophilic and tends to accumulate in aquatic organisms, such as, oyster, crustaceans, mollusks, mussels, fish and algae. Freshwater species will bioaccumulate more TBT than marine organisms due to the relationship between bioavailability and aqueous solubility (Extoxnet, 1996).

a) Marine and estuarine organisms

In the presence of TBT, reduction of growth rate of a marine angiosperm was detected (Waite *et al*., 1989). Tributyltin is highly toxic to marine mollusks. It has been shown experimentally to affect shell deposition of growing oysters, affect gonal development and gender of adult oysters, and increase motality of larval oysters and other bivalves (IPCS, 1990; Lawler and Aldrich, 1987; Thain and Waldock, 1986). TBT causes imposex, the development of male characteristics in female gastropods (Smith, 1981). In crustacean group, TBT reduces reproductive performance, neonate survival and juvenile growth rate (Hall *et al*., 1988; IPCS, 1990; Laughlin *et al*., 1983).

The toxicity of tributyltin to marine fish is highly variable. Larval stages are more sensitive than adult. In an effect of dose, a temporary opacity of the surface eyes may develop. Other symptoms include sluggishness and difficulties with balance. Malanophores in the skin were found to be constricted but TBT did not seem to affect feeding behavior (Hall *et al*., 1988).

b) Freshwater organisms

Freshwater angiosperms were inhibited by TBT oxide and killed in high concentration (IPCS, 1990). Freshwater mollusk and snails were sensitive to TBT acetate (IPCS, 1990). Nevertheless, TBT causes growth obstacle and the death of mollusk (Upathem *et al*., 1980). Imposex, the development of male characteristics in females, has been initiated by TBT exposure in several snail species. Consequently, reproduction was inhibited when female snail expose to TBT developed male characteristics (USEPA, 1985). Also the inhibition in growth rate and mortality of crustaceans was reported (Laughlin *et al*., 1983). In the exposure of TBT to freshwater fish, there was a dose-related obstacle of growth, resulting in a decrease in body weight. In the sensitive high level, remaining group showed significant reduction in the hemoglobin titre in the blood and in body weight (Seinen *et al*., 1981).

4.4 Effect on terrestrial organisms

Tributyltin compounds can be used as wood preservative. They can affect to terrestrial organisms. However, little information is available. TBT compounds are toxic to insects expose topically or via feeding on treat wood.

Tributyltin oxide is fairly toxic to bird. It does not affect the bird mortality but reduce egg production, eggshell thickness, fertility and hatchability (IPCS, 1990).

5. Endocrine Disrupting Chemical (EDCs)

Environmental pollution has been the source of much public discussion and media attention. Endocrine disrupting chemicals (EDCs) have caused particular concern because they may interfere with the normal function of the hormonal systems of humans and animals. Endocrine disrupting properties are found in several classes of chemicals released into the environment such as some insecticides and fungicides, dioxin and anti-fouling paint. TBT is an endocrine disrupting chemical (Metthiessen and Gibbs, 1988).

Endocrine disruptors are naturally occurring compounds or man-made chemicals that may interfere with the production or activity of hormones of the endocrine system leading to adverse health effect. Many of these chemicals have been linked with production, release, transport, metabolism, binding, biologic action or climination of natural ligands in the body that are responsible for the maintenance of homeostasis and the regulation of developmental process (Zacharewski, 1998). These chemicals also may be adversely affecting human health in similar ways resulting in declined fertility and increased incidences or progression of some diseases including endometriosis and cancers (NIEHS, 2006). These chemicals have also been referred to as endocrine modulators, environmental hormones and endocrine active compounds.

Despite of the lack of information on the effect on humans of EDCs in the environment, strong evidence links EDCs exposure to effects on some organisms in the environment, most notably the effect of tributyltin on mollusks. The action of EDCs has resulted in the localized destruction of certain species and is a cause for grave concern. The possible effect of EDCs on human are: reproductive (sperm quality, fertility, sex ratio and abnormalities of male sex organs), endometriosis, precocious puberty, nervures system function, immune function and cancer (breast cancer, endometrial cancer, testicular cancer, prostate cancer and thyroid cancer) (WHO, 2002). Even when there is no firm evidence on the interaction, the biological plausibility of possible damage to certain human functions from exposure to EDCs seems to strong when viewed against the background of known influences of endogenous and exogenous hormones on many of these processes. Therefore, despite the difficulties and uncertainties, concern remains about the possible role of exposure to EDCs in adverse health effect in humans. It is pertinent to describe the endocrine system briefly and discussing the mechanisms of endocrine disruption.

6. Environmental problem

Tributyltin (TBT) is the most toxic synthetic chemical that has ever been introduced into the marine and fresh water environment. TBT compounds are active ingredient in biocides used as antifoulants in marine paints. Other uses include wood treatment and preservation, antifungal action in textiles and industrial water systems, such as cooling towers and refrigeration water systems, wood pulp and paper mill systems, and breweries. TBT can leach from hulls or enter the water through vessel maintenance and cause detrimental effects to non-target marine organisms even at low concentration (ng/L) due to its effectiveness as a biocide. Tributyltin is an endocrine disruptor which interferes with the endocrine system in organisms and humans. It causes physical damage, reproductive effects, teratogenic effects and, the most worrying, imposex of gastropod (Smith, 1981). Imposex is the imposition of male organs (penis, vas deferens) on female organisms, causing infertility. The very low levels of TBT (about 1 μg/L) are lethal or cause reduced growth and reproduction of commercial shellfish (Navio *et al*., 1996). The legislation and banning of tributyltin compound was brought into world concern after its toxicity was detected. Regrettably, an enormous amount of this compound has already been introduced into the terrestrial and aquatic environment. It is also classed as a Persistent Organic Pollutant (POP) by United Nations Environment Programe (UNEP) (Wikipedia, 2010). Therefore, the compound is regarded as an organic compound that is a resistant to environmental degradation and will contaminate for a long period of time. The accumulation of tributyltin in environmental media and organism’s tissue has become an important issue, as it can biomagnify in the food chain which impact greatly on human.

Thailand is one of the fastest growing developing countries in Southeast Asia. Human and industrial activities in Thailand have recently increased, and trading is flourishing because of the increase of economic activity. The sailing of foreign flag vessels is, therefore, increasing in the Gulf of Thailand. This imposes a potential risk for considerable antifouling biocides. Kan-atireklap and others monitored of the contamination by butyltin compounds in sediment and green mussels (*Perna viridis L.*) from coastal areas of Thailand coastal areas in 1994 and 1995, and found that coastal areas of Thailand were heavily contaminated. Nine years have passed since that study was conducted, so it is very important to investigate the current status of organotin contamination in Thailand (Hiroya, 2006).

Maximum concentration limits for pollutants, called Environmental Quality Standard (EQS), have been established to protect aquatic environments and organisms in the ecosystem. EQS value specific to Scotland is used by Scottish Environmental protection Agency (SEPA) in regulating use of TBT. Tributyltin compound in freshwater has limit of 0.02 μg/L and marine water 0.002 μg/L. USA standard values of TBT compound are separated into acute concentration and chronic concentration. In freshwater, EQS are 0.46 and 0.063 μg/L for acute and chronic, respectively. In marine water, EQS are 0.37 and 0.01 μg/L for acute and chronic, respectively. In Thailand, Pollution Controlled Department (PCD) has defined the limit of concentration of TBT. In marine water, TBT has limit of 0.10 μg/L.

7. Determination of organotin compounds

7.1. Extraction and derivatisation of organotin compound

Tributyltin, dibutyltin and monobutyltin have to be extracted, pre-treated and concentrated before analysis. As these compounds are complexed in water, they cannot be analysed directly. Therefore, extraction methods are used to provide butyltins in a suitable form to apply analytical techniques. Several methods for the extraction and analysis of butyltins had been described. The chromatographic methods, GC and HPLC, are the techniques extensively used.

For GC analysis, the polar ionic butyltin species needs to be extracted from the sample matrix and converted into their fully alkylated which are more volatile forms, which can be separated by this analytical system. Extraction and derivatisation have to be done before analysis. Extraction of water samples, acid leaching followed by alkylation with Grignard reagent is the most basic approach. Grignard reagent is sensitive towards water, as the consequence, these two techniques are applied as multi-step to extract organotin into non-polar aprotic solvent before alkylation. The insitu process was also introduced by adding organic solvent together with alkylation reagent (Columbini *et al*., 2004). The HPLC analysis can be determined directly or extraction step is required when normal phase condition is performed (Inoue *et al*., 2000).

a) Extraction

The extraction process can use non-polar solvent and temperature gradients desorption from a purge and trap apparatus.Various solvent can be used in the extraction such as hexane (Landmeyer *et al*., 2004), cyclohexane (Paton *et al*., 2006), cyclopentene (Huang *et al*., 2004), isooctane (Columbini *et al*., 2004), and benzene (Harino *et al*., 1997). Moreover, double extractions were introduced using acetone before and followed by hexane-dichloromethane (Suehiro *et al*., 2006). In the extraction process, pH is controlled by adding acid which can be hydrochloric acid or acetic acid. A number of different solvent have been shown to be satisfactory for the extraction of TBT from water samples. DBT and MBT are more difficult to extract quantitatively due to their more ionic nature. For this reason, most methods used tropolone and sodium diethyldithio carbamate added to the solvent as a complexing agent to increase the recoveries.

Basically, liquid-liquid extraction uses shaking techniques to partition organotin between a polar and non-polar solvent. Microwave-assisted extraction (MAE) system for extraction of organotin is another alternative technique (Wang *et al*., 2006).

Utilization of solid phase extraction (SPC) techniques to separate and pre-concentrate alkyltin compounds from sample matrix has been developed (Bowles *et al*., 2003). The butyltins are then eluted from the cartridges with appropriate organic solvents, for example diethyl ether or hexane, and are ready for derivatisation with Grignard reagent. The solid-phase micro extraction (SPME) has also applied to the derivatised organotin (Campillo *et al*., 2004). Furthermore, single drop micro extraction (SDME) was developed on the same principle to compare the potential of the methods (Columbini *et al*., 2004).

b) Derivatisation

For GC, the derivatisation step by Grignard reaction uses n-propylmagnesium bromide for propylation or n-pentylmagnesium bromide to pentylate butyltin compounds (Harino *et al*., 1997; Landmeyer *et al*., 2004). A Grignard reagent is represented by formular RMgX where R can be any alkyl group and X is a halide group. These organometallic compounds behave as strong bases and are attracted to electron-deficient centers. Grignard reagents are sensitive to water, thus usually dissolved in ether and keep under an inert atmosphere. Exposure to water or the atmosphere can result in spontaneous reaction. When reagent are added to organic extracts containing butyltin compounds, Grignard reagent react with the butyltins by adding alkyl groups to form tetra-alkyltin derivative. The following reactions show the derivatisation of TBT, DBT and MBT by n-hexylmagnesium bromide:

$$\text{(n-butyl)}_3\text{Sn}^+ \quad + \quad \text{n-hexylMgBr} \longrightarrow \text{(n-hexyl)(n-butyl)}_3\text{Sn}$$

$$\text{(n-butyl)}_2\text{Sn}^{2+} \quad + \quad \text{2(n-hexylMgBr)} \longrightarrow \text{(n-hexyl)}_2\text{(n-butyl)}_2\text{Sn}$$

$$\text{(n-butyl)Sn}^{3+} \quad + \quad \text{3(n-hexylMgBr)} \longrightarrow \text{(n-hexyl)}_3\text{(n-butyl)Sn}$$

The tetraalkyltin compounds produced are thermally stable, easily separated by gas chromatography and produced characteristic mass spectra. Although many different derivatising reagent have been used for the alkylation of organotin compounds, derivatives formed by reaction with methyl and ethyl Grignard reagent are considerably more volatile than those form with larger alkyl (pentyl or hexyl) groups. The impurity in Grignard reagents may contaminate samples, particularly those that have low concentration of TBT. Therefore, addition step to clean the derivatised sample may be required.

Apart from alkyl Grignard reagent, there is also an insitu derivatisation using sodium tetraethylate ($NaBEt_4$) as a reagent (Huang and Matzner, 2003). This method has become more popular due to its faster and easier reaction. Recently, sodium tetra(n-propyl)borate ($NaBPr_4$) was introduced (Columbini *et al.*, 2004). A comparison between $NaBEt_4$ and $NaBPr_4$ gave similar derivatisation efficiency and limits of detection (Schubert *et al.*, 2000). In addition to use in-situ process, the pH must be controlled by buffers (pH 5).

7.2. Detection and measurement of organotin compounds

Normally, standard methods to determine organotin is gas chromatography (GC) couple with sensitive and specific detector. The detectors used together with GC for organotin determination are mass spectrometer (MS) (Devosa *et al*., 2005), inductive couple plasma and mass spectrometer (ICP-MS) (Huang *et al*., 2004), quartz furnace and atomic adsorption spectrophotometer (QF-AAS) (Bowles *et al*., 2003), microwave induce plasma and atomic emission spectrophotometer (MIP-AES) (Minganti *et al*., 1995), inductive couple plasma and atomic emission spectrophotometer (ICP-AES) (Tutschku *et al*., 1994).

An internal standard should be used to reliably quantify low concentration of butyltin in environmental samples. The internal standard should have similar chemical properties to the analyte so that relative recoveries are similar throughout the analytical procedure. Accurate butyltin speciation in different matrices requires the use of appropriate internal standards in order to sufficiently reduce matrix effects and systematic errors occurring during the sample preparation steps. Tripropyltin (TPrT) and triethyltin (TEtT) are commonly used as internal standard for the analysis of organotin compound in environmental samples (Columbini *et al*., 2004; Huang and Matzner, 2003; Inoue *et al*., 2000). In addition, isotope labeled standard, such as enriched TBT and TPrT (^{117}Sn, ^{118}Sn, ^{119}Sn or ^{120}Sn), have been introduced resulting in more reliable and accurate results for MS detection (Columbini *et al*., 2004; Tan, 2003). Also deuterated organotin compounds can be used for internal standardization applied for GC/MS analysis (Devosa *et al*., 2005; Landmeyer *et al*., 2004).

8. Degradation of organotin compound

Degradation of organotin compound occurs naturally in the environment which involves progressive debutylation. In this process, first, tributyltin is degraded and then, dibutyltin (DBT) and monobutyltin (MBT) are produced as products. These butyltin compounds are less toxic than TBT, so degradation of TBT can reduce the effect to the environment and organism expose to the substance (Maguire, 1984). It is theoretically into the tin compound.

$$R_3SnX \longrightarrow R_2SnX2 \longrightarrow RSnX_3 \longrightarrow SnX_4$$

8.1. Biodegradation

The effective biodegradation depends on environmental conditions including temperature, dissolved oxygen, pH, level of mineral elements or nutrient, the present of biodegradable organic substances of co-metabolism and, the nature of the microorganisms and its ability for adaptation. The high level of TBT over the lethal or inhibitory concentration would be toxic to the bacteria and, therefore, reduce the degradation efficiency. Biodegradation is a progressive oxidative debutylisation on the splitting of the carbon-tin bond. Dibutyl derivatives are formed, which are more readily degraded than tributyltin. Monobutyltin is mineralized slowly. Anaerobic degradation does occur but is considered slow, thus aerobic degradation is more rapid (IPCS, 1990). Species of bacteria, algae and fungi have been identified that can degrade TBT. Moreover, estimates of the half-life of TBT in the environment depend on environmental conditions (Dowson *et al*., 1996).

8.2. Abiotic degradation

Degradation of TBT can proceed via physico-chemical mechanisms, including hydrolysis, photodegradation and chemical cleavage. However, the hydrolysis of tributyltin compound occurs under conditions of extreme pH, it is hardly ever evident under normal environmental conditions (Maguire and Tkacz, 1985). Photodegradation occurs during laboratory exposure of solutions to UV light at a specific range of wavelength which depends on the energy required to breakdown the tin-carbon bond. UV light with a wavelength longer than 290 nm processes energy of 300 kJ/mol, whereas the adequate energy for photolysis is 190-22- kJ/mol (Champ and Saligman, 1996; Craig, 2003). Consequently, TBT species are degraded very slowly by natural sunlight. Furthermore, the UV photodegradation of TBT leads to the formation of partially oxidized products from the organic groups attached to the tin atoms. Accordingly, new methods must be developed. Heterogeneous photocatalysis has been shown to be an attractive process for the degradation of many water pollutants. Powdered titanium dioxide, TiO_2, is one of the most promising photocatalysts for the detoxification of organic or inorganic contaminants in the aquatic environment (Navio *et. al*., 1996).

9. Titanium dioxide (TiO_2)

Titanium dioxide (TiO_2) has been used in worldwide applications such as photovoltaic cells, photocatalysis, environmental purification, photoinduced superhydrophilicity as well as an ingredient in a pigment. There are three principal crystal structures, anatase , rutile and brookite (orthorhombic) found in nature (Figure 4). There are diverse methods to effectively synthesize powder, thin-film and membrane TiO_2 or modified TiO_2, namely precipitation (co-), solvothermal, sol-gel, microemulsion, electrochemical, chemical/physical vapor deposition, ion-implantation and ball milling methods.

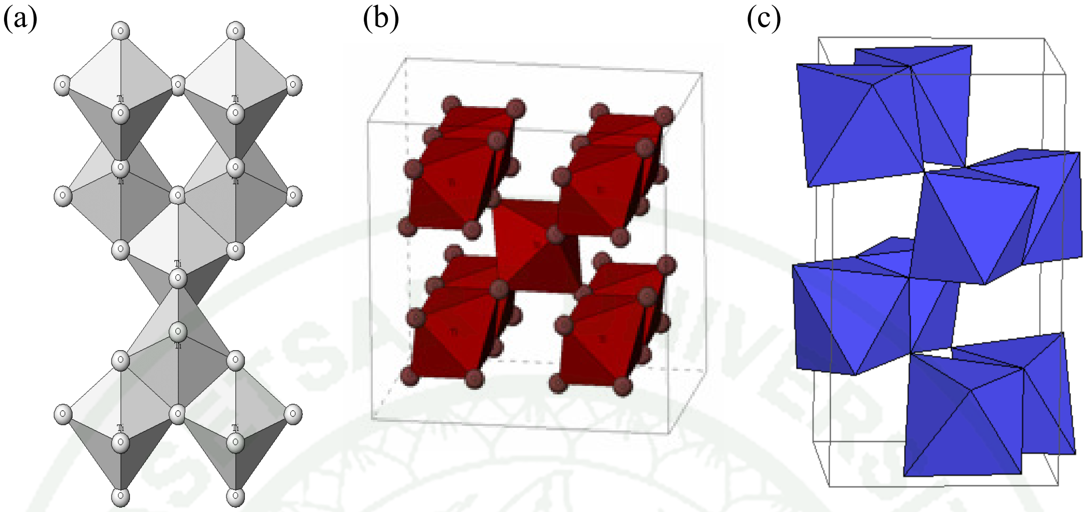


Figure 4 Crystal structures of (a) anatase, (b) rutile and (c) brookite.

Source: AIST-Kansai (2002)

TiO_2 is close to being an ideal photocatalyst due to its properties. In photocatalytic reactions, TiO_2 can degrade not only organic compounds such as hydrocarbons, chlorinated compounds and nitrogen- or sulfur-containing compounds but also inorganic compounds such as nitrogen oxide species (NO_x) and organtin compounds. Overall, photocatalytic reactions can be generally summarized as displayed in Figure 5. Initially, e^- and h^+ are generated by using photon energy ($h\nu$) which has equal or higher energy than band gap energy of TiO_2. Some electrons (e_{cb}^-) are excited into the conduction band while holes (h_{vb}^+) still stay in the valence band and then both of them will move to the TiO_2 surface with a view to reducing or oxidizing. On the other hand, e^- and h^+ are able to recombine again which can occur at the bulk and at the surface. The recombination process is usually considered as the deactivation process in photocatalytic reaction.

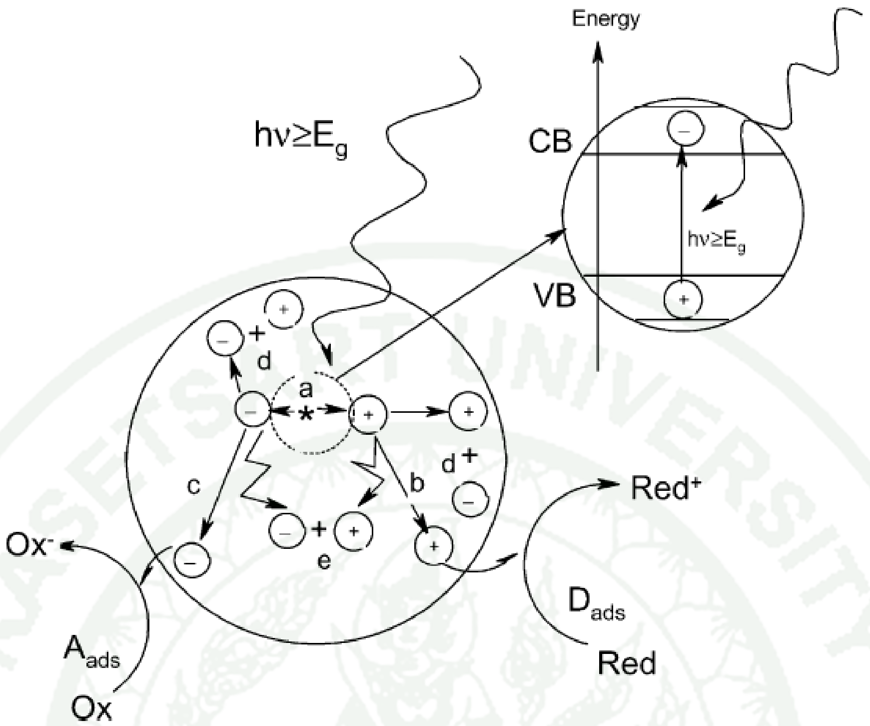


Figure 5 Principal processes on the TiO_2 particles; (a) $e^- + h^+$ generation, (b) oxidation of donors (D), (c) reduction of acceptors (A), (d) and (e) e^-- h^+ recombination at surface and in bulk, respectively.

Source: Mills and Hunte (1997)

OBJECTIVES

This work aims to study the photodegradation of organotin compounds including optimization of extraction and degradation condition. There are two main objectives that this work focuses on.

1. To study the condition and parameters which are suitable for the extraction and analysis of organotin compounds such as, amount of Grignard reagent, amount of NaCl, concentration of tropolone and pH.

2. To study rate of photodegradation of organotin compounds in various light sources such as UV light, visible light (xenon lamp) and natural light and compare with various catalyst such as commercial TiO_2 (P25), undoped TiO_2 and N-doped TiO_2.

LITERATURE REVIEW

The previous researches on degradation of organotin compound are under reviewed as followed.

Maguire *et al.* (1984) reported some physical and chemical characteristics of the tri-n-butyltin moiety from bis(tri-n-butyltin) oxide (TBTO) which indicated that TBTO may be moderately persistent in water. The tri-n-butyltin species dissolved in water neither volatilizes nor loses butyl groups over a period of at least 2 months in the dark at 20°C; in sunlight, however, it undergoes slow photolytic decomposition ($t_{1/2} > 89$ days), at least partially by stepwise debutylation to inorganic tin. At 20°C, log K_{ow} of the tributyltin species is 3.2 at pH 6; for the parent TBTO at 20°C, the aqueous solubility is 0.7-7 mg/L at pH 5-7, and the vapor pressure is estimated to be 6.4×10^{-7} mmHg.

Navio *et al.* (1993) studied the UV degradation of tributyltin (TBT), dibutyltin (DBT) and monobutyltin (MBT) chlorides. The effect of surrounding gases such as air, nitrogen and oxygen were studied. TBT in water could be photodegraded to inorganic tin via DBT and MBT as intermediates. All samples were analyzed by UV spectrophotometer. From this research, it conclude that, on UV illumination in an air-equilibrated atmosphere solution, the photodegration of butyltin species increase as the number of butyltin groups attached to the tin metal decrease. This indicated that the surrounding environment influences the efficiency of photodegration of these compounds.

Navio *et al.* (1996) studied the degradation of butyltin compounds by photocatalyst under UV illumination in air-equilibrated aqueous TiO_2 suspension. They examined several factors affecting the degradation rate, such as the extent of adsorption on the surface of catalyst particles and the effect of pH values. The adsorption of tributyltin (TBT) at the TiO_2 surface can be described by a Langmuir isotherm with an equilibrium constant, K of 13.6×10^{2} (mM^{-1}) and a limit extent for the solute adsorption equal to 2.1×10^{-6} mol/g. The IR results infer that the adsorption of TBT at the TiO_2 surface seems to proceed through the surface hydroxyl groups acting as bridges between Ti^{4+} and Sn^{4+}. The photoassisted degradation, in the presence of TiO_2, of n-butyltin compounds follow pseudo-first-order kinetics with the following sequence for rates of photodegradation: $k_{TBT} < k_{DBT} << k_{MBT}$, under experimental conditions. Increasing the pH of the solution leads to a progressive increase in the rate of photodegradation. The prolonged illumination (46 h) of TBT species in air-equilibrated aqueous TiO_2 specimens leads to a TiO_2 surface free of carbonaceous species; tin, however, remains at the TiO_2 surfaces as metallic tin and/or SnO_x.

Navio *et al.* (1997) studied the UV degradation of triphenyltin (TPT), diphenyltin (DPT) and monophenyltin (MPT). From the results of degradation of TPT, up to 135 min of illumination, they found that both the DPT and MPT species accumulated in the medium with increasing illumination time, and their concentrations progressively increased and in an almost parallel manner. This implied that the rate of degradation of TPT to DPT and TPT to MPT were very close. The balance of material which was sum of concentration of TPT, DPT and MPT during 120 min of illumination was practically constant, remaining around 1 μg/l. This seems to indicate a certain resistance to inorganic tin in dephenylation processes. So inorganic tin did not appear in a detectable amount in the medium, at least before 120 min and it was below limit of detection by atomic absorption. However, the presence of inorganic tin very low concentration in the medium could not be ruled out. Results were also presented concerning the photodegradation of TPT and DPT in different atmospheric gases such as, oxygen and nitrogen. GC-MS analysis of the photo assisted degradation of TPT showed peaks attributable to the photogenerated intermediate products present in the liquid phase. In an atmosphere open to the air, the major product was phenol, while under molecular nitrogen, the major products found were chloro-phenols.The presence or absence of oxygen gas seems to affect the photodegradation rate of the TPT species, although not that of DPT.

Kawai *et al.* (1998) studied the degradation of tributyltin by using bacteria (no. 4 strain) which was isolated from polluted river water in Osaka City. This bacterial strain degraded TBT within 24 h when the initial water concentration was 4-20 µg Sn/liter, and the addition of organic nutrient broth promoted the degradative ability. Samples were determined by gas chromatography equipped with a frame photometric detector. Following TBT degradation, dibutyltin (DBT) and monobutyltin (MBT) were produced, and finally MBT was transformed into inorganic tin. The growth of the no. 4 strain was inhibited by the addition of TBT of more than 20 µg Sn/liter in the medium and, consequently, TBT degradation might have been suppressed with the elapse of time.

Bolt *et al.* (1999) studied degradation of tributyltin chloride in water photoinduced by iron(III). Upon irridation at 365 nm, the light was only absorbed by iron(III) species. The formation of hydroxyl radical ($^{\cdot}OH$), upon irradiation was confirmed by ESR spectroscopy. From the result, 1:2:2:1 quartet (a = 14.6 G) was observed which was a characteristic of the stable adduct with $^{\cdot}OH$ radical. TBT-iron(III) mixture with 40% of monomeric species $Fe(OH)^{2+}$ under the irradiation of UV lamp at 365 nm, the concentration of TBT decreased continuously. The disappearance of TBT emerged to follow first-order kinetic and $k_{obs} = 0.039\ min^{-1}$. Simultaneously, they observed the formation of iron(II) increased quickly, then reached a plateau for longer irradiation times. This plateau can be assigned to the establishment of a steady state with the re-oxidation of iron(II) species. The analysis by GC-FID, after derivatisation with $NaBEt_4$, showed that several photoproducts, DBT and MBT, were formed during the degradation of TBT photoinduced by iron(III). The concentration of TBT, DBT and MBT were determined from calibration curves obtained with authentic sample. DBT and MBT were the major photoproducts in the early stages of the reaction. Other photoproducts were identified by GC-MS analysis. Inorganic tin, identified as $SnEt_4$, was present in the irradiated solution. Several oxidized organotin derivatives, ketone and alcohol, were identified at very low concentrations. Moreover, a mixture of TBT and iron(III) was exposed to solar light during a sunny day. After 2 h, about 50% of the TBT had disappeared and the photoproducts were analogous in nature to those observed upon excitation at 365 nm.

Inoue *et al.* (2000) studied degradation of triphenyltin (TPT) by fluorescent pseudomonad. Triphenyltin-degrading bacteria were selected by a simple technique using a post-column high performance liquid chromatography. 3, 3', 4', 7-tetrahydroxyfravone was used as a post-column reagent for determination of TPT and its metabolite, diphenyltin (DPT). An isolated strain, strain CNR15, was identified as *Pseudomonas chlororaphis* on the basis of its morphological and biochemical features. The incubation of strain CNR15 in succinate-glycerol medium and 130 μM of TPT resulted in the rapid degradation of TPT and the accumulation of approximately 40 μM DPT as the only metabolite after 48 hours. The culture supernatants of strain CNR15, grown with or without TPT, exhibited a TPT degradation activity, whereas the resting cells were not capable of degrading TPT. Triphenyltin was stoichiometrically degraded to DPT by the solid-phase extract of the culture supernatant, and benzene was detected as another degradation product. They found that the TPT degradation was catalyzed by low-molecular-mass substances (approximately 1,000 Da) in the extract termed the TPT-degrading factor. The other fluuorescent pseudomonads, *P. chlororaphis* ATCC 9446, *Pseudomonas fluorescens* ATCC 13525, and *Pseudomonas aeruginosa* ATCC 15692, also showed TPT degradation activity similar to strain CNR15 in the solid-phase extracts of their culture supernatants. These results suggest that the extracellular low-molecular-mass substance that is universally produced by the fluorescent pseudomonad could function as a potent catalyst to cometabolite TPT in the environment.

Tam *et al.* (2002) studied the removal of tributyltin (TBT) from artificial wastewater by dead and live cells of four microalgal species, *Chlorella miniata, C. sorokiniata*, *Scencedesmus dimorphus* and *S. platydiscus*. Dead cells were generally more efficient in removing TBT during three days exposure. More than 90% and 85% TBT were removed by dead cells of *Scenedesmus* and *Chlorella*, respectively. Although the removal percentages of live microalgae were smaller, TBT was continuously absorbed and degraded, and TBT removal percentages similar to respective dead cells were achieved at the end of 14 days treatment. Degradation products, DBT and MBT, were recorded mainly inside the cells, and intracellular MBT concentrations were significantly higher than DBT. In terms of TBT removal, *Scenedesmus* cells were more effective than *Chlorella*, probably due to larger cell sizes and biomass. However, TBT specific uptake and degradation by *Chlorella* was higher than in *Scenedesmus*.

Dlugonski and Bernat (2006) examined the effects of synthetic medium ingredients and culture incubation conditions on growth and tributyltin chloride (TBT) degradation activity of the fungus *Cunninghamella elegans*. The best efficiency of TBT conversion to less toxic derivatives: dibutyltin and monobutyltin was noticed on media which contained glucose, NH_4Cl, K_2HPO_4 and $MgSO_4$. Then, the constructed M3 medium (with the above components) ensured vigorous growth of *C. elegans* and allowed the reduction of 80% of the initial TBT content (10 mg/l), after 3 days of biodegradation. The further acceleration of the biocide utilization by *C. elegans* was achieved by additional oxygen supply to the growing fungus. The efficient xenobiotic biodegradation was related to the intensity of fungal growth. The obtained results suggested a cometabolic nature of TBT utilization by *C. elegans*.

Luan *et al*. (2006) studied the removal and degradation of TBT at 10, 50 and 100 mg Sn/l contamination levels by alginate-immobilized *Chlorella vulgaris* beads during six consecutive cycles (4 days each), and compare the performance with blank alginate beads (without algae). More than 90% of TBT was rapidly removed, within 1 day, by both algal and blank beads, irrespective to the spiked TBT concentrations and the number of cycles. This indicated that the initial removal was mainly by biosorption and alginate matrix provided many binding sites. For algal beads, TBT was mostly adsorbed onto alginate matrix with some on algal cell walls, and less than 10% of the spiked TBT accumulated inside cells. The amounts of debutylated products, dibutyltin (DBT) and monobutyltin (MBT) in medium increased gradually with treatment cycles and with the spiked TBT concentrations. At the contamination levels of 50 and 100 mg Sn/l, both DBT and MBT in algal bead treatments increased to more than 5 mg Sn/l in cycle 6 while little DBT and MBT were detected in blank beads throughout the cycles. The accumulation of DBT and MBT, same as TBT, inside cells was relatively small compared to that in medium and alginate matrix. For the high TBT level of 100 mg Sn/l, 60% of the spiked TBT was biodegraded by algal beads at the end of the six cycles. These results suggested that the alginate immobilized alga, *C. vulgaris* was able to continuously detoxify TBT into DBT and MBT for six consecutive cycles even at the highest TBT contamination level.

Paton *et al.* (2006) studied the degradation and toxicity of phenyltin compounds in autoclaved, autoclaved-reinoculated and non-sterilised soil in a 231 day incubation experiment following a single application. Degradation and toxicity of phenyltin compounds in soil was monitored by using both chemical and microbial methods (lux-based bacterial biosensors). Degradation was significantly slower in the sterile soil when compared to non-sterilised soils. In the non-sterilised treatment, the half-life of triphenyltin was 27 and 33 days at amendments of 10 and 20 mg Sn/kg, respectively. As initial triphenyltin degradation occurred, there was a commensurate increase in toxicity, reflecting the fact that metabolites produced may be both more bioavailable and toxic to the target receptor. Over time, the toxicity reduced as degradation proceeded. The toxicity impact on non-target receptors for these compounds may be significant.

Dlugonski and Bernat (2007) studied the relationship between TBT concentrations, the fatty acids composition and the ability of the biocide degradation of *Cunninghamella elegans*. The major fatty acids of this fungus are palmitate, stearate, oleate, linoleate and g-linolenate. The decreasing of fatty acid unsaturation index and the conversion of stearic acid in oleic acid was significantly inhibited the presence of TBT. Changes in fatty acid compositions during TBT degradation in *Cunninghamella elegans* revealed that the degree of saturation was correlated with biotransformation of the xenobiotic to less toxic compounds: dibutyltin and monobutyltin. Their results suggested that the high TBT resistance in *Cunninghamella elegans* was associated with the modulation of the fatty acids composition and the biocide degradation.

Mendo *et al.* (2007) isolated and identified bacteria resistant to TBT that could be used and developed as biosensors for TBT pollution. With this purpose, 50 strains were isolated from sediment and water from Ria de Aveiro. From this research, the Gram negative bacteria exhibited more tolerance to TBT than Gram positive bacteria. One isolate, *Aeromonas veronii*, highly resistant to TBT uses this compound as carbon source and degrades it to less toxic compounds.

Heroult *et al.* (2008) studied the degradation of organotin compounds (OTC) in agricultural and forest soil. The samples were sandy soil. Individual experiments involving the three butyl- and the three phenyltins were carried out during 90 days in controlled conditions (darkness, 28 ºC, aerobic conditions, 13% moisture) and with spiking concentration representative of environmental levels (20–50 µg Sn/kg). After 90 days, TBT and TPhT degradation levels were 58% and 94% whereas MBT and MPhT ones are only 27% and 50%, respectively. Besides, significant formation of inorganic tin appears after 30 days for TPhT spiked samples whereas it only appears after 60 days for TBT ones. The degradation of mono-organotins (MBT, MPhT), di-organotins (DBT, DPhT) and TBT is clearly identified as a single successive loss of an organic group whereas TPhT is directly degraded to MPhT. The half-life times were dependent on their substitution degree, ranging from 24 (TPhT) to 220 (MBT) days. The comparison of half-life times shows the influence of substitution degree and organic group nature on OTC persistence. According to these values, the following corresponding scale of persistence can be proposed: TPhT < DPhT < TBT ~ MPhT < DBT < MBT. In the range of pH 4.3–5.7 does not seem to influence OTC degradation under the present operating conditions. Finally this study shows the significant persistence in soil samples in our experimental conditions for most of studied organotins and highlights the potential impact on soil quality.

Jiang *et al*. (2008) studied the degradation of monomethyltin trichloride (MMT), dimethyltin dichloride (DMT) and trimethyltin chloride with their new developed HPLC-FPD hyphenated system, which enables rapid and sensitive detection of methyltins. The half-life times and kinetic rate constants of their degradation at different pH were calculate. All the degradation curves of methyltins are in according with pseudo-first-order rate equation except for the MMT at pH 4 and 6, which are in according with zero-order rate equation. For all studied methyltins, the highest degradation rate was obtained at pH 6, while the lowest one was obtained at pH 8. The degradation rate of methyltins has a sequence of TMT < DMT < MMT because of the reverse sequence of methyl groups which hinder the reaction. An unknown intermediary product, which is more stable and has higher concentration at pH 8 for MMT and DMT, of methyltin photodegradation was detected for the fist time. This unknown intermediary product was identified as $CH_3O\text{-}Sn^{3+}$, $CH_2OH\text{-}Sn^{3+}$ or $(CHO)\text{-}Sn^{3+}$ with electrospray mass spectrometry, and possible mechanism was proposed base on the intermediary product. The effects of some environmental parameters such as salinity and humic acid on the degradation rate of methyltins were also investigated. Results suggest that salinity and humic acid has strong effect on their degradation, especially for MMT, which was almost never degraded in the solutions containing NaCl and humic acid.

Bernat and Dlugonski (2009) studied the degradation of butyltin compounds by *Streptomyces* sp. isolated from plant waste composting heaps. Five initial concentrations (10, 20, 40, 60 and 80 mg/l) of DBT were utilized in universal medium supplemented with *Streptomyces* sp. IM P102.The xenobiotic degradation in the concentrations of 10, 20 and 40 mg/l was the most significant. Starting from 60 mg l^{-1} the degradation efficiency rapidly decreased. Because at 60 or 80 mg/l of DBT a stepwise decrease in actinobacterium biomass concentrations was observed, it seemed that *Streptomyces* sp. IM P102 better resisted the toxicity of DBT at 10–20 mg/l than at 60 or 80 mg/l. After 1 day of incubation, 90% of DBT was converted to less toxic derivative such as monobutyltin (MBT). DBT metabolism was inhibited by metyrapone addition, a known cytochrome P-450 inhibitor. It could provide evidence that cytochrome P-450 system is involved in DBT metabolismin Streptomyces sp. IMP102.

MATERIALS AND METHODS

Materials

Reagents

1. Tetrabutyltin ($C_{16}H_{36}Sn$, Lab. Grade, Aldrich, St. Louis, USA)
2. Tributyltin chloride ($C_{12}H_{27}SnCl$, Lab. Grade, Aldrich, St. Louis, USA)
3. Dibutyltin chloride ($C_8H_{18}SnCl_2$, Lab. Grade, Aldrich, St. Louis, USA)
4. Monobutyl chloride ($C_4H_9SnCl_3$, Lab. Grade, Aldrich, St. Louis, USA)
5. Tropolone ($C_7H_6O_2$, Lab. Grade, Aldrich, St. Louis, USA)
6. Titanium(IV) tetraisopropoxide ($C_{12}H_{28}O_4Ti$, Lab. Grade, ACROS, New Jersey, USA)
7. Titanium(IV) oxide nanopowder (TiO_2, 99.99%, Comercial Grade, Aldrich, St. Louis, USA)
8. Hexylmagnesium bromide ($C_6H_{11}MgBr$, Lab. Grade, Aldrich, St. Louis, USA)
9. Hexane(C_6H_{12}, HPLC grade, Fisher, Leicestershire, England)
10. Methanol (CH_3OH, AR. Grade, BDH, Poole, England)
11. Sodium chloride(NaCl, Lab Grade, BDH, Poole, England)
12. Sodium sulfate (Na_2SO_4, AR. Grade, Merck, Hohenbrunn, Germany)
13. Ammonia solution (NH_4OH, 25%, AR. Grade, Merck, Darmstadt, Germany)

Methods

1. Optimization of extraction

The solutions were prepared by using stock solution 1000 mg/L of TBT, DBT and MBT. The concentrations of compounds were studied at 5 mg/L in water. The solutions were used all of this section.

1.1. Amout of Grignard reagent

In this experiment, the concentrations of TBT, DBT and MBT were studied at 10 mg/L in hexane. 1 mL of sample solution was transferred into vial. The amount of hexylmagnesium bromide was varied by 0.1 mL, 0.3 mL and 0.5 mL. The sample solution was kept in ice bath for 1 hour. After that, the reaction was stopped by adding 3 mL of 2M HCl. Then, 1 mL of organic phase was collected and performed by GC/MS.

1.2. Effect of tropolone

Sample solution was added NaCl 30 mg and concentrated HCl 30 µl. Then, the solution was extracted by 10 mL of tropolone in hexane for triplicates. The amount of tropolone in hexane was varied by 0.02%, 0.04%, 0.05%, 0.06%, 0.07% and 1.00%. After that, the extracted solutions were derivatized and were performed by GC/MS.

1.2.1. Stoichiometric determination of tributyltin, dibutyltin and monobutyltin complexes with tropolone

Pipette 0.00, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90 and 1.00 mL of 1 ppm of tributyltin chloride into each of eleven 10 mL volumetric flasks. Then, 1.00, 0.90, 0.80, 0.70, 0.60, 0.50, 0.40, 0.30, 0.20 and 0.10 mL of 0.0005% tropolone were separately pipette into each volumetric flask, respectively.

The absorbances of the solutions were measured by UV-Vis spectrophotometer in the range of 200 to 400 nm. For dibutyltin and monobutyltin complexes, they were prepared by similar method.

1.3. Effect of HCl (pH)

60 mg of NaCl was added into sample solution. The pH was adjusted by concentrated HCl which was varied pH 1.5, 1.6, 1.7, 1.8 and 2.0, respectively. So the sample solutions were extracted by 0.05% tropolone for triplicates and derivatised. The analyte was performed by GC/MS.

1.4. Effect of NaCl

The pH of sample solution was adjusted to 1.7 by concentrated HCl. The amount of NaCl having varied was 10, 30, 60, 80, 100 and 200 mg, and then, was extracted by 0.05% tropolone for three replicates. The extracted samples were derivatised and analyzed by GC/MS.

2. Determination of organotin compounds

2.1. Extraction of organotin compounds

Organotin compounds were extracted using the method adapted by Bangkedphol (Bangkedphol et. al., 2010). 2 mL of water sample was collected and then transferred into test tube. 4 mg of NaCl was added to the sample and pH was adjusted to 1.7 with concentrated HCl so as to increase ionic strength of water. The sample was extracted 3 times with 1 mL of 0.05% tropolone in hexane. All organic phases collected from each step were mixed into one portion. After that 0.5 mL of 16M TeBT which was divided from 25 mL of 1000 mg/L stock solution was added to the extracted solution as internal standard and then made up with hexane in 4 mL volumetric flask. For the derivatization, 2 mL of extracted sample was transferred into vial and then 0.5 mL of *n*-hexylmagnesium bromide was added. This process was allowed to proceed for 1 hour in inert atmosphere. After that the reaction was stopped by adding 3 mL of 2M HCl and the solution was set aside for 30 min. The organic phase was separated for analysis and dried with anhydrous ammonium sulphate.

2.2. GC/FPD

The derivatised solution 2 µl was introduced into Agilent 7890A Gas chromatograph tandem with Flame Photoemission Detector (FPD). The chromatographic capillary column was a Varian CP-Sil 8, 30m x 0.25mm i.d., 0.25 µl film thicknesses. The carrier gas was helium with the flow rate of 0.1 mL/min. Injector and detector temperature were held at 250 ºC. The solvent delay was 5 min. The column oven temperature was programmed from the initial temperature of 100 ºC, held for 1 min, to final temperature of 300 ºC at the rate of 20 ºC/min, and held for 1 min. Sample injection was splitless for 1 min followed by the split mode. The temperature of Flame Photoemission Detector was adjusted to 250 ºC.

2.3. GC/MS

2 µl of derivatised solution was introduced into Varian CP-3800 gas chromatograph attach to a 1200L quadrupole mass spectrometer. The chromatographic capillary column was used as same as in GC/FPD. Injector was set at 250 ºC. The solvent delay was 5 min. The carrier gas was helium with the flow rate of 1.0 mL/min. The column oven temperature was programmed from an initial temperature of 100 ºC, held for 1 min, to final temperature of 300 ºC with 10 ºC/min of rate, and held for1 min. Sample injection was splitless. The mass spectrometer was full scan in EI mode. The detector acquisition method employed to select ion monitoring for TeBT, TBT, DBT and MBT between *m/z* 205 and 390, over total ion. The peak area and total spectra (Total ion Chromatogram, TIC) were recorded.

3. Catalyst Preparation

The titanium dioxide doped nitrogen (N-doped TiO_2) was prepared by the sol-gel method which was adapted from Sirisaksoontorn (Sirisaksoontorn et. al. 2009). Firstly, 5.00 mL of 25% ammonia solution as a nitrogen source was continually added into 10.00 mL titanium (IV) tetraisopropoxide as a titania precursor under the constantly stirring rate (400 rpm) at 30ºC. After ten minutes, the condensed solution was occurred; arise out of the rapid hydrolysis and condensation reactions. This condition was held for 1 hour at 30ºC. Consequently, yellow gel powder was obtained and then dried at 160ºC in the oven for hour to evaporate the remaining ammonia solution and some organic by-products generating from the hydrolysis reaction. Finally, as-prepared N-doped TiO_2 was calcined in the muffle furnace at 400 ºC for 1 hour. The undoped titanium dioxide (TiO_2) was prepared by the similar sol-gel method. However, distilled water was used instead of 25% ammonia solution.

4. Catalyst characterization

4.1. X-ray Diffraction (XRD)

4.1.1. Determination of the crystalline phase

The crystalline phase was obtained by a Philips Pw 1830 X-ray diffractometer (XRD) operated at 40 kV and 35 mA and a Philips X′ Pert X-ray diffractometer operated at 40 kV and 30 mA, both of which used Cu K_α radiation source at λ of 1.54 Å. XRD data were collected from 2θ of 20-60 degree. Each of the crushed samples was either coated on the inverse side of cello tape and made its surface smooth by pressing with a spatula or spread on a small piece of glass and pressed with another smooth-surfaced glass. The crystalline phase of all samples was identified by comparison with the Joint Committee on Powder Diffraction Standards (JCPDS) files.

4.1.2. Determination of the crystallite size

The crystallite size was also calculated applying the Scherer's equation as shown in equation 1 (Patterson *et al.,* 1939).

$$d = \frac{k\lambda}{\beta \cos\theta_B} \qquad \text{.....(1)}$$

where d is the crystallite size (nm)

k is the constant whose value is approximately 0.9

λ is the wavelength of the X-ray radiation source (0.154 nm for Cu K_α)

β is the full width at half maximum intensity (FWHM) (radians)

θ_B is the Bragg angle at the position of the peak maximum

The example of the calculation is shown in the Appendix A.

4.1.3. Determination of the unit cell volume

The unit cell volume was calculated from the product among three lattice parameters (a, b and c), which can be equated for the tetragonal system (a≠b=c) as follows;

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{l^2 + k^2}{c^2} \qquad \text{.....(3)}$$

where *d* is a lattice spacing between the planes in the atomic lattice

h, k and l are the Miller indices

a, b and c are the lattice parameters

The example of the calculation is shown in the Appendix B.

4.2. Scanning Electron Microscopy (SEM)

The morphology of all N-doped TiO_2 catalysts was determined by SEM recorded on a JEOL JSM-5600Lv scanning electron microscope fitted with tungsten filament. Each of the powdered samples was spread on a carbon tape mounted on a SEM stub and needed to be coated with Pt/Pd particles prior to SEM operation.

4.3. Transmission Electron Microscopy (TEM)

The morphology and particle size of all catalysts were investigated by TEM recorded on a JEOL 1200 EX electron microscope fitted with a standard tungsten filament and operated at 80 keV. Images were recorded digitally using a Mega View II digital camera with Soft Imaging System GmbH analysis 3.0 image analysis software and/or on KODAK Electron Image Film SO-163. Samples diluted in ethanol solution were deposited onto Formvar-coated, carbon-reinforced, 3-mm-diameter copper electron microscope grids and left to air-dry prior to analysis.

4.4. Elemental Analysis (EA)

The nitrogen and carbon contents were carried out on LECO CHNS-932 Elemental Analyzer. Before operating, a blank sample of which the weight was set up at 2.000 mg needed to be run for many times until the percentages of C, H, N and S were constant. About 2.000 mg standard reference, sulfamethazine, was also necessary to be operated in order to check the instrumental accuracy which shows that the percentages of C, H, N and S should be congruent with the standard values, that is, C of 51.78%, H of 5.07%, N of 20.13% and S of 11.52%. Then set blank again for one time before three-replicated samples weighted in tin capsules about 2.000 mg in each replica were run.

4.5. Diffuse Reflectance UV-Vis Spectrophotometry

Diffuse reflectance UV-Vis spectra from 200 nm to 700 nm of all catalysts with slit width of 2 nm were collected on a Perkin Elmer Lambda 650 spectrophotometer. The powdered sample was mounted on a glass by using acetone to help the sample adhere to the glass plate during running time. Then, the sample was pressed by a spatula to have a smooth surface and moved into the analysis chamber.

5. Preparation of organotin solutions for photodegradation reaction

5.1. Preparation of stock solution

The stock solution of tetrabutyltin (TeBT), tributyltin chloride (TBT), dibutyltin dichloride (DBT) and monobutyltin trichloride (MBT) were prepared distinctly to a concentration of 1000 mg/L in hexane. TeBT standrad solution, 23.70 µl was transferred and made up with hexane in 25 mL volumetric flask. 21.70 µl of the TBT standard solution was transferred into a 25 mL volumetric flask and made up to the volume with hexane. The solid standard of DBT was accurately weighed 26.04 mg, then dissolved and made up with hexane in 25 mL volumetric flask. MBT standard solution, 15.40 µl was transferred and made up to the volume with hexane in 25 mL volumetric flask. The stock solutions were kept at a temperature close to 0 ºC in the dark condition. For preparing water samples, the stock solution of TBT, DBT and MBT were prepared separately in methanol.

5.2. Preparation of organotin solutions for linear calibration curves

Stock solution 1000 mg/L of TBT, DBT and MBT were mixed in one portion and were diluted in hexane to form working solutions of concentrations 0.5 mg/L, 1.0 mg/L, 2.0 mg/L, 3.0 mg/L, 4.0 mg/L and 5.0 mg/L, respectively. However, 2.0 mg/L of TeBT was added as internal standard.

6. Photoreactor

6.1. Visible photoreactor

The photodegradation reaction of organotin compounds were studied by using a photoreactor as shown in figure 6. 90/100W of the Xe lamp as a light source has been fitted, which can be selected to operate 90W, 100W or 190W per one lamp. The current adaptor has necessarily been used for the adjustment of AC 220V to DC 12V. Inside the reactor; it contained a set of magnetic stirrer, including a 400 mL foil-covered beaker equipped with a HOYA UV 385 cutoff filter. Besides, this reactor can control the inside temperature in 30 ºC during 5 hours of the reaction.

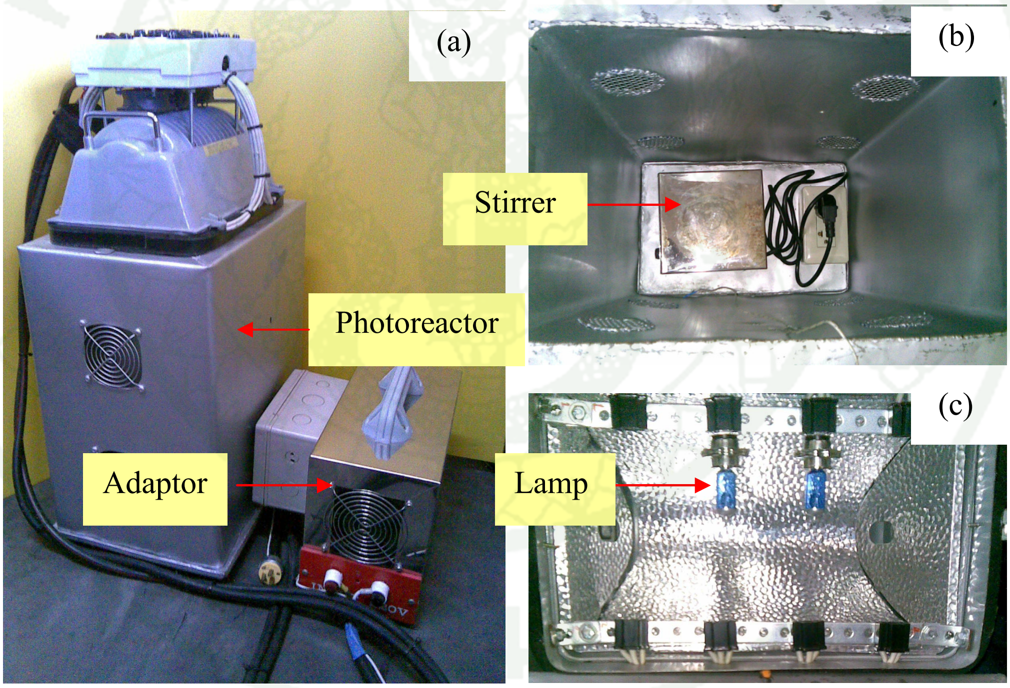


Figure 6 The graphic picture of the visible photoreactor; (a) the photoreactor set, (b) the stirrer set and (c) the lamp set.

6.2. UV photoreactor

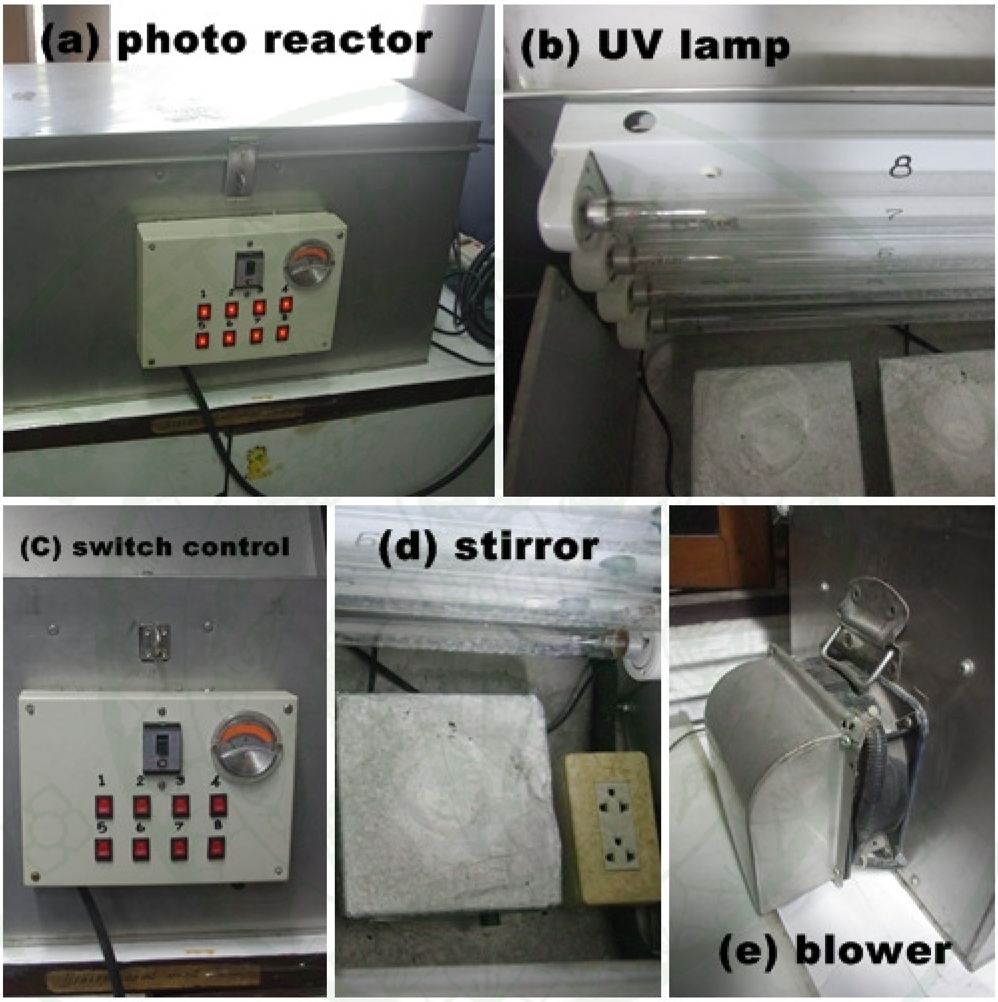


Figure 7 The graphic picture of the UV photoreactor; (a) the photoreactor set, (b) the lamp set, (c) swith control, (d) the stirrer set, and (e) blower.

The light source of UV photoreactor used 120W which consisted of 8 lamps of 15W SANYO DENKI G15T8 UV-lamp. A set of magnetic stirrer was contained inside the reactor, including a 400 mL beaker. Besides, this reactor can control the inside temperature in 30 ºC during 5 hours of the reaction.

7. Phodegradation study

7.1. Artificial light

The general procedure used to study the photodegradation activity of each photocatalyst is as follows;

Initially, 10 mL of 1000 mg/L stock solution of butyltin which was dissolved in methanol was measured out and diluted to 10 mg/L with distilled water in the 1000 mL volumetric flask. After that the solution was sonicated in water bath in order to enhance the solubility of butyltin and the homogeneity of solution. In case of visible light irradiation, the solution was poured into a 400 mL beaker cover with foil which equipped with a HOYA UV 385 cut-off filter was used. The HOYA UV 385 cut-off filter was not be used in case of UV irradiation. Then 0.1 g of the photocatalyst was added. The degradation reaction was operated under dark reaction for half an hour and then under artificial light reaction. The dark reaction was done in order to make the system reach the equilibrium point before degradation. In this condition, solution was stirred under the constant temperature in the photoreactor during the period of degradation and 2 mL of sample was collected by autopipette for initial concentration (C_0). Before samples were picked up, however, the stirrer was switched off by 5 min in order to abate the suspension of the catalyst in solution. All of collected samples were extracted and derivatised. Finally, the analysts were performed by GC/FPD. The kinetics of photodegradation may be expressed as $\ln(C_0/C)= kt$, where k is the apparent reaction rate constant, and C_0 and C are the concentrations of initial butyltin and butyltin after time, respectively.

Based on the general procedure, the period of time for Photodegradation of organotin compounds was set on 5 hours after half an hour in dark. 2ml of sample was tripicately collected in every hour. Then, the samples were extracted by 1 ml of 0.05% tropolone in hexane for triplicate. The total amount of extracted solution was 3 mL. After that, 0.5 mL of 16M TeBT was added as internal standard and made up with hexane until 4 mL. The analyses were derivatised by 0.5 mL of hexylmagnesium bromide and kept in ice bath for 1 hour. 3 mL of 2M HCl was added in order to stop reaction. The analyses were performed by GC/FPD and GC/MS.

7.2. Solar irradiation

Firstly, Water sample that consisted 10 ppm of TBT, DBT and MBT were separately prepared by diluting from 1000 ppm of stock solution with the volume of 100 mL. The solution was stirred in dark condition for 30 min. 2 mL of sample was collected for initial concentration (C_0). After that, samples were irradiated by natural light for 5 hours and collected 3 times every hour. Then, sample was extracted and derivatised. The extract solutions were performed by GC/FPD and GC/MS.

8. Determination and photodegradation of butyltin in sea water from Lam Chabang Gulf of Thailand

Due to the concentration of organotin compounds in natural samples is very low, preconcentration is required. 400 mL of netural water sample from Lam Chabang Harbour was transferred into separatory funnel. Then, the pH was adjusted to 2 with concentrate HCl and added 0.8 mg NaCl. The sample was extracted for triplicate with 20 mL of 0.05% tropolone in hexane for 30 min each time. The extracts were dried with nitrogen purging and reconstituted in 3 mL of hexane. After that, 0.5 mL of 16M of TeBT was added as an internal standard and made up into 4 mL with hexane. The solution was derivertised with 0.5 mL of hexylmagnesium bromide for 1 hour and then 3 mL of 2M HCl added to stop the reaction. The moisture was removed by small amount of anhydrous of ammonium sulphate. The analyzed samples were determined by GC/MS. Using the linear regression equation from the calibration graph, the peak areas were quantified and the concentration of organotin compounds calculated.

For photodegradation, the experiment was performed in Bangkok, December, 2009. 400 mL of natural water sample was transferred into beaker which contained 0.4 mg of N-doped TiO_2. The solution was stirred under sunlight for 5 hours. After that, the solution was rested in order to abate the suspension of the catalyst in solution. Then, the solution was extracted and derivatised as mention above. The analyzed sample was determined for organotin compounds by GC/FPD.

RESULTS AND DISCUSSIONS

1. Analysis of butyltin compound

1.1. GC/FPD

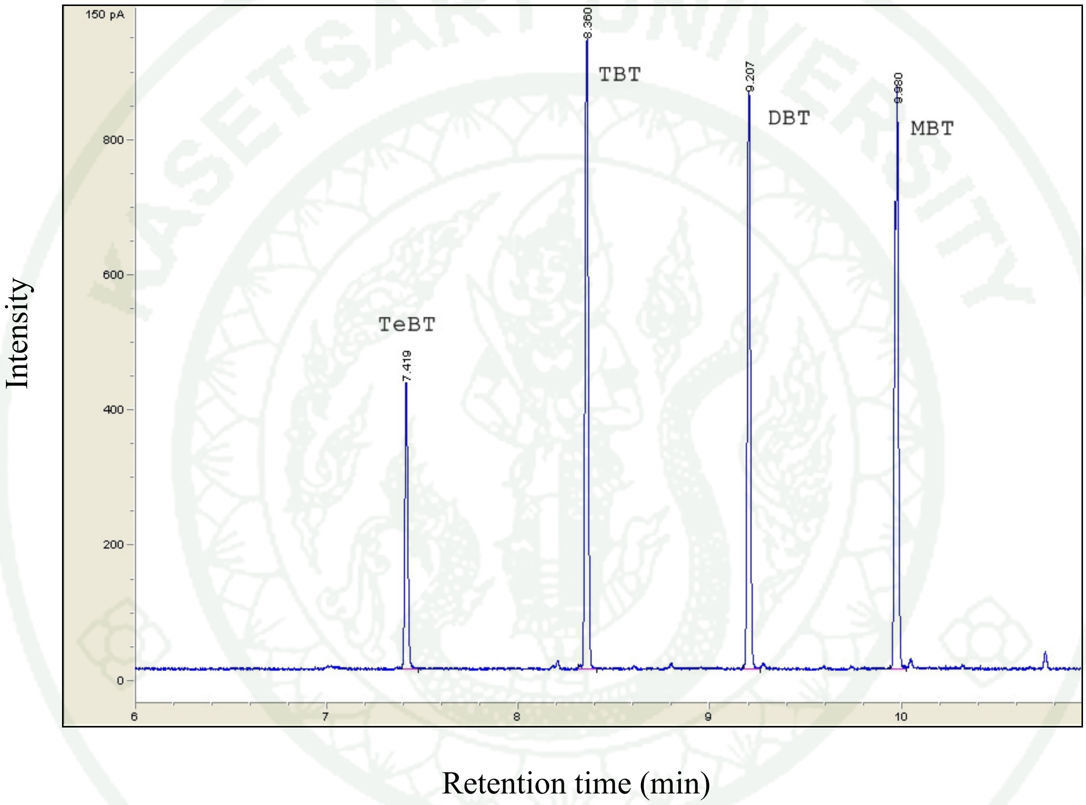


Figure 8 The chromatogram of organotin compounds determined by GC/FPD; monobutyltin(MBT), dibutyltin(DBT), tributyltin(TBT) and tetrabutyltin(TeBT) with the retention time of 9.980, 9.207, 8.360 and 7.491 minutes, respectively.

Figure 8 shows the total ion chromatogram of organotin compounds which was determined by GC/FPD. The retention times were 9.980, 9.207, 8.360 and 7.491 minutes for MBT, DBT, TBT and TeBT, respectively. The order of organotin compounds that was eluted from the capillary column are in line with charge of molecule. TeBT was eluted from the column at first because it has the lowest molecular weight and then TBT, DBT and MBT were eluted, respectively.

1.2. GC/MS

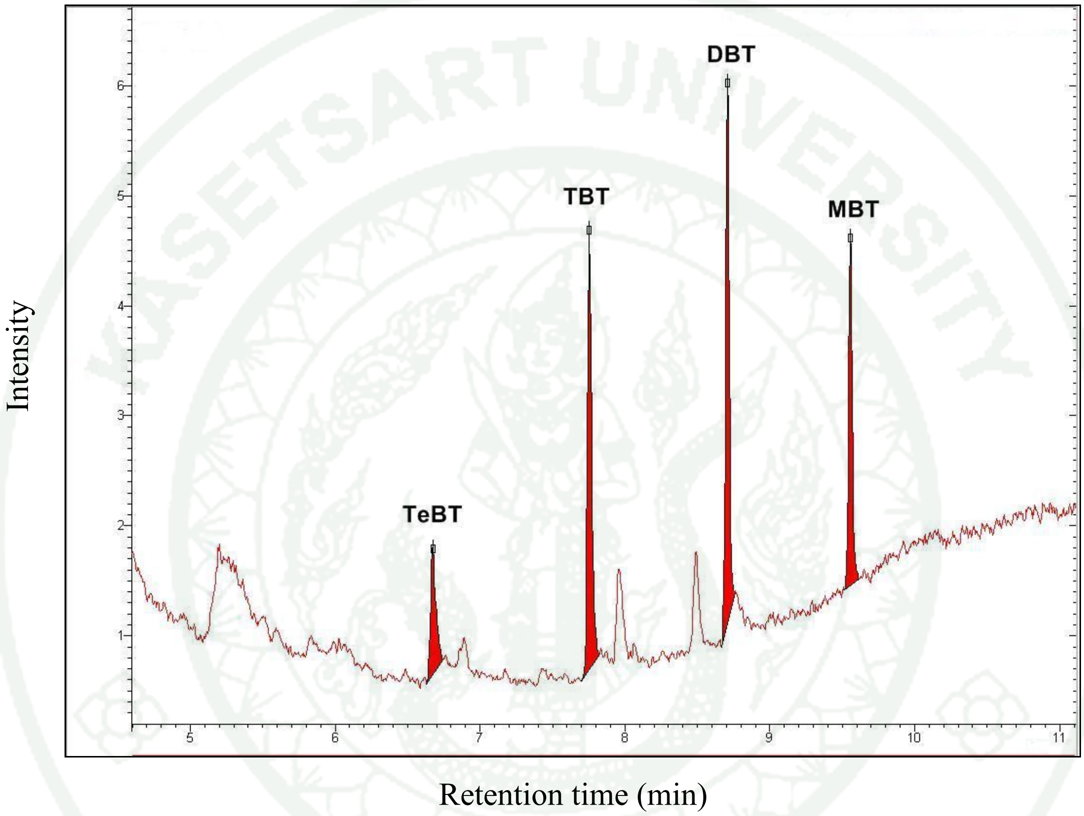


Figure 9 Total ion chromatogram of organotin compounds determined by GC/MS; monobutyltin(MBT), dibutyltin(DBT), tributyltin(TBT) and tetrabutyltin(TeBT) with the retention time of 10.377, 9.622, 8.773 and 7.846 minutes, respectively.

Figure 9 shows the total ion chromatogram of organotin compounds determined by GC/MS. The retention times were 10.377, 9.622, 8.773 and 7.846 minutes for MBT, DBT, TBT and TeBT, respectively. Mass spectra of organotin compounds determined by GC/MS with EI mode are shown in figure 10 to 13.

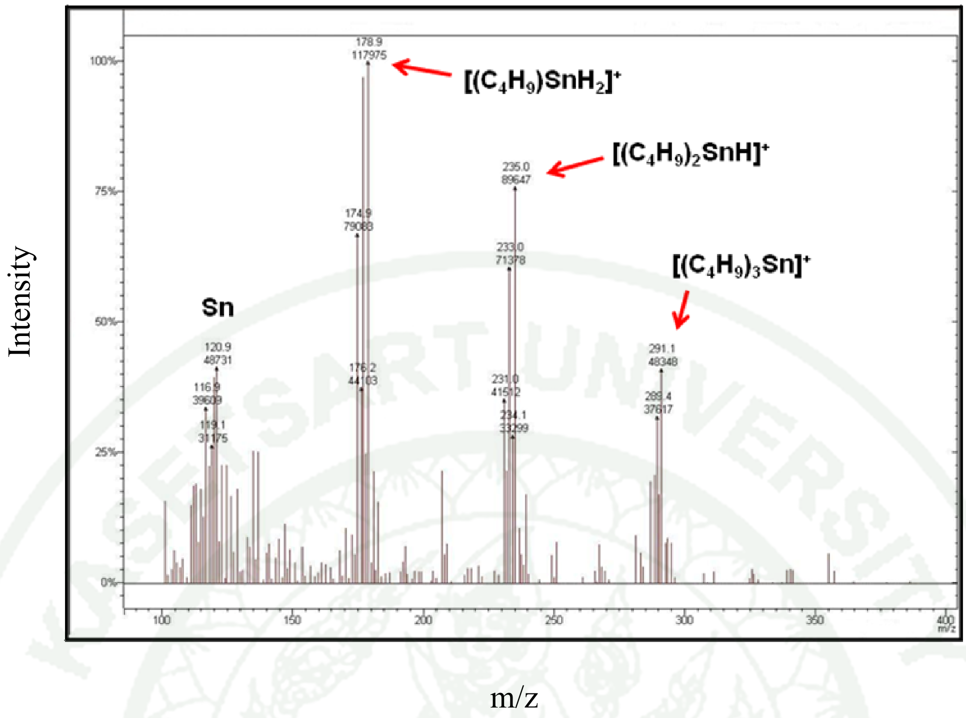


Figure 10 Mass spectra of tetrabutyltin (TeBT)

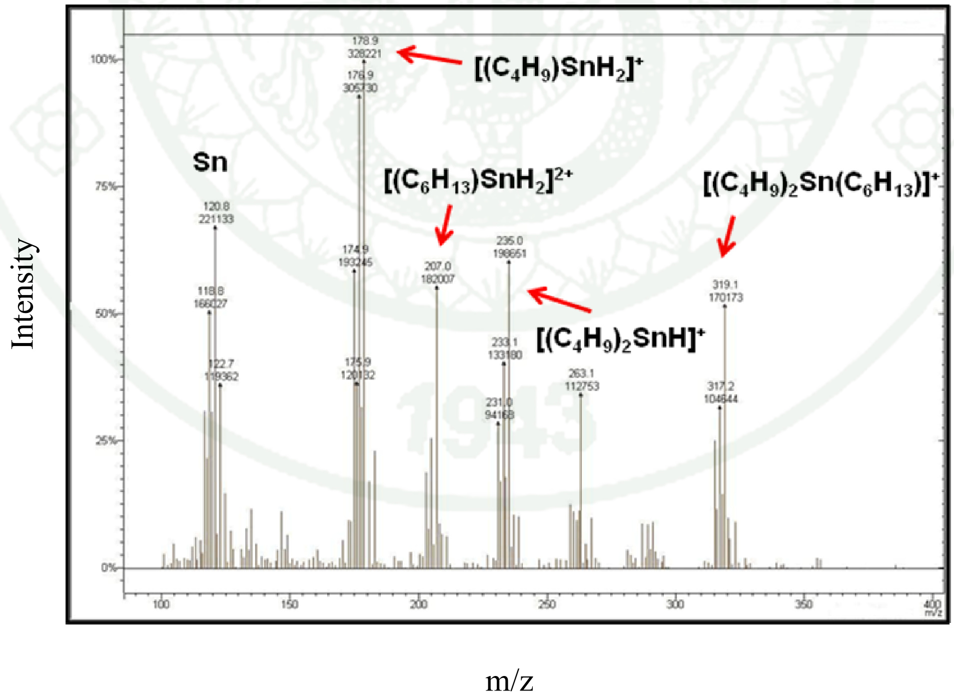


Figure 11 Mass spectra of tributyltin chioride (TBT)

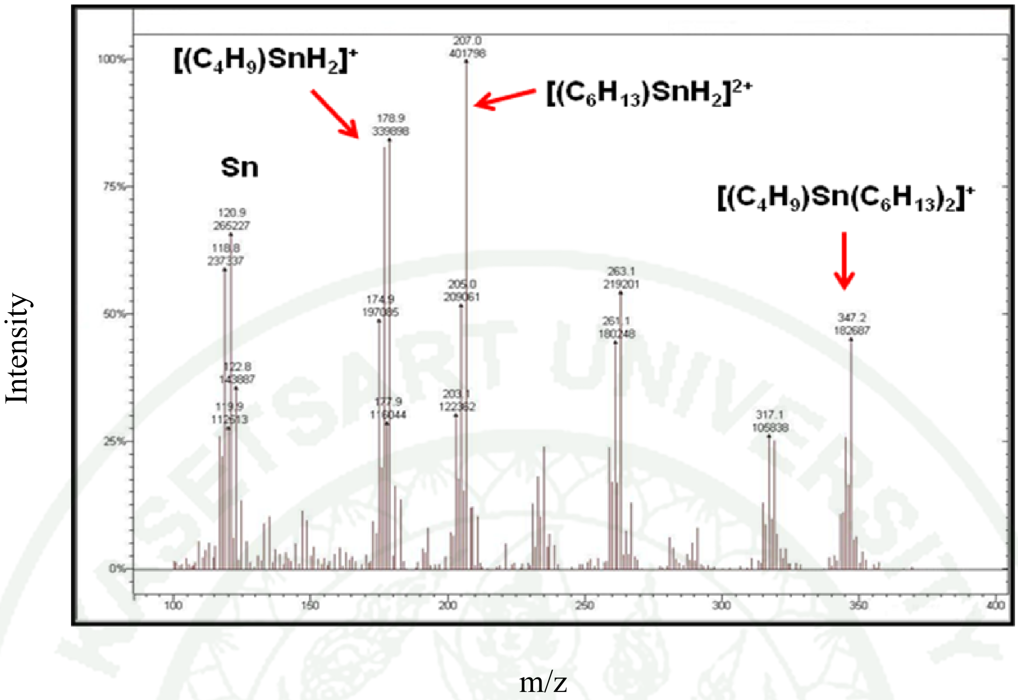


Figure 12 Mass spectra of dibutyltin chioride (DBT)

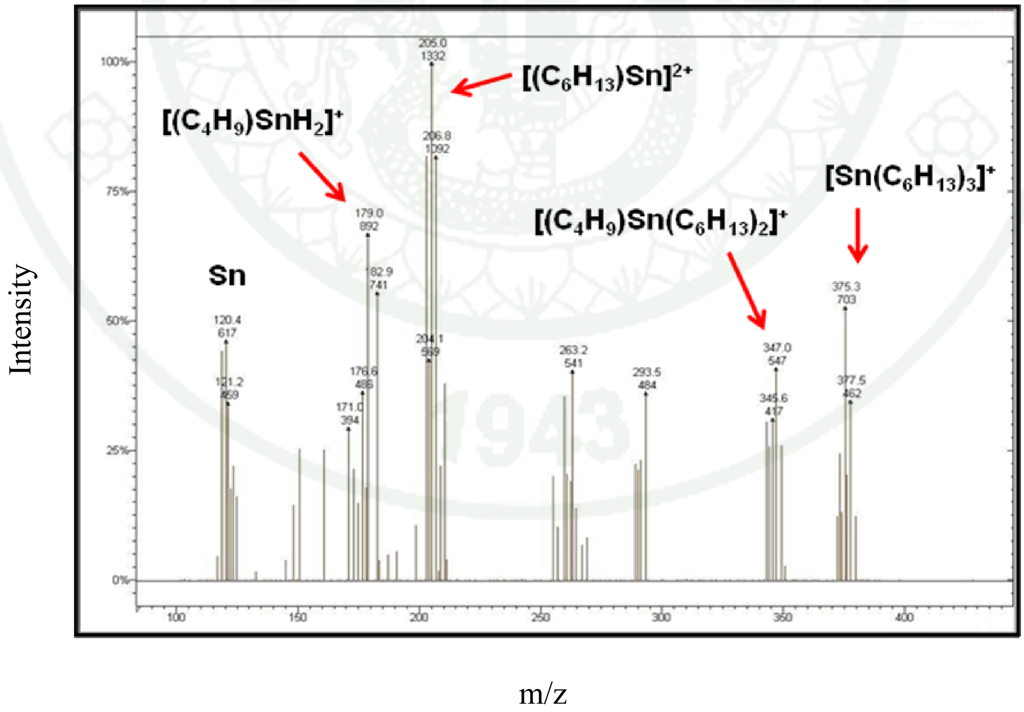


Figure 13 Mass spectra of monobutyltin chioride (MBT)

1.3. Effect of Grignard reagent

In general, Organotin compounds have a high boiling point temperature so it cannot be analyzed by gas chromatography technique. Derivatization method was used in order to decrease boiling point temperature of organotin compounds. When 0.1 and 0.3 mL of hexylmagnesium bromide were used in derivatization, the recovery of organotin compounds was lower than 0.5 mL. The result shows the good recovery of TBT, DBT and MBT when used 0.5 mL of hexylmagnesium bromide as shown in table 2.

Table 2 The recovery of MBT, DBT and TBT in water samples when 0.5 mL of hexylmagnesium bromide was used in the derivatization.

sample	Added (mg/L)	Founded (mg/L)	%Recovery	Average (%)	S.D.
TBT	10.00	9.45	94.50	105.51	1.06
	10.00	11.56	115.57		
	10.00	10.65	106.46		
DBT	10.00	10.57	105.69	108.10	0.29
	10.00	10.74	107.37		
	10.00	11.13	111.25		
MBT	10.00	10.45	104.52	108.88	0.50
	10.00	11.43	114.30		
	10.00	10.78	107.82		

2. Optimizations of extraction

2.1. Effect of tropolone on extraction efficiency

Table 3 The recoveries of tributyltin (TBT) and dibutyltin (DBT) extracted from water samples which used hexane containing tropolone as extracting solvent.

Analyte	% Tropolone in hexane	Found (mg/L)			Average (mg/L)	Recovery ± R.S.D. (%)
		1	2	3		
TBT	0.000	4.0129	4.0152	4.0102	4.0128	80.26±0.06
	0.020	4.0367	4.0354	4.0381	4.0367	80.73±0.03
	0.040	4.3506	4.352	4.3493	4.3506	87.01±0.03
	0.050	4.4104	4.4027	4.4077	4.4069	88.14±0.09
	0.060	4.4104	4.4126	4.4072	4.4101	88.20±0.06
	0.070	4.3893	4.3915	4.3937	4.3915	87.83±0.05
	0.100	4.4149	4.4175	4.4135	4.4153	88.31±0.05
DBT	0.000	0.7701	0.7695	0.7718	0.7705	15.41±0.15
	0.020	4.2860	4.2836	4.2873	4.2856	85.71±0.04
	0.040	4.7213	4.7228	4.7195	4.7212	94.42±0.04
	0.050	4.9482	4.9492	4.9472	4.9482	98.96±0.02
	0.060	4.9490	4.9492	4.9513	4.9499	99.00±0.03
	0.070	5.0048	5.0025	5.0062	5.0045	100.09±0.04
	0.100	4.9465	4.9474	4.9480	4.9473	98.95±0.01

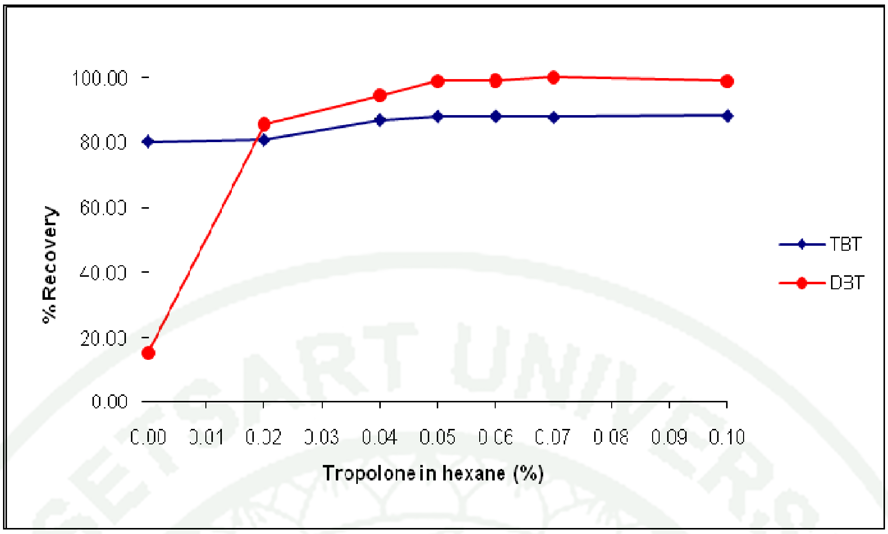


Figure 14 The recoveries of TBT and DBT at different concentrations of tropolone in hexane

The ligand tropolone has been used to enhance the extraction efficiency of organotin compounds. Tropolone forms stable complexes with MBT and DBT in solution, but not with TBT (Astruc *et al*., 1992). Figure 15 and 16 show the absorption spectra measured at the wavelength in the range of 200 to 400 nm of tropolone complexes with MBT and DBT at various ratios, respectively. The stoichiometry of complexes between MBT and DBT with tropolone was determined by continuous variation method (Job's method) using the experiment results from figure 15 and 16. The Job's plot of complex between absorbance of MBT and tropolone as shown in figure 17 indicated that the stoichiometric ratio between MBT and tropolone was 1:2. From figure 18, the Job's plot of complex between DBT and tropolone shows that the stoichiometric ratio between DBT and tropolone was 1:1.

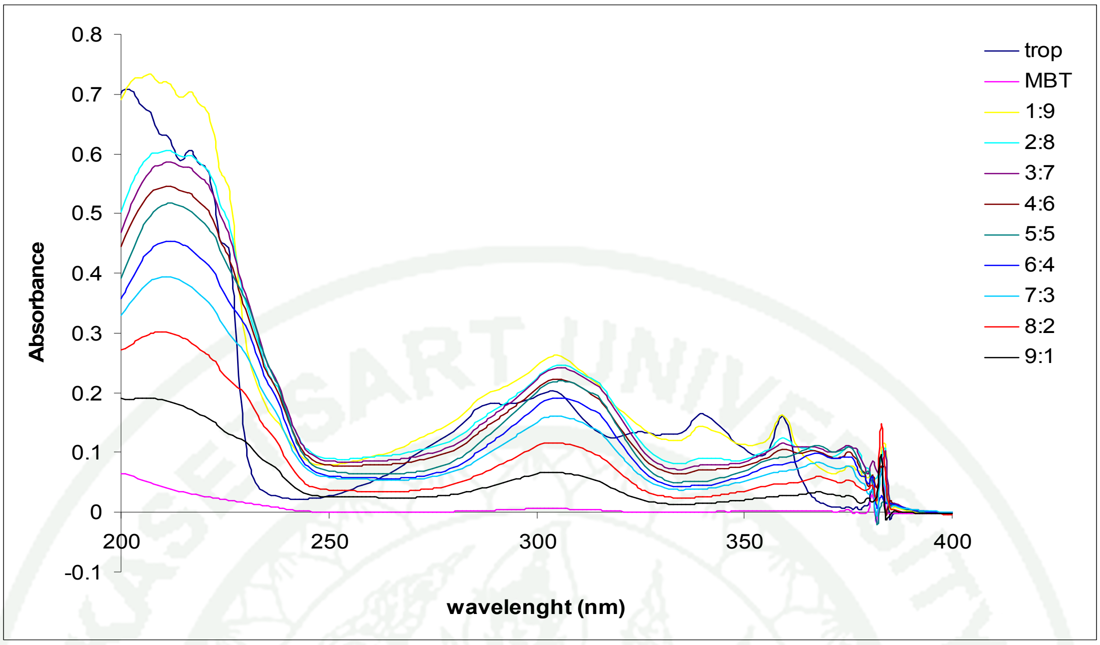


Figure 15 The spectra of complexes between butyltin trichloride (MBT) and tropolone in various ratio.

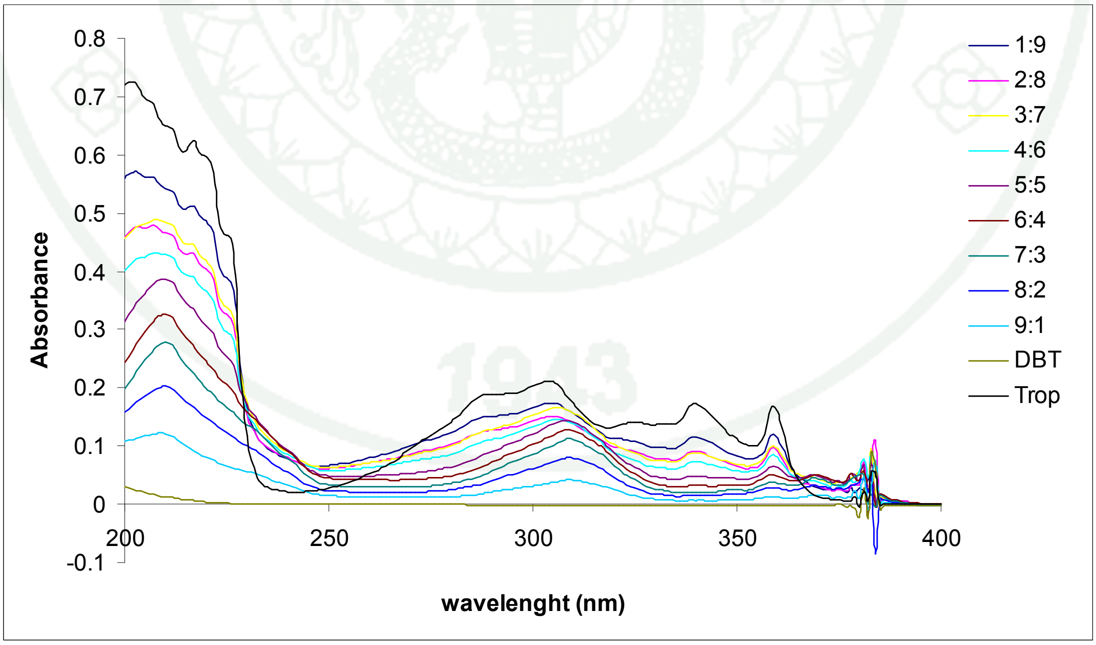


Figure 16 The spectra of complexes between dibutyltin dichloride (DBT) and tropolone in various ratio.

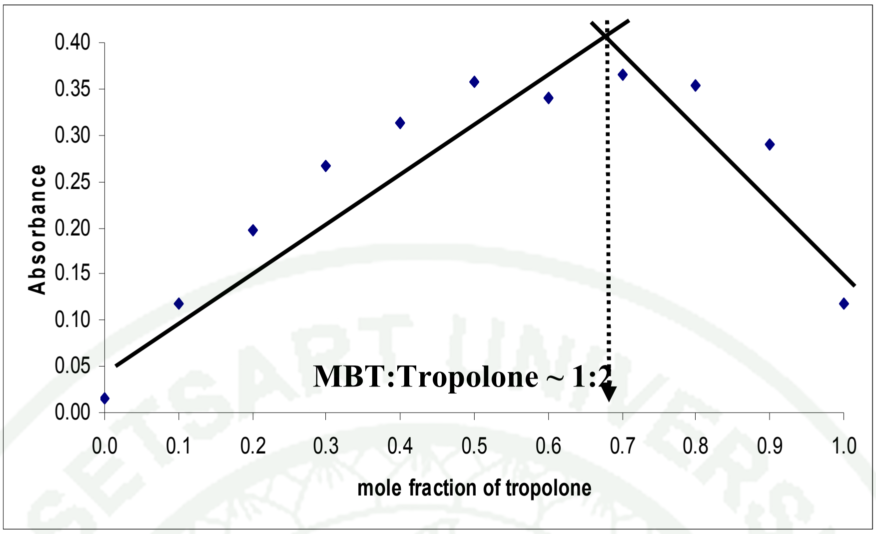


Figure 17 Job’s method plot of complex between monobutyltin chloride and tropolone in hexane, measured at wavelength 230 nm.

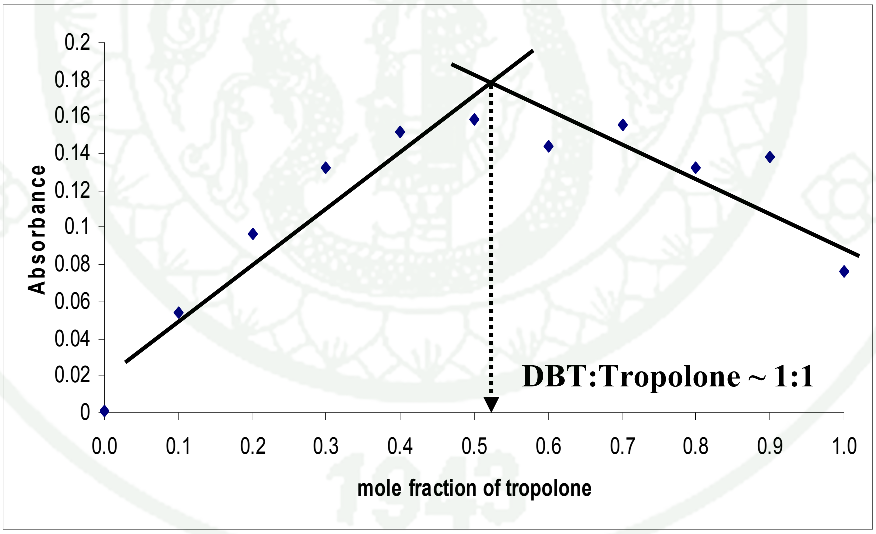


Figure 18 Job’s method plot of complex between dibutyltin chloride and tropolone in hexane, measured at wavelength 231 nm.

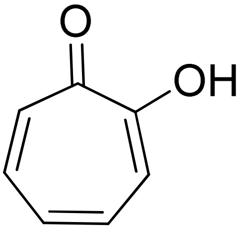


Figure 19 Chemical structure of tropolone

Tropolone is a bidentate ligand which can donate two electron pairs to butyltin compound through each terminal oxygen atoms. Tin is a p-block metal which usually forms complexes with ligands and give maximum 5 coordinating compounds of trigonal bipyramidal structure (Greenwood and Earnshaw, 1997). For this reason, monobutyltin theoretically can form a complex with two molecules of tropolone giving trigonal bipyramidal structure while dibutyltin can form complex with only one molecule of tropolone giving tetrahedral structure. The possible chemical structures of both complexes are shown in figure 20. The free molecule of tributyltin, in general will form a trigonal planar molecule and three bulky butyl groups will hinder the formation of tropolone complex.

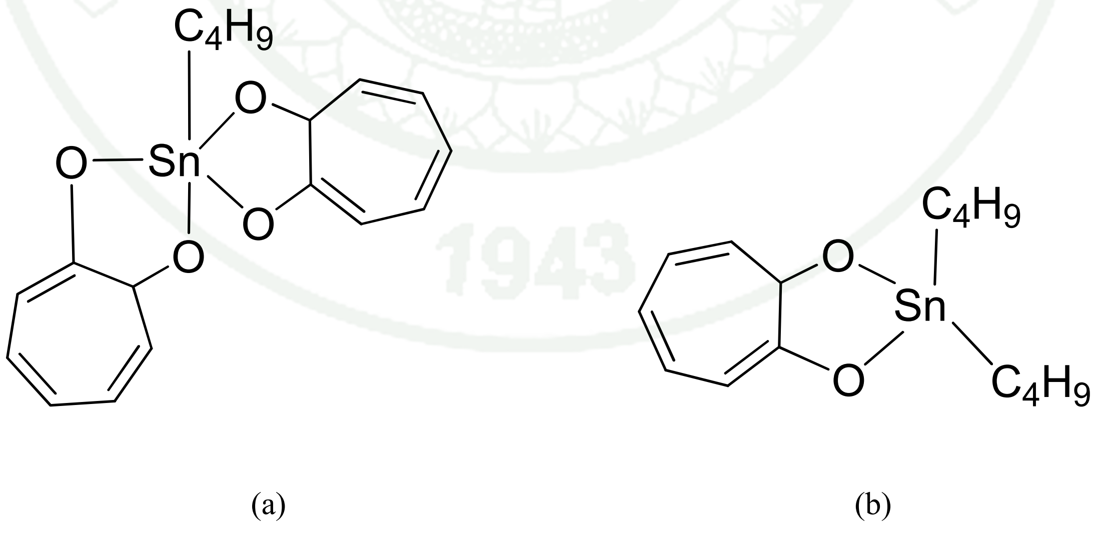


Figure 20 The proposed structure of complexes between (a) monobutyltin (MBT) with tropolone and (b) dibutyltin (DBT) with tropolone

Water is very high polarity that can strongly retain tin compounds. The complex formation of tropolone will reduce the positive charge of MBT and DBT. Therefore, complexation decreases the solubility of organotin compound in water. Consequently, organotin compounds can be soluble in organic phase. From the result in figure 14, tropolone can form complexes with DBT compound. It successfully increased the recoveries of DBT in water sample from 15.41% to highest recoveries of 100.09%. The recoveries were increased after the adding of 0.02% tropolone in hexane. The enhancement in the extraction efficiency related to the increase in concentration of tropolone was observed until stable at 0.05% of tropolone. This result indicated that tropolone has significant effect on the extraction of DBT compound. Although tropolone does not form a complex with TBT, the recoveries of TBT slightly increase from 80.26% to 88.14%. Therefore, tropolone may also decrease the solubility of TBT in water. From the graph in figure A, at 0.05% of tropolone in hexane was found to be the suitable concentration for the extraction of organotin compounds in water samples.

2.2. Effect of pH on extraction efficiency

Table 4 The recoveries of organotin compounds extracted from pH adjusted water sample using 0.05% tropolone in hexane as extracting solvent

Analyte	Conc. HCl (µl)	pH	Found (mg/L)			Average (mg/L)	Recovery ± R.S.D. (%)
			1	2	3		
TBT	0	5.70	4.0367	4.0358	4.0354	4.0360	80.72±0.02
	20	2.00	4.0381	4.0394	4.0372	4.0382	80.76±0.03
	30	1.77	4.4104	4.4027	4.4077	4.4069	88.14±0.09
	40	1.66	4.9008	4.9084	4.907	4.9054	98.11±0.08
	50	1.56	4.8729	4.8747	4.8761	4.8746	97.49±0.03
	60	1.50	4.8882	4.8855	4.8913	4.8883	97.77±0.06
DBT	0	5.70	4.286	4.2873	4.2852	4.2862	85.72±0.02
	20	2.00	4.4945	4.4928	4.4967	4.4947	89.89±0.04
	30	1.77	4.9441	4.9492	4.9472	4.9468	98.94±0.05
	40	1.66	4.9992	5.0000	4.9994	4.9995	99.99±0.01
	50	1.56	4.9828	4.9834	4.9843	4.9835	99.67±0.01
	60	1.50	4.9774	4.9785	4.9762	4.9773	99.55±0.02

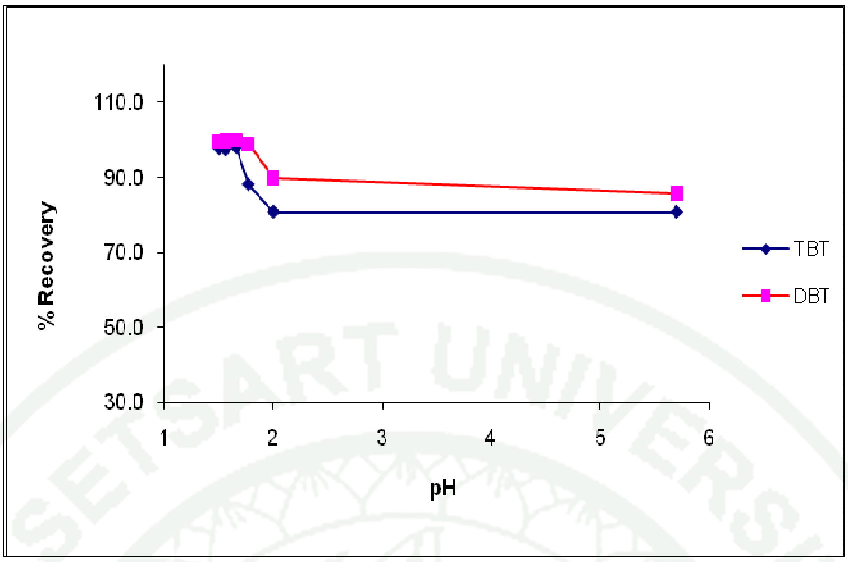


Figure 21 The recoveries of TBT and DBT compounds at various pH

Extraction of dissolved organotin compounds from acidified waters by a solution of tropolone in hexane is characterized by a good recovery (Astruc *et al.*, 1992). The recoveries of TBT and DBTwere increased about 14% and 17% after the acid addition. Generally the concentration of H^+ is high at low pH so the extraction of hexane will give better results compared to the natural pH. From figure 21, pH in the range of 1.66 to 1.50 gave a better recovery percentage for both TBT and DBT compared to the higher pH.

Essentially, pH of natural water samples are in the range of 6.0 – 7.0, therefore, organotin compounds could be hydrolysed into a more stable form. Acid added into water can protect the sample by preventing hydrolysis which keeps the compound in the cationic form. Thus, pH adjustment can also support the complexation of tropolone. In contrast, excess acid may reduce the recoveries. It is possible that under condition with extremely low pH, the acid may break tin-carbon bonds and reduce the actual amount of organotin compound recovery (IPCS, 1990). Therefore, the pH of samples should be carefully controlled.

2.3. Effect of salt on extraction efficiency

Table 5 The recoveries of organotin compounds extracted from water samples with different amount of NaCl at pH 1.66 using 0.05% tropolone in hexane as extracting solvent

Analyte	NaCl (mg)	Found (mg/L)			Average	Recovery ±
		1	2	3	(mg/L)	R.S.D. (%)
TBT	0	4.2532	4.2518	4.2545	4.2532	85.06±0.03
	10	4.3484	4.3506	4.3466	4.3485	86.97±0.05
	30	4.5087	4.5074	4.5105	4.5089	90.18±0.03
	60	4.9008	4.9084	4.9070	4.9054	98.11±0.08
	80	4.9043	4.9026	4.9030	4.9033	98.07±0.02
	100	4.8612	4.8626	4.8500	4.8579	97.16±0.14
	200	4.7759	4.7817	4.7746	4.7774	95.55±0.08
DBT	0	4.6111	4.6121	4.6103	4.6112	92.22±0.02
	10	4.7566	4.7553	4.7574	4.7564	95.13±0.02
	30	4.9200	4.9209	4.9190	4.9200	98.40±0.02
	60	4.9992	5.0000	4.9994	4.9995	99.99±0.01
	80	5.0010	5.0021	5.0002	5.0011	100.02±0.01
	100	4.9573	4.9565	4.9590	4.9576	99.15±0.03
	200	4.9008	4.9003	4.8933	4.8981	97.96±0.09

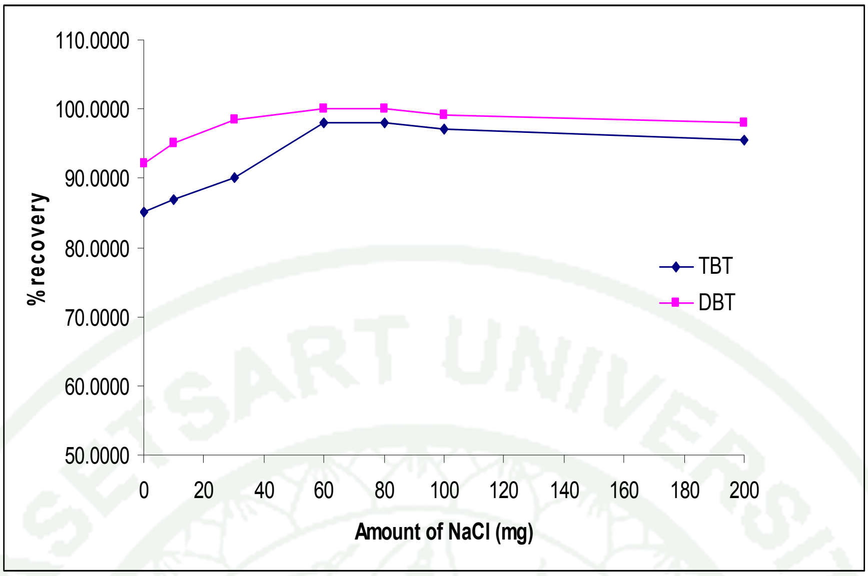


Figure 22 The recoveries of organotin compounds when different amount of NaCl were added into water samples

Sodium chloride is a powerful ionic compound. It is present as sodium ion (Na^+) and chloride ion (Cl^-) when dissolved in water phase. It increases the ionic strength of water. The sodium cation in water causes “salting out” effect, which may then force butyltin compounds to transfer into organic phase (Rydberg, 2004). From the results show in figure 22, gradually improvement of extraction was found after addition of sodium salt. At 60 mg or 0.02% NaCl in water samples, the optimum condition was obtained. The recoveries were increased from 85.06% to 98.11% for TBT and from 92.22% to 99.99% for DBT. The recoveries decreased slightly, by 2 to 3%, when more than 0.02% of NaCl were added. Due to the overload salt added, the transferring of organotin compounds to organic phase has been blocked by the greater viscosity.

Therefore, the optimum condition for extraction was determined to be 0.02% NaCl with pH adjusted to 1.66 of water sample, extracted with 0.05% tropolone in hexane. This condition was then used in the following experiments.

3. Catalyst characterization

3.1 X-ray Powder Diffraction (XRD)

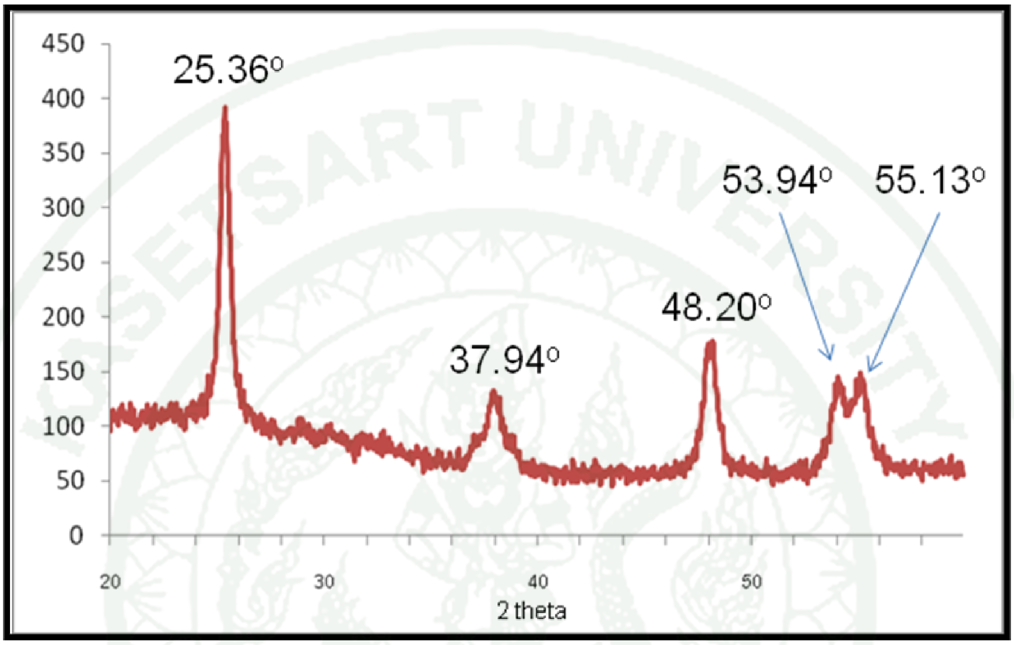


Figure 23 The XRD patterns of N-doped TiO2 using titanium(IV) tetraisopropoxide as a titania precursor with calcination temperature of 400°C (Sirisaksoontorn et. al., 2009).

The XRD patterns in figure 23 shows 2θ peaks at 25.36°, 37.94°, 48.20°, 53.94°, 55.13° which are regarded as an attributive indicator of the anatase phase of titania (JCPDS files No. 21-1272). The average particle size was calculated by applying Scherrer's equation to the anatase (101) diffraction peaks which represented the highest intensity peak for each pure phase .As prepared catalyst had a particle size equal to 11.30 nm. Unit cell volume was calculated from the product among three lattice parameters (a, b and c), which can be equated for the tetragonal system ($a \neq b = c$).

3.2 Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM)

The SEM images (Figure 24a) exhibit that the surface morphology of N-doped TiO_2 using titanium(IV) tetraisopropoxide is mainly like fluffy grains. These results are in good agreement with TEM images (Figure 24b) for the N-doped TiO_2 samples that the particle morphology is somewhat spherical in both the analysis. Furthermore, the average sizes of N-doped TiO_2 calcined at 400°C is 15.03 nm based on the diameter calculation of randomly selected 50 particles.

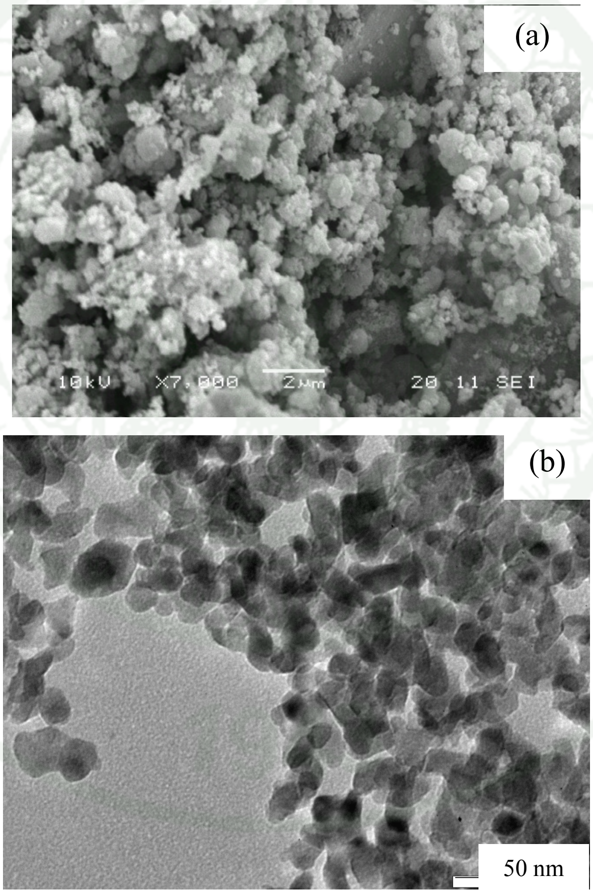


Figure 24 (a) SEM and (b) TEM images of N-doped TiO_2 using titanium(IV) tetraisopropoxide as a titania precursor and calcined at 400°C (Sirisaksoontorn et. al., 2009).

3.3. Elemental Analysis (EA)

Table 5 shows the amount of nitrogen of N-doped TiO_2. The titanium(IV) tetraiso- propoxide precursor was hydrolyzed with NH_3. Nitrogen was able to be doped into TiO_2 lattice with strong bonds, like Ti-N. The average percentage of nitrogen content was 0.054.

Table 6 The amount of nitrogen of N-doped TiO_2 (Sirisaksoontorn et. al., 2009).

Titania precursor	Calcination temperature (°C)	Nitrogen content (%)			Average nitrogen content (%)
		N_1	N_2	N_3	N_{ave}
Titanium(IV) tetraisopropoxide	400	0.059	0.054	0.048	0.054

3.4. Diffuse Reflectance UV-Vis Spectrophotometry (UV-Vis/DR)

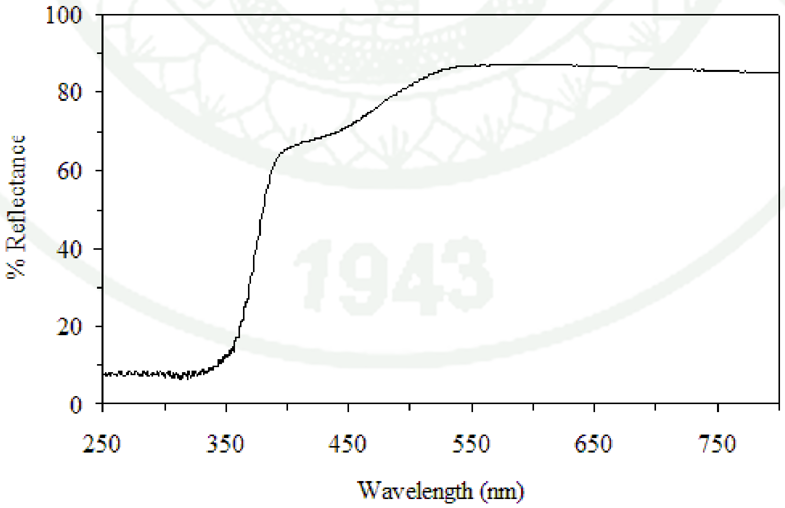


Figure 25 The UV-Vis/DR spectrum of N-doped TiO_2 calcined at 400 °C. (Sirisaksoontorn et. al., 2009)

UV-Vis/DR spectra in figure 25 exhibit two-step absorption edges of yellow N-doped TiO_2 calcined at 400 °C. The first edges are located at 392 nm. (the procedure for the determination of the absorption edge will be shown in Appendix F). Besides, the second edges are apparently shown at 507 nm. These edges indicate that nitrogen doping had a significant impact on the band structure of TiO_2. The band energy could be calculated by the equation as follows (Fernandes *et al*., 2005);

$$E_g = \frac{1239.8}{\lambda}$$

where E_g is band gap energy (eV)

λ is wavelength (nm)

The Energy band gap (E_g) values of N-doped TiO_2 calcined at 400 °C were 3.16 and 2.45 eV.

4. Photodegradation of organotin compounds

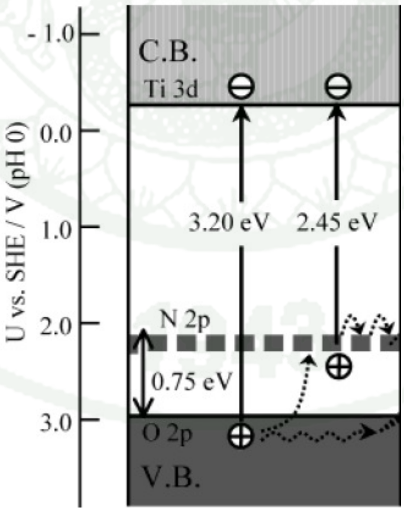


Figure 26 Schematic illustration of the expected energy bands for N-doped TiO_2 (anatase) together with some photoinduced electronic process.

Source: Nakato *et al.* (2004)

In general TiO_2 will be active when irradiated with UV light. Moreover, there is only 3-4% of an ultraviolet part in the solar light that shines through the earth (Shifu *et al.*, 2005). In order to enhance the photocatalytic activity of TiO_2, many researchers try to extend the range of photoefficiency of TiO_2 into visible light. One of the most applicable approaches is to doping semiconductors with various types of transition metal ions or anions species, which causes the band gap narrowing. Nitrogen anion dopants seem to be the most fashionable anions because its anion size closes to that of oxygen anion in TiO_2 lattice. The modified band structure of N-doped TiO_2 is shown in figure 26. The additional states are induced to appear near the valence band of TiO_2.

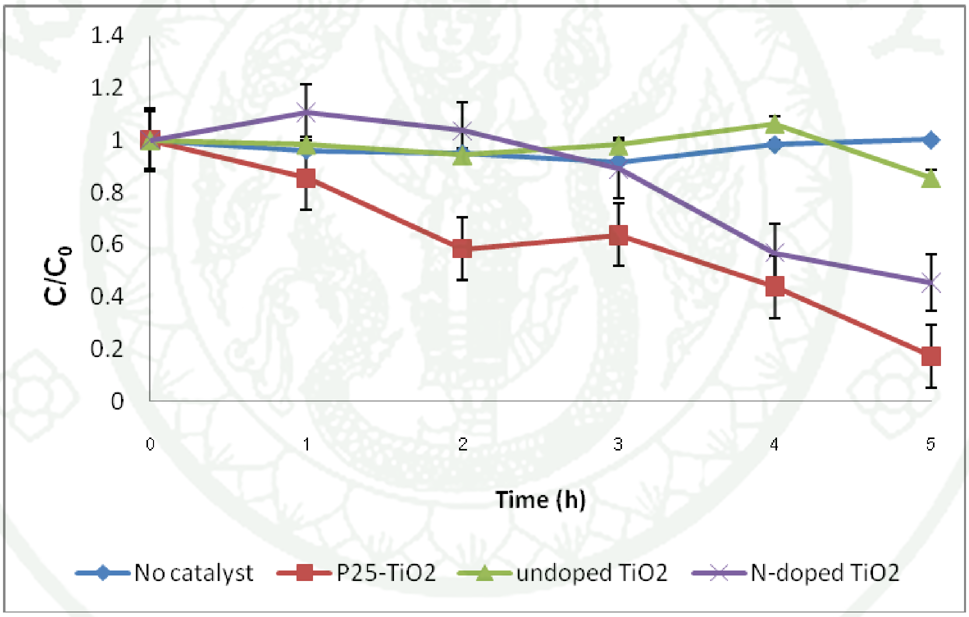


Figure 27 Photodegradation of TBT under UV-light illumination by using (a) P25-TiO_2 (●), (b) undoped TiO_2 (▲), (c) N-doped TiO_2(■) and (d) without catalyst (♦). Error bars represent one standard deviation for n=3.

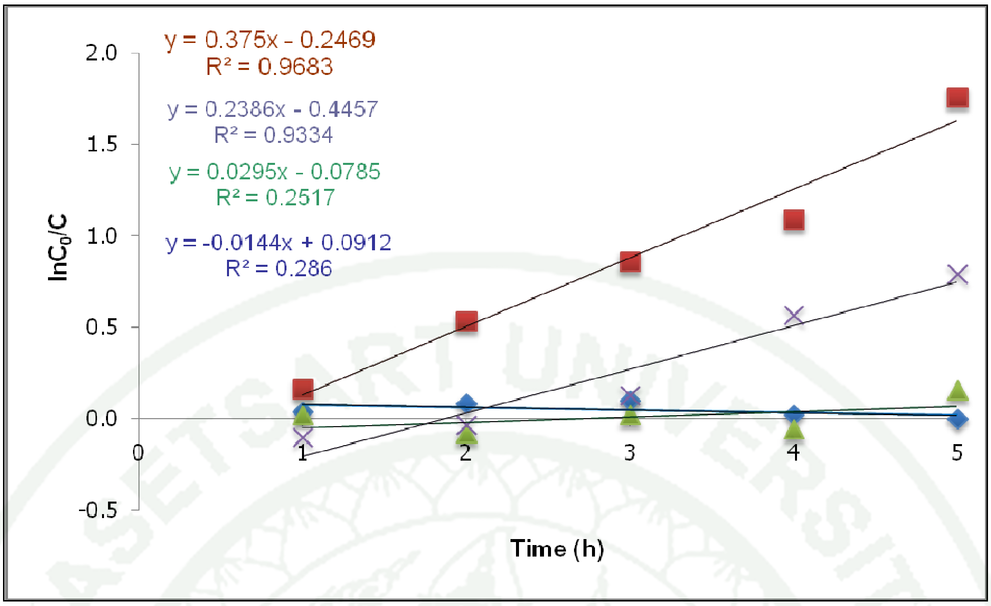


Figure 28 The relation between $\ln C/C_0$ and time (h) of TBT photodegradation reaction under UV light by (a) P25-TiO_2 (■), (b) undoped TiO_2 (▲), (c) N-doped TiO_2 (X) and (d) without catalyst (♦)

The results of photodegradation of TBT compound under UV-light irradiation by using P25-TiO_2, undoped TiO_2, and N-doped TiO_2 compared to without catalysts are shown in figure 27. The photocatalytic efficiency was determined by calculating the relative concentration (C/C_0), where C is the concentration at the sampling time and C_0 is the initial concentration. The procedure used to find rate constant was adapted from previous research by Navio (Navio *et al.* 1996). They assumed that the degradation of tributyltin in the presence of photocatalyst was the first-order kinetic reaction because they plotted a graph between $\ln C_o/C$ and degrading time (h). Then, they obtained the correlation coefficient (R^2) which was close to 1.000 and the slope of the graph could be considered as the rate constant of the photodegradation reaction. Figure 28 shows the relation between $\ln C_0/C$ and time (h) of TBT photodegradation reaction under UV light by P25-TiO_2, undoped TiO_2, N-doped TiO_2 and without catalyst. It is indicated that P25-TiO_2 was able to degrade TBT with the highest conversion of 82.72% and rate constant of 0.3750 h^{-1}. This phenomenon can be explained by the synergistic interaction between anatase and rutile phases, as the previous study (Smirniotis and Sun, 2003). When anatase attached to rutile, it would cause band bending which reduced the possibility of electron-hole recombination. This might enhance the photocatalytic activity of P25-TiO_2. Even though N-doped TiO_2 has narrow band gap energy (2.45 eV) compared with P25-TiO_2 (3.20 eV), its percent conversion had lower than P-25 TiO_2 (54.70% with the rate constant of 0.2386 h^{-1}). This is because of fact that the excess energy from UV light source which is enough to activate a bunch of electrons from valence band of N-doped TiO_2 not having band bending increases the chance of recombination between electrons and holes. In case of undoped TiO_2, it shows 14.36% of percent conversion with the rate constants of 0.0295 h^{-1}. It has the lowest efficiency when compare with P25-TiO_2 and N-doped TiO_2.

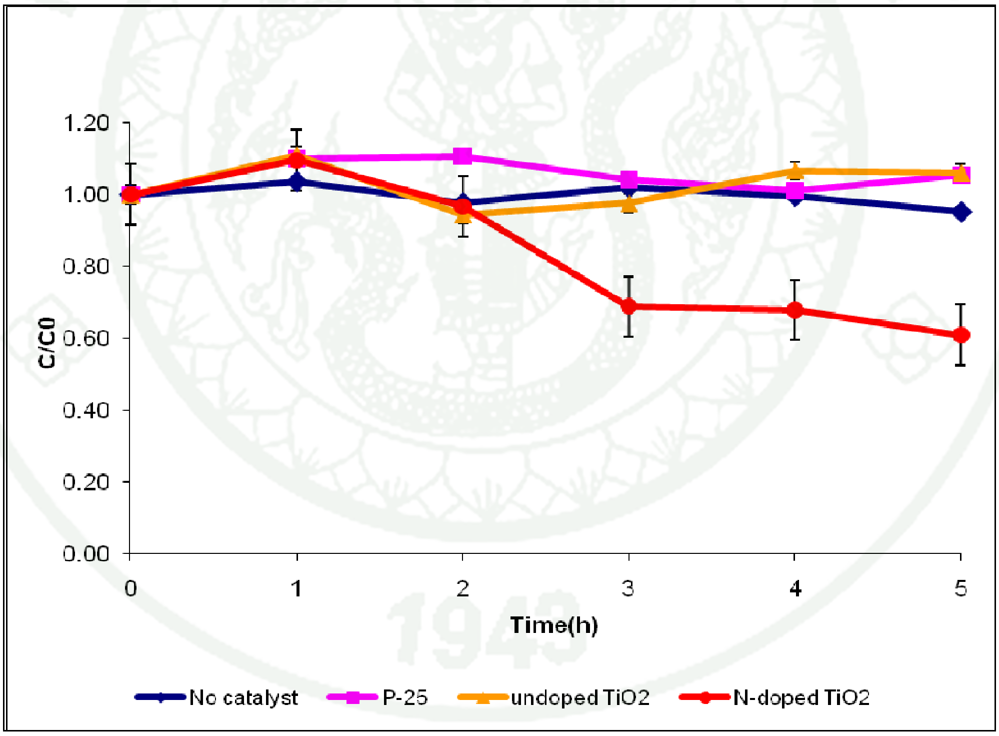


Figure 29 Photodegradation of TBT under visible-light illumination by using (a) P25-TiO_2 (■), (b) undoped TiO_2 (▲), (c) N-doped TiO_2 (●) and (d) without catalyst (♦)

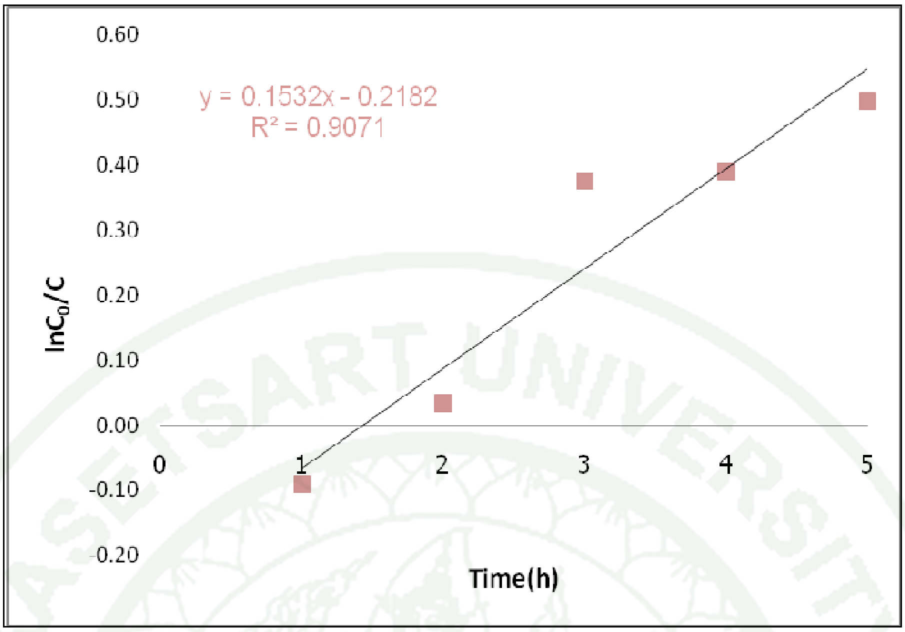


Figure 30 The relation between lnC/C$_0$ and time (h) of TBT photodegradation reaction under visible light illumination by N-doped TiO$_2$ (■).

Results of photodegradation of TBT compound under visible light illumination are shown in figure 29. The P25-TiO$_2$ and undoped TiO$_2$ do not show any degradation activity under visible light irradiation. Since the band gap energy of undoped TiO$_2$ and P25-TiO$_2$ are high (anatase and rutile are 3.2 and 3.0 eV, respectively), electron in the valence band cannot be excited to the conduction band by the low energy of visible light. The N-doped TiO$_2$ provided the best catalytic efficiency. It was able to degrade TBT with conversion of 39.20% and rate constant of 0.1532 h^{-1} because of its band gap energy suitable for absorb energy in the range of visible light region. In addition, the visible light could not degrade the TBT as no degradation activity occurs in the blank experiment.

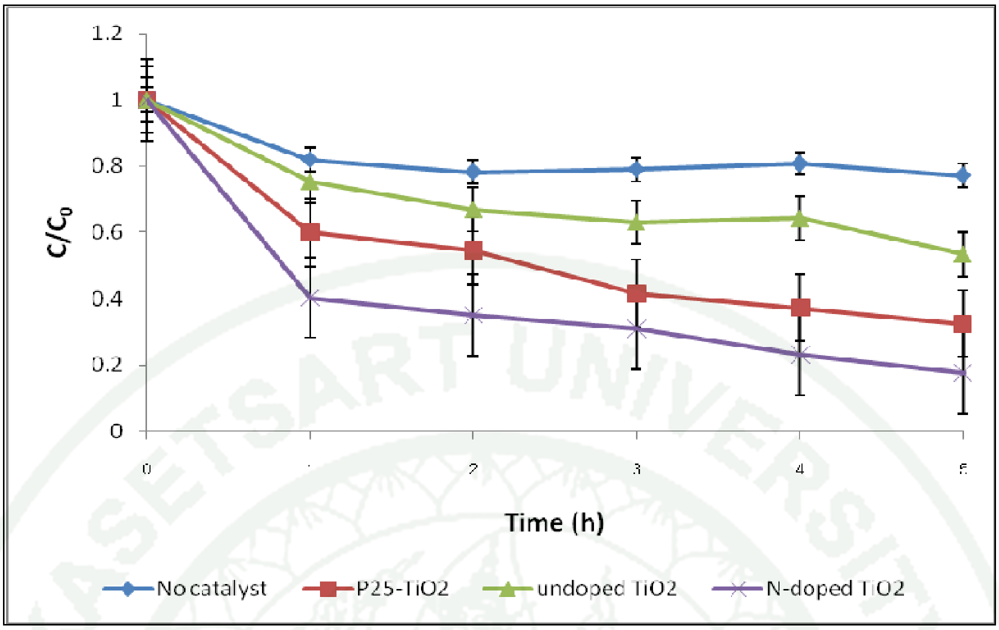


Figure 31 Photodegradation of TBT under natural light illumination by using (a) P25 TiO_2 (■), (b) undoped TiO_2(▲), (c) N-doped TiO_2 (♦) and (d) without catalyst (●)

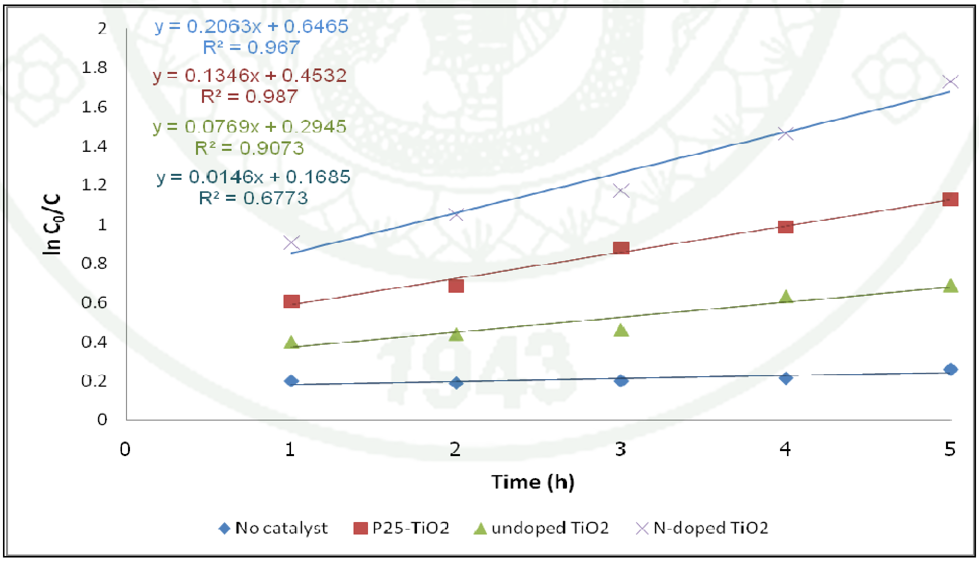


Figure 32 The relation between $\ln C/C_0$ and time (h) of TBT photodegradation reaction under natural light by using (a) P25-TiO_2 (■), (b) undoped TiO_2 (▲), (c) N-doped TiO_2 (X) and (d) without catalyst (♦).

Figure 31 shows the relative concentration plot of photodegradation of TBT using various catalysts under natural light illumination. It indicated that N-doped TiO_2 could enhance the photodegradation of TBT under natural light illumination with the highest conversion of 82.2% and the rate constant of 0.2063 h^{-1}. The N-doped TiO_2 displayed successful degradation activity in natural light which is a result of “band gap narrowing”. In natural light, the existence of UV wavelengths causes the degradation of TBT by P25-TiO_2 and undoped TiO_2 .The higher degradation activity of P25-TiO_2 which have 67.60% of conversion with the rate constant of 0.1346 h^{-1} than undoped TiO_2 which have 49.70% of conversion with the rate constant of 0.0769 h^{-1} resulted from the developed crystallinity containing anatase and rutile with the ratio of 75:25. This prevents the recombination between holes and electrons after “the line up of Fermi levels of anatase and rutile”.

Table 7 %Degradation, rate constants and haft-life of photodegradation reactions of tributyltin by using P25-TiO_2, undoped TiO_2, N-doped TiO_2 and without catalyst under different light source.

Catalyst	Light source								
	UV-light			Visible light			Natural light		
	%Degradation[a]	Rate constant[b] (h^{-1})	$t_{1/2}$[c] (h)	%degradation[a]	Rate constant[b] (h^{-1})	$t_{1/2}$[c] (h)	%degradation[a]	Rate constant[b] (h^{-1})	$t_{1/2}$[c] (h)
No catalyst	-	-	-	-	-	-	22.85	0.0146	47.47
P25	82.72	0.3499	1.85	-	-	-	67.60	0.1346	5.15
Undoped-TiO_2	14.36	0.0295	23.49	-	-	-	49.70	0.0769	9.01
N-doped TiO_2	54.70	0.2386	2.90	39.20	0.1532	4.52	82.20	0.2063	3.36

[a] %Degradation was calculated from ($C_{initial} – C_{final}$ / $C_{initial}$) x100%.

[b] The procedure to calculate rate constants are also shown in Appendix D.

[c] Haft life ($t_{1/2}$) was calculated from 0.693/k.

$TiO_2 \longrightarrow (h^+ \sim e^-)$	excitation formation	eqn. 1
$(h^+ \sim e^-) \longrightarrow$ heat, photon	recombination process	eqn. 2
$(h^+ \sim e^-) \longrightarrow h^+ + e^-$	excitation dissociation	eqn. 3
$O_2(g) \rightleftharpoons O_2(ads)$	oxygen adsorption equilibrium	eqn. 4
$O_2(ads) + e^- \longrightarrow O_2^{-\bullet}\ (ads)$	electron trapping	eqn. 5
$OH^-(ads) + h^+ \longrightarrow OH^\bullet(ads)$	hole trapping by adsorbed hydroxyl group	eqn. 6
$(C_4H_9)_3SnOH(ads) + h^+ \longrightarrow (C_4H_9)_3SnOH^{\bullet+}$		eqn. 7
$\longrightarrow OH^\bullet + (C_4H_9)_3Sn^+$		eqn. 8
$(C_4H_9)_3SnOH^{\bullet+} \longrightarrow C_4H_9^\bullet + (C_4H_9)_2SnOH^+$		eqn. 9
$\longrightarrow C_4H_9^+ + (C_4H_9)_2SnOH^\bullet$		eqn. 10
$(C_4H_9)_2SnOH^\bullet + OH^\bullet \longrightarrow (C_4H_9)_2Sn(OH)_2$		eqn. 11
$C_4H_9^\bullet + O_2(ads) \longrightarrow C_4H_9O_2^\bullet \longrightarrow \xrightarrow{[O]}$		eqn. 12
$C_4H_9^\bullet + O_2^{-\bullet} \longrightarrow \xrightarrow{[O]} \longrightarrow$		eqn. 13
$C_4H_9O_2^\bullet + O_2^{-\bullet} \longrightarrow \xrightarrow{[O]} \longrightarrow$		eqn. 14
$C_4H_9^+ \xrightarrow{HO_2} C_4H_9OH \longrightarrow \xrightarrow{[O]} \longrightarrow$		eqn. 15
$(C_4H_9)_3Sn^+ + O_2(ads) \qquad (C_4H_9)_2Sn^{2+} + C_4H_9^\bullet + O_2^-$		eqn. 16

Scheme 1 Sequence for the TiO_2-photocatalytic degradation of organotin compounds

Source: Navio *et al.* (1996)

Navio reported about mechanistic feather and photodegradation activity of butyltin compound as shown in scheme 1 (Navio *et al.*, 1996). Illumination of titanium dioxide powder with protons of energy equal to or greater than its band gap energy results in the formation of an electron (e^-) and hole (h^+) pair (eqs. 1). Recombination of e^- - h^+ (eqs. 2) can be hindered by electron trapping by adsorbed oxygen (eqs. 4 and 5), which is renewed the air saturation as it is consumed at the photocatalyst surface. The oxidative degradation of organometallic compounds adsorbed on the semiconductor can then be initiated by direct trapping of the photogenerated hole (eqs. 7). This results in the formation of a singly oxidized species (the organometallic radical cation) as has been point out by other authors using various groups IVA organometallic compounds. Such organometallic cation radicals or butylcation could fragment to give either hydroxyl or butyl radicals or butyl cations (eqs. 8 and 10). These intermediates initiate thermal reactions of oxidative degradation, leading finally to carbon dioxide and water as shown in the remaining steps (eqs. 11-16).

In fact the degradation of TBT should be in line with debutylation process to generate DBT and MBT as by product but they were undetectable in photodegradation of TBT on UV or visible light illumination. These results indicated that the photodegradation of TBT may exhibit the characteristics of a sequential debutylation process. The non-detection of DBT and MBT during the photodegradation of TBT could be associated with the photodegradation of DBT and MBT to inorganic tin which may be faster than the formation of DBT and MBT via the photodegradation of TBT. In order to prove this assumption, experiments were performed to study, independently, the photodegradation of organotin compounds (TBT, DBT and MBT, respectively) and mix solution of butyltin using N-doped TiO_2 as a photocatalyst.

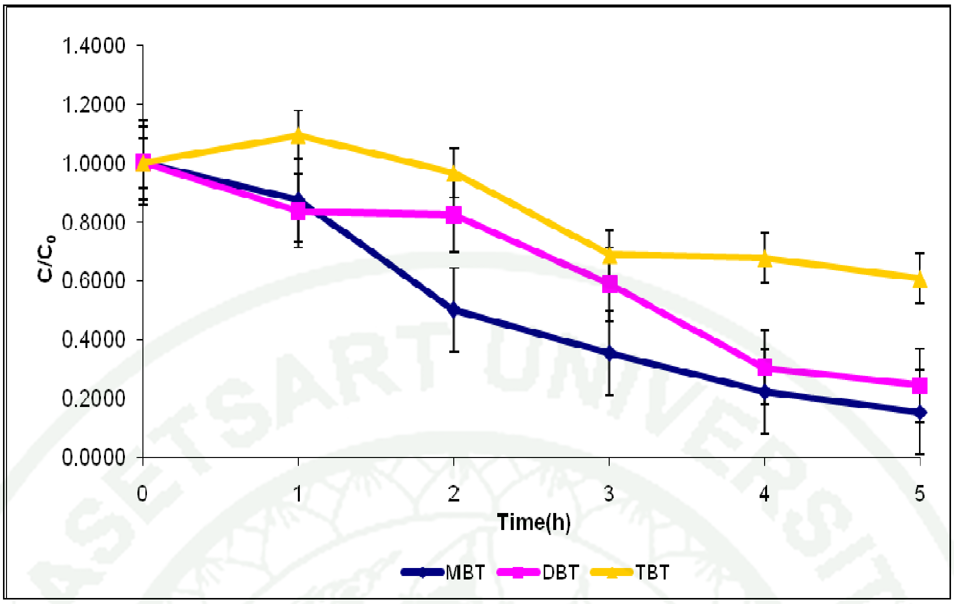


Figure 33 The photodegradation of monobutyltin (MBT) (♦), dibutyltin (DBT) (■) and tributyltin (TBT) (▲) by using N-doped TiO_2 under visible light

From figure 33 under visible light illumination, it can be observed that with fix amount (10 mg/L) of organotin compounds, DBT and MBT were degraded with 75.55% and 84.68% conversion with the rate constant of 0.2973 h^{-1} and 0.3950 h^{-1}, respectively, whereas TBT was reduced with 39.20% conversion and rate constant of 0.1532 h^{-1}. According to these results, the sequence of the rates of photodegradation, under our experimental conditions, is as followed: MBT > DBT > TBT.

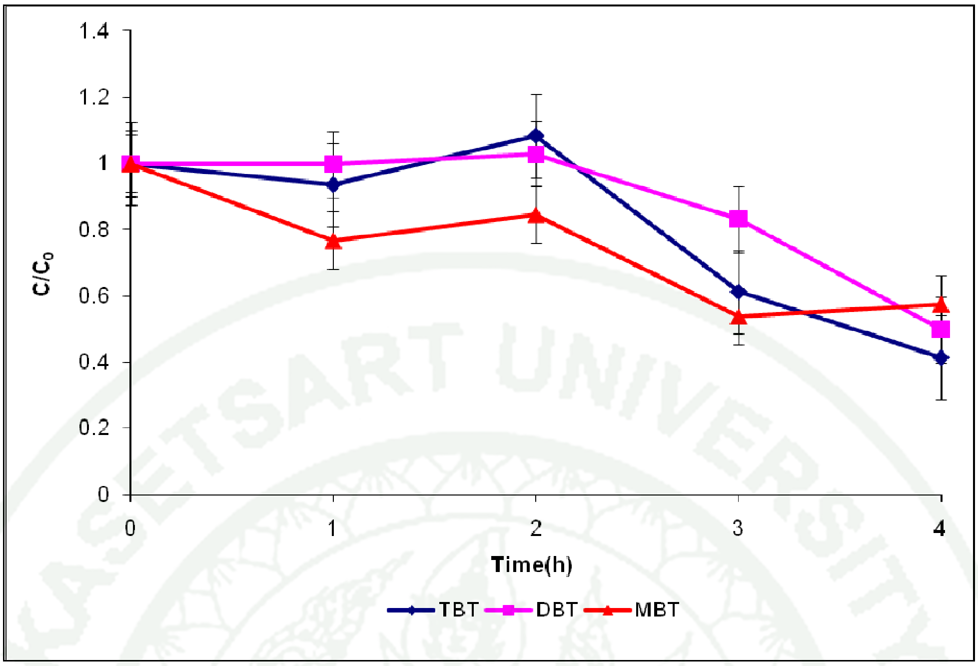


Figure 34 Photodegradation of mix solution (a) TBT (♦), (b) DBT (■) and MBT (▲) by using N-doped TiO_2 in visible light illumination

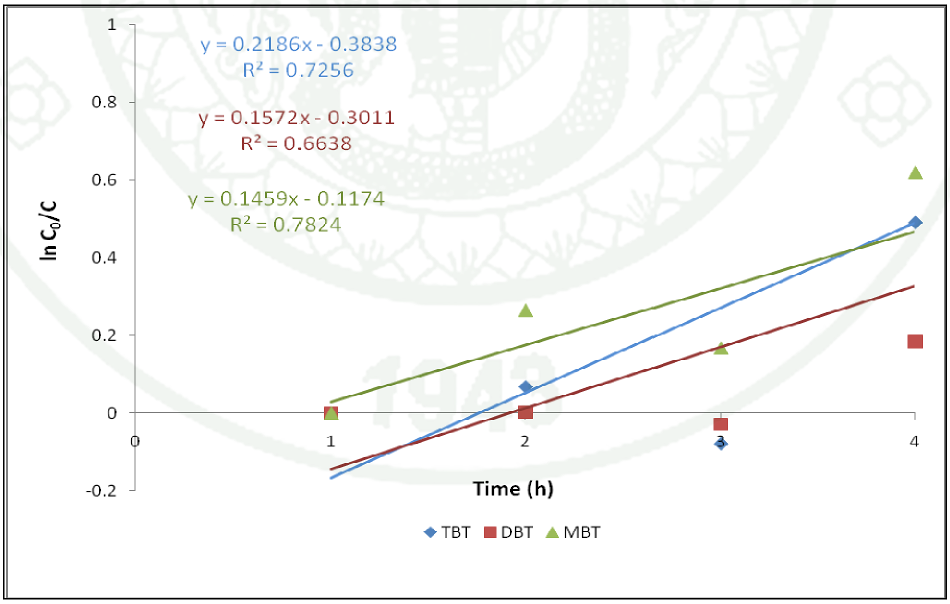


Figure 35 The relation between $\ln C_0/C$ and time (h) of mix organotins solution; (a) TBT (♦), (b) DBT (■) and (c) MBT (▲),photodegradation reaction under visible light illumination using N-doped TiO_2

This experiment was performed in order to prove the assumption that when TBT decrease DBT and MBT will increase. As shown in figure 34, after samples were illuminated for 1 hour, the concentration of mix organotins solution, TBT and MBT, were decreased. However, the concentration of DBT was not decreased. After 2 hours, concentration of DBT started to decreased and MBT increased cause debutylation of DBT. In case of TBT, the amount of TBT was unexpected increase after 2 hours which may causes from the recombination process. In the sample solution, among the illumination process, TBT, DBT and MBT were oxidized to radical form or cation as shown in equation 8 to 10 on scheme 1. Since a great number of radical or cation, recombination process may be occurred to generate TBT. Moreover, the rate constant of DBT and MBT in mix solution were lower than previous experiment in pure solution as shown in table 8. This is because, TBT was degraded to DBT or MBT causing the concentration of DBT and MBT in mix solution increased.

Table 8 The rate constant of organotin compounds in photodegradation reaction under visible light illumination using N-doped TiO_2

Sample	Rate constant of organotin compounds (h^{-1})	
	mix solution	pure solution
TBT	0.2186	0.1532
DBT	0.1572	0.2973
MBT	0.1459	0.3950

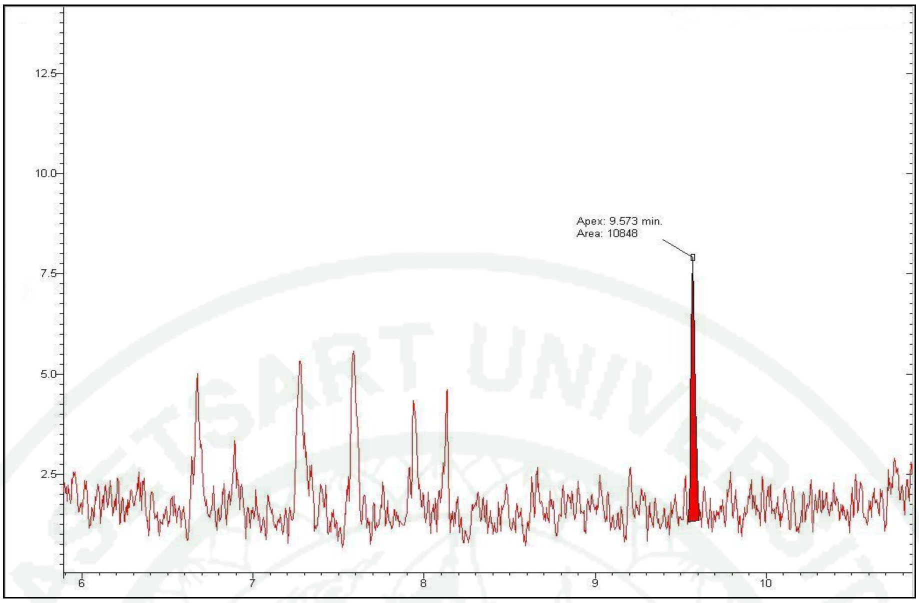


Figure 36 Total ion chromatogram of monobutyltin chioride (MBT) which occurred after illuminated natural light

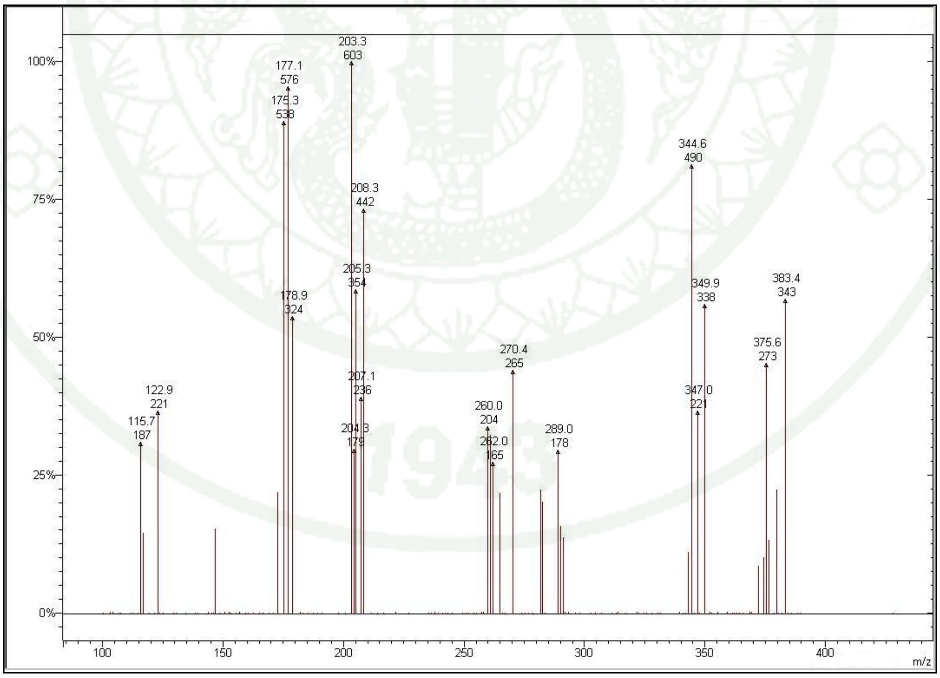


Figure 37 Mass spectra of monobutyltin chioride (MBT) which occurred after illuminated natural light

In case of photodegradation of DBT using N-doped TiO_2 under natural light illumination, after 1 hour, the signal of DBT was not detected but MBT occurred instead. The total ion chromatogram and mass spectra of monobutyltin (MBT) after natural light illumination onto DBT are shown in figure 36 and 37. The amount of MBT which was detecting by GC/MS was 6.67 mg/L. After illuminated for 2 hours; it could not detect any signal. This result confirmed that the degradation of butyltin compounds involved sequential debutylation through inorganic tin. Moreover, photodegradation of MBT with N-doped TiO_2 under natural light illumination (figure 38), it was completely degraded with the rate constant of 0.4514 h^{-1} which is shown in figure 39. The rate constant of MBT was higher than the rate constant of TBT as the same condition after illuminated light for 5 hours.

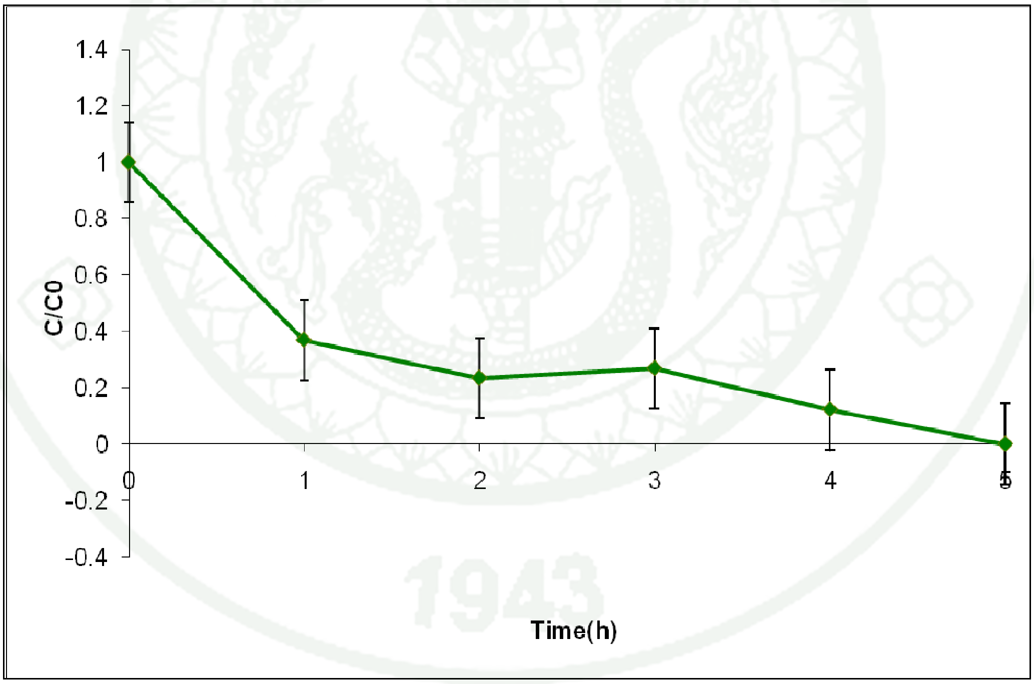


Figure 38 Photodegradation of monobutyltin (MBT) by using N-doped TiO_2 under natural light

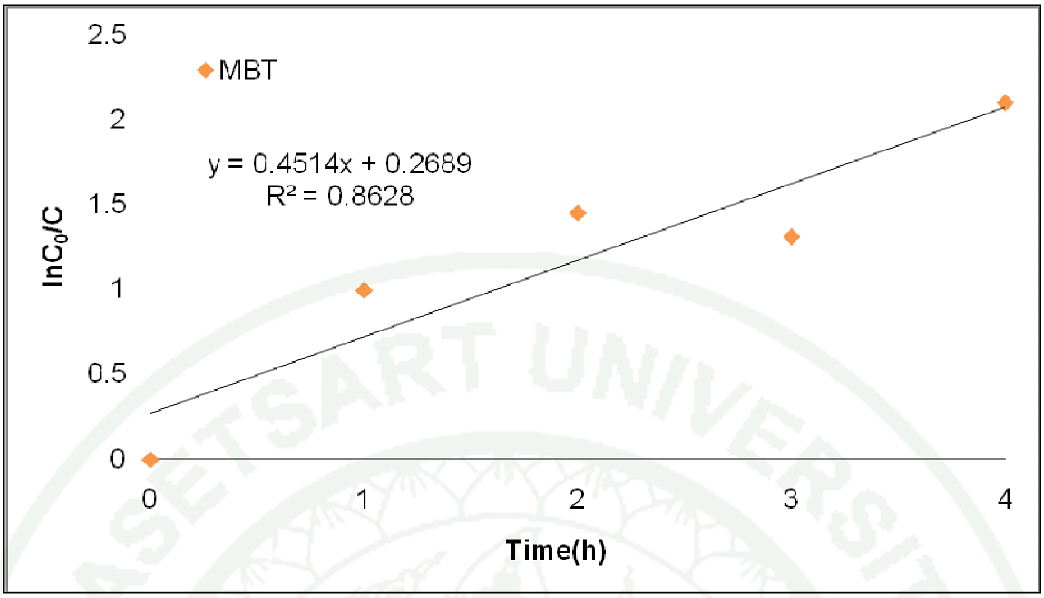


Figure 39 The relation between $\ln C_0/C$ and time (h) of MBT photodegradation reaction under natural light by N-doped TiO_2

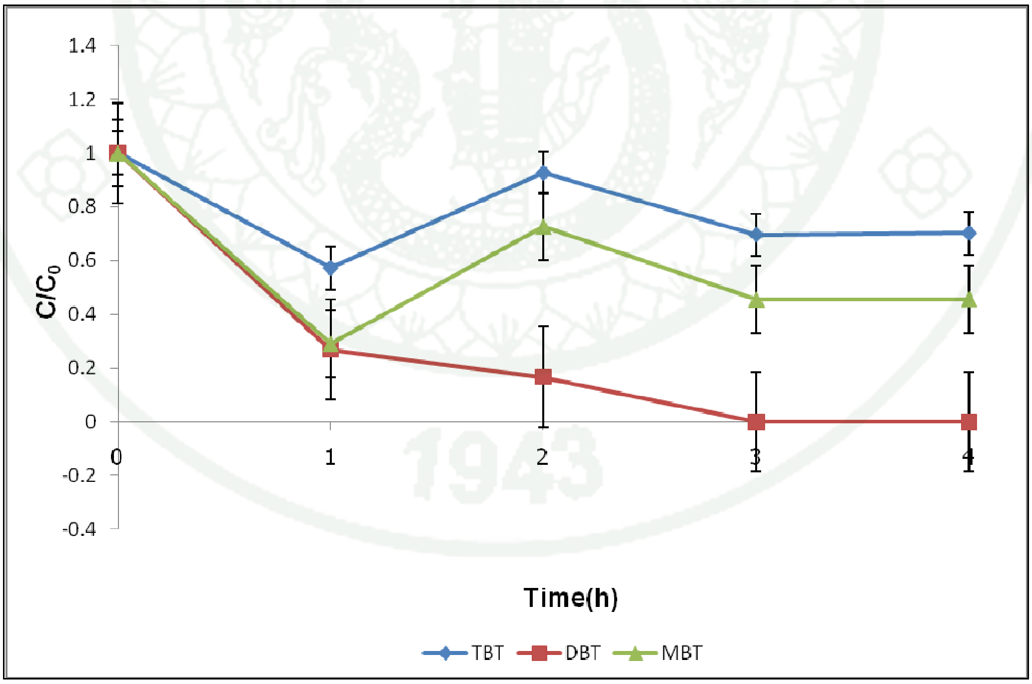


Figure 40 Photodegradation of mix solution of MBT, DBT and TBT by using N-doped TiO_2 in natural light illumination; (a) TBT (◆), (b) DBT (■) and MBT (▲)

Figure 40 shows the photodegradation of mix solutions by using N-doped TiO_2 in natural light illumination. In the range of 1 hour, mix solutions were effectively degraded but after time passed 2 hours, DBT was degraded about 83.35% whereas concentration of MBT increased due to the debutylation of DBT to MBT. In case of TBT, the amount of TBT was also increased causes recombination process as mention in the previous section. After 3 h, DBT was completely degraded while TBT and MBT were degraded by 30.54% and 54.16%, respectively.

5. Determination and photodegradation of butyltin in sea water from Gulf of Thailand

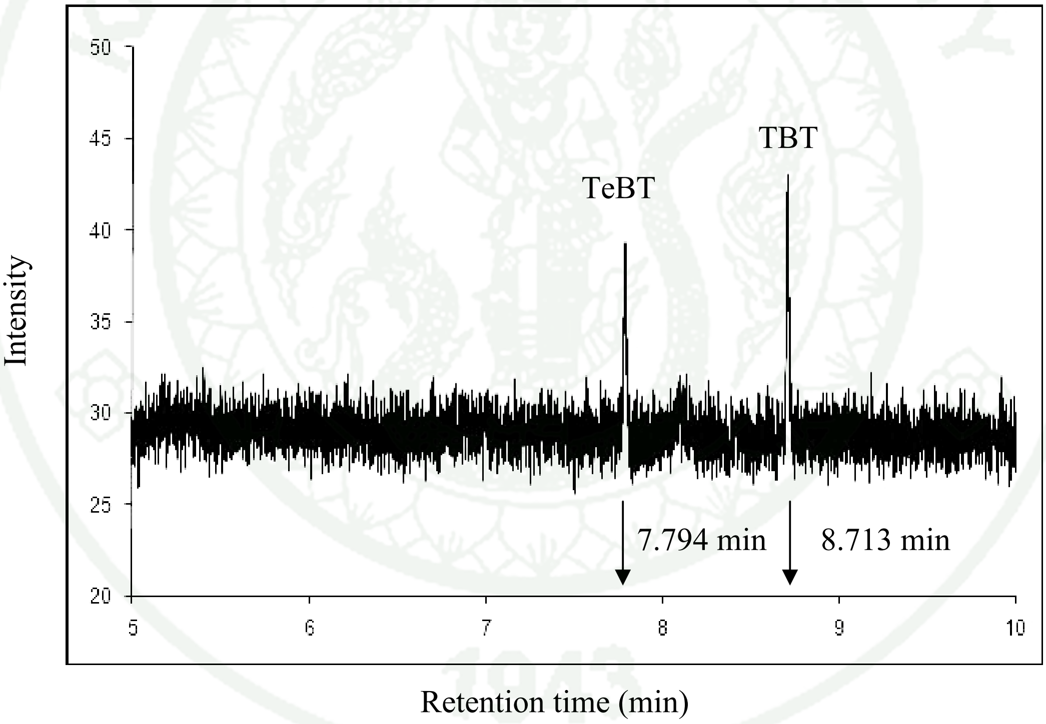


Figure 41 Total ion chromatogram of TBT extracted from Lam Chabang Gulf of Thailand

Figure 41 shows the result of total ion chromatogram of TBT extracted from Lam Chabang Gulf of Thailand. The sample was collected on November 2009. The sharp peaks were observed at 7.794 min and 8.713 min, respectively. The first peak refers to TeBT which was added as internal standard and the next refers to TBT which contaminated in sea water from Gulf of Thailand. The concentration of TBT was 1.46 μg/L. Then, the sea water sample was degraded with N-doped TiO_2 for 5 hours. After the sample was analyzed, the signal of TBT disappeared as shown in figure 42. It concluded that N-doped TiO_2 could be enhancing the photodegradation of TBT in environmental sample.

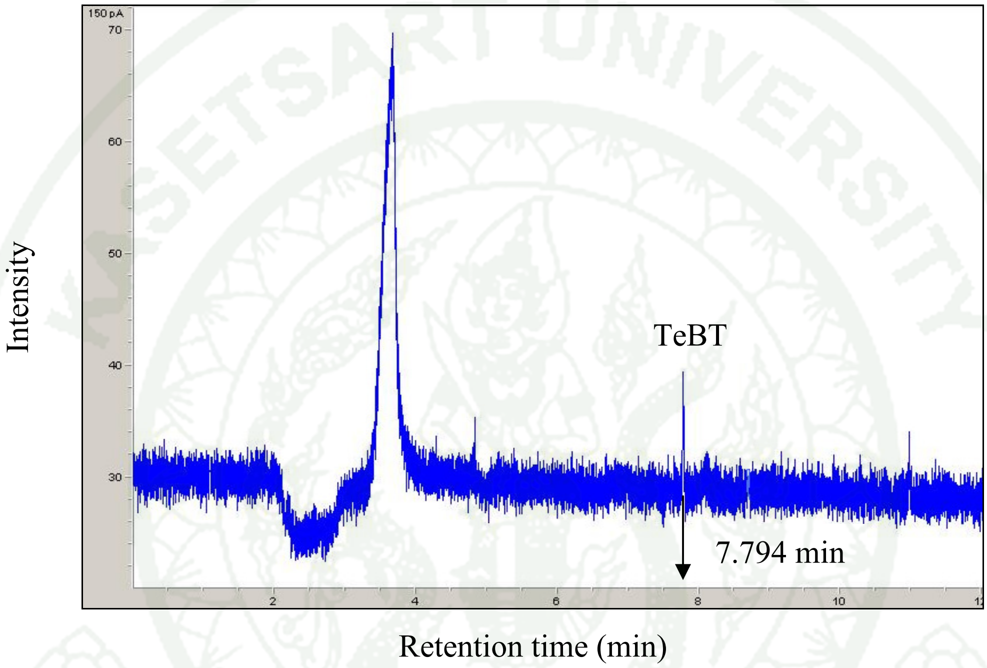


Figure 42 Total ion chromatogram of TBT extracted from Lam Chabang Gulf of Thailand after illuminated by natural light for 5 hours.

CONCLUSION

The photodegradation of organotin compounds (TBT, DBT and MBT) in aqueous TiO_2 suspension were studied. Procedure for the extraction and determination of organotin compounds in water samples were optimized. The extraction efficiency of organotin compounds depends on three parameters. First, tropolone could coordinate with MBT and DBT but not with TBT because of steric effect. The stoichiometric ratio between MBT:tropolone is 1:2 and DBT:tropolone is 1:1. The complex formation of tropolone will reduce the polarity of MBT and DBT which reduce the solubility of organotin compound in water. Consequently, organotin compounds can be soluble in organic phase. Second, NaCl which could increases the ionic strength of water, which may then force organotin compounds to transfer into organic phase. Third, pH of solution, organotin compounds could be hydrolyzed into a more stable form so acid added into water can protect the sample by preventing hydrolysis which keeps the compound in the cationic form. Thus, pH adjustment can also support the complexation of tropolone. . The appropriate extraction condition for 30 ml solution was pH 1.66, 0.05% of tropolone in hexane and 60 mg of NaCl. The condition of GC-FPD and GC-MS which were used to determine organotin compounds were optimized. For GC-MS, injector was set at 250 ºC. The solvent delay was 5 min. The carrier gas was Helium with flow rate of 1.0 ml/min. The column oven temperature was programmed from an initial temperature of 100 ºC, held for 1 min, to final temperature of 300 ºC with 10 ºC/min of rate, and held for1 min. Sample injection was splitless. The mass spectrometer was fully scanned in EI mode. The detector acquisition method employed to select ion monitoring for TeBT, TBT, DBT and MBT between *m/z* 205 and 390, over total ion. For GC-FPD, Injector and detector temperature were held at 250 ºC. The solvent delay was 5 min. The column oven temperature was programmed from the initial temperature of 100 ºC, held for 1 min, to final temperature of 300 ºC at the rate of 20 ºC/min, and held for1 min. Sample injection was splitless for 1 min followed by the split mode. The temperature of Flame Photoemission Detector was adjusted to 250 ºC.

The photocatalyst, N-doped TiO_2, was prepared via the sol-gel method using titanium(IV) tetraisopropoxide as a precursor. The photocatalyst was calcined at 400°C. From all characterization techniques, the prepared photocatalyst has anatase phase and crystallite size is 11.30 nm. The percentage content of nitrogen is 0.054. The UV-Vis/DR spectrum of N-doped TiO_2 shows that photocatalyst absorbs light in the visible region with the band gap of 2.45 eV. The photodegradation of organotin compounds comparing between N-doped TiO_2, P25-TiO_2 and undoped TiO_2 and without catalyst were studied. Under UV-light irradiation indicated that P25-TiO_2 was able to degrade TBT with the highest rate constant of 0.3499 h^{-1} with 82.72% conversion. This phenomenon can be explained by the synergistic interaction between anatase and rutile phases. Under visible light illumination, N-doped TiO_2 provided the best catalytic efficiency for TBT, DBT and MBT because of its band gap energy suitable for absorb energy in the range of visible light region. It was able to degrade TBT, DBT and MBT with 39.20%, 75.55% and 84.68% conversion and the rate constant of 0.1532 h^{-1}, 0.2973 h^{-1} and 0.3950 h^{-1}, respectively. The degradation of TBT should be in line with debutylation process to generate DBT and MBT as by product but they were undetectable in photodegradation of TBT. The rate constant of photodegradation of DBT and MBT were higher than TBT with the order of MBT > DBT > TBT. The non-detection of DBT and MBT during the photodegradation of TBT could be associated with the photodegradation of DBT and MBT to inorganic tin which was faster than the formation of DBT and MBT via the photodegradation of TBT. In natural light, TBT and MBT was effectively degraded by N-doped TiO_2 with 82.2% and 100% conversion with the rate constant of 0.2063 h^{-1} and 0.4514 h^{-1}, respectively. MBT was detected as intermediate product of the photodegradation of DBT under natural light illumination.

In case of the photodagradation of mix organotins solution, under visible light illumination, the concentration of mix organotins solution, TBT and MBT, were decreased. However, the concentration of DBT was not decreased. After 2 hours, concentration of DBT started to decreased and MBT increased cause debutylation of DBT. In case of TBT, the amount of TBT was unexpected increase after 2 hours which may causes from the recombination process. In the experiment of natural light illumination, after 2 h, the amount of TBT was also increased causes recombination process. For the real sample from Lam Chabang Harbour Gulf of Thailand which was contaminated by TBT, the concentration of TBT was 1.46 μg/L. N-doped TiO_2 could degrade TBT under optimized condition for 5 hour.

LITERATURE CITED

AIST-Kansai. 2002. **Crystal Structure Gallery.** Available Source: http://staff.aist.go.jp/nomura-k/english/itscgallary-e.htm, September 6, 2010.

Astruc, A., M. Astruc, R. Pinel and M. Potin-Gautier. 1992. Speciation of butyltin compounds by on-line HPLC-ETAA of tropolone complexes in environmemtal samples. **Appl. Organomet. Chem.** 6: 39-47.

Bangkedphol, S., H.E. Keenan, C.M. Davidson and A. Sakultantimetha. 2010. Enhancement of tributyltin degradation under natural light by N-doped TiO_2 photocatalyst. **J. Hazard. Mater.** 184: 533-537.

Batt, J.M. n.d. **The world of organotin chemical: Application, Substituted and the environment.** Available Source: http://www.arkemainc.com/pdf/additives/World_of_Organotin_Chemicals.pdf , October 1, 2009.

Blunden, S.J. and C.J. Evans. 1990. Organotin compounds, pp. 1-44. *In* O. Hutzinger, eds. **The handbook of environmental chemistry. volumn 3, Part B, Anthropogenic compound.** Springer, Berlin, Germany.

Bolt, M., G. Mailhot and M. Astruc. 1999. Degradation of tributyltin chloride in water photoinduced by iron(III). **Appl. Organomet. Chem.** 13: 53-61.

Bowless, K.C., S.C. Apte and L.T. Hales. 2003. Determination of butyltin species in natural waters using aqueous phase ethylation and off-line room temperature trapping. **Anal. Chim. Acta.** 477: 103-111.

Campillo, N., N. Aguinaga, P. Vinas, I. Lopez-Garcia and M. Hernandez-Cordo. 2004. Speciation of organotin compounds in waters and marine sediments using purge-and-trap capillary gas chromatography with atomic emission detection. **Anal. Chim. Acta.** 525: 273-280.

Champ, M.A. and P.F. Seligman. 1996. An introduction of organotin compounds and their use in antifouling coating, pp. 1-25. *In* Chapman and Hall, eds. **Organotin: Environmental Fate and Effects.** London, UK.

Clarkson, T.W. 1991. Inorganic and organometal pesticides, *In* W.J. Hayes and E.R. Laws, eds. **Handbook of pesticide toxicology.** Academic press, New York, USA.

Columbini, V., C. Bancon-Montigny, L. Yang, P. Maxwell, R.E. Turgeon and Z. Mester. 2004. Head space single-drop microextraction for the detection of organotin compounds. **Talanta.** 63: 555-560.

Craig, P.J. 2003**. Organometallic compounds in the environment: Principles and reaction.** 2nd ed. John Wiley & Son, New York, USA.

Devosa, C., D. Vliegena, B. Willaert, F. Davida, L. Moensc and P. Sandra. 2005. Automated headspace-solid-phase micro extention-retention time locked-isotope dilution gas chromatography-mass spectrometry for the analysis of organotin compounds in water and sediment samples. **J. Chromatogr.** 1079: 408-414.

Dlugonski J. and P. Bernat. 2006. Acceleration of tributyltin chloride (TBT) degradation in liquid cultures of the filamentous fungus Cunninghamella elegans. **Chemosphere.** 62(1): 3-8.

Dlugonski J. and P. Bernat. 2007. Tributyltin chloride interactions with fatty acids composition and degradation ability of the filamentous fungus Cunningham Ella elegans. **International Biodeterioration & Biodegradation.** 60: 133–136.

Dowson, P.H., J.M. Bubb and J.N. Nester. 1996. Persistent and degradation pathways of tributyltin in freshwater and estuarine sediments. **Estuarine, Coastal and Shelf Science.** 42(5): 551-562.

Extoxnet. 1996. Extention toxicology network, pesticide formation profile, Oragon State University. Available Source: http://extoxnet.orst.edu/pips/tributyltin.htm, May 15, 2009.

Fang, X., Z. Zhang, Q. Chen., H. Ji and X. Gao. 2007. Dependence of nitrogen doping TiO_2 precursor annealed under NH_3 flow. **J. Solid State Chem**. 180: 1325-1332.

Fernandes, J.B. and A.R. Gandhe. 2005. A simple method to synthesize N-doped rutile titania with enhanced photocatalytic activity in sunlight. **J. Solid State Chem.** 178: 2953-2937.

Goh, C.L. 1985. Irritant dermatitis from tri-n-butyltin oxide in paint. **Contact dermatitis.** 12: 161-163.

Greenwood, N.N. and A. Enshaw. 1997. Germanium, Tin and Lead, pp. 367-404. *In* Butterworth-Heinemann, eds. **Chemistry of element.** 2nd ed. Oxford, UK.

Hall, L.W., S.J. Bushong, W.S. Hall and W.E. Johnson. 1988. Acute and chronic effects of tributyltin on a Chesapeake Bay copepod. **Environ Toxicol Chem.** 7: 41-46.

Hall, L.W., M.S. Scott, W.D. and M.A. Unger. 2000. A probabilistic ecological risk assessment of tributyltin in surface waters of the Chesapeake Bay watershed. **Hum Ecol Risk Assess.** 6: 141-179.

Harino, H., M. Fukushima, Y. Kurokawa and S. Kawai. 1997. Susceptibility of bacterial populations to organotin compounds and microbial degradation of organotin compounds in environmental water. **Environ. Pollute.** 98(2): 157-162.

Heroult, J., Y. Nia, L. Denaix, M. Bueno and G. Lespes. 2008. Kinetic degradation processes of butyl- and phenyltins in soils. **Chemosphere.** 72: 940-946.

Hiroya, H., M. Ohji, G. Wattayakorn, T. Arai, S. Rungsupa and N. Miyazaki. 2006. Occurrence of antifouling biocides in sediment and green mussels from Thailand. **Arch. Environ. Contam. Toxicol.** 51: 400-407.

Huang, J.H. and E. Matzner. 2003. Degradation of organotin compounds in organic and mineral forest soils. **J. Plant Nutr. Soil Sci.** 167(1): 33-38.

_______, E. Matzner and D. Schwesig. 2004. Organotin compounds in precipitation, fog and soils of a forested ecosystem in Germany. **Environ. Pollut.** 130(2): 177-186.

IPCS (International Program on Chemical Safety). 1990. **Environmental health criteria 116.** Tributyltin compounds. Available Source: http://www.inchem.org/documents/ehc/ehc116.htm#SubSectionNumber:4.2.1, September 6, 2010.

Inoue, H., O. Takimura, H. Fuse, K. Murakami and Y. Yamaoka. 2000. Degradation of triphenyltin by fluorescence pseudomonad. **Appl. Environ. Microbiol.** 66(8): 3492-3498.

Jiang, G., J. Liu, B. He, J. Zhang, Q. Zhou and G. Zhai. 2008. Ultraviolet degradation of methyltins: Elucidating the mechanism by identification of a detected new intermediary product and investigating the kinetics at various environmental conditions. **Chemosphere**. 72: 389-399.

Kaloyanova, F.P. and M.A. El Batawi. 1991. In **Human toxicology of pesticides.** CRC Press, Florida, USA.

Kamruddin, S.K., T.K. Chattopadhyaya, A. Roy, and E.R.T. Tierkink. 1995. Biocidal organotin compounds. Part 2. Synthesis characterization and biocidal properties of triorgaotin(IV) hidantoic acid derivatives and the crystal structures of triphenyltin and tricyclohexyltin hidantoates. **Appl. Organomet. Chem.** 10: 513-521.

Kawai, S., Y. Kurokawa, H. Harino and M. Fukushima. 1998. Degradation of tributyltin by a bacterial strain isolated from polluted river water. **Environ. Pollut.** 102: 259-263.

Kerk, G.J.M. van der. 1975. Present status of the use of organotin compounds. **Chem ztg.** 99: 26-32.

Landmayer, J., T. Tanner and B. Watt. 2004. Biotransformation of tributyltin to tin in freshwater river-bed sediments contaminated by organotin release. **Environ. Sci. Technol.** 38: 4106-4112.

Lascourreges, J.F., P. Caumette and O.F.X. Donard. 2000. Toxicity of butyltin, phenyltin and inorganic tin compounds to sulfate-reducing bacteria isolated from anoxic marine sediment. **Appl Organomet Chem.** 14(2): 98-107.

Laughlin, R. and O. Linden. 1982. Sublethal responses of the tadpoles of the europeam frog *Rana temporaria* to two tributyltin compounds. **Bull Environ. Contam. Toxicol.** 28: 494-499.

Laughlin, R., W. French and H.E. Guard. 1983. Acute and sublethal toxicity of tributyltin oxide (TBTO) and its putative environmental product, tributyltin sulfide (TBTS) to zoeal mud crab, *Rhithropanopeus harrisii*. **Water Air Soil Pullut.** 20: 69-79.

_______, _______ and _______. 1986. Accumulation of bis(tributyltin)oxide by the marine mussle, *Mytilus Edulis*. **Environ. Sci. Technol.** 20: 884-890.

Lawler, I.F. and J.C. Aldrich. 1987. Sublethal effects of bis(tri-n-butyltin)oxide on *Crassostrea gigas spat*. **Mar Pollut Bull.** 18: 274-278.

Lespes, G., C. Carlier-Pinasseau and M. Astruc. 1997. Determination of butyl- and phenyltin compounds in sediments by GC-FPD after $NaBEt_4$ ethylation. **Talanta.** 44: 1163-1171.

Lewis, P.G. and E.A. Emmett. 1987. Irritant dermatitis from tri-n-butyltin oxide and contact allergy from chlorocresol. **Contact Dermatitis.** 17:129-132.

Luan, T.G., J. Jin, S.M.N. Chan and N.F.Y. Tam. 2006. Biosorption and biodegradation of tributyltin (TBT) by alginate immobilized *Chlorella vulgaris* beads in several treatment cycles. **Process Biochem.** 41(7): 1560-1565.

Maguire, R. J. and A.J. Tkacz. 1985. Degradation of tri-n-tin species in water and sediment from Toronto Harbour. **J. Agric. Food Chem.** 33: 947-953.

_______, H. C. John and J. H. Elizabeth. 1984. Degradation of the Tri-n-butyltin Species in Water. **J. Agrlc. Food Chem.** 31: 1060-1065.

Mendo, S., A. Cruz, T. Caetano and S. Suzuki. 2007. Aeromonas veronii, a tributyltin (TBT)-degrading bacterium isolated from an estuarine environment, Ria de Aveiro in Portugal. **Mar. Environ. Res.** 64: 639-650.

Metthiessen, P. and P.E. Gibbs. 1998. Critical appraisal of the evidence for tributyltin-mediated endocrine disruption in mollusks. **Environ Toxicol Chem.** 17: 37-43.

Mills, A. and S.L. Hunte. 1997. An overview of semiconductor photocatalysis. **J. Photochem. Photobiol. A: Chem.** 108: 1-35.

Minganti, V., R. Capelli and R. De Pellegrini. 1995. Evaluation of different derivatisation methods for the multi-element detection of Hg, Pb and Sn compounds by gas chromatography-microwave induced plasma-atomic emission spectroscopy in environmental samples. **Fresenius J. Anal. Chem.** 351: 471-477.

Nakato, Y., R. Nakamura and T. Tanaka. 2004. Mechanism for visible light responses in anodic photocurrents at N-Doped TiO_2 film electrodes**. J. Phys. Chem. B.** 108: 10617-10620.

Navio, J.A., C. Cerrillos, M.A. Pradera. E. Morales and J.L. Gomez-Ariza. 1997. UV-photoassisted degradation of phenylltin(IV) chlorides in water. **J. Photochem. Photobial. A.: Chem.** 108: 59-63.

_______, _______, F. Pablos and F.J. Marchena. 1993. UV photolytic degradation of butyltin chlorides in water. **J. Photochem. Photobial. A.: Chem.** 71: 97-102.

_______, _______, _______, _______ and M.A. Pradera. 1996. Photoassisted Degradation of n-Butyltin Chlorides in Air-Equilibrated Aqueous TiO_2 Suspension. **Langmuir.** 12: 2007-2014.

NIEHS (National Institute of Environmenttal Health Sciences). 2006. **Endocrine Disruptors.** Available Source: http://www.niehs.nih.gov, September 6, 2010.

Paton, G.I., W. Cheewasedtham, I.L. Marr and J.J.C. Dawson. 2006. Degradation and toxicity of phenyltin compounds in soil. **Environ. Pollut.** 144: 746-751.

Patterson, A.L. 1939. The Scherrer formula for X-Ray particle size determination. **Phys. Rev.** 56: 978-982.

Rydberg, J., M. Cox, C. Musikas, G.R. Choppin. 2004. **Solvent extraction principles and practice.** 2nd ed. Marcel Dekker Inc., New York, USA.

Schubert, P. E. Rosenberg and M. grasserbaure. 2000. Comparison of sodium tetrahydroborate and sodium tetra(n-propyl)borate as derivatisation reagent for the speciation of organotin and organolead compounds in water samples. **Fresenius J. Anal. Chem.** 366: 356-360.

Seinen, W., T. Helder, H. Vernij, A. Penninks and P. Leeuwangh. 1981. Short term toxicity of tri-n-butyltinchloride in rainbow trout (*Salmo gairdneri Richardson*) York sac fry. **Sci. Total Environ.** 19: 155-166.

Shifu, C., C. Lei, G. Shen and C. Gengyu. 2005. The preparation of nitrongen-doped photocatalyst $TiO_{2-x}N_x$ by ball milling. **Chem. Phys. Lett.** 413: 404-409.

SIGMA-ALDRICH. 2007. **Tributyltin product.** Product. Available Source: http://www.sigmaaldrich.com, April 28, 2009.

Sirisaksoontorn, W., S. Tacheepan and A. Songsasen. 2009. Photodegradation of phenanthrene by N-doped TiO_2 photocatalyst. **J. Environ. Sci. Health, Part A.** 44: 841-846.

Smirniotis, P.G. and B. Sun. 2003. Interaction of anatase and rutile TiO_2 particles in aqueous photooxidation. **Catal. Today.** 88: 49-59.

Smith, B.S. 1981. Male Characteristics on female mud snails caused by antifounling paints. **J. Appl. Toxicol.** 1: 22-25.

Sonia, M., C. Andreia, C. Tania and S. Satoru. 2007. *Aeromonas veronii*, a tributyltin (TBT)-degrading bacterium isolated from an estuarine environment, Ria de Aveiro in Portugal. **Marine Environmental Research.** 64: 639–650

Suehiro, F., T. Kobayashi, L. Nonaka, B.C. Tuyen and S. Suzuki. 2006. Degradation of tributyltin in microcosm using Mekong River sediment. **Microb. Ecol.** 52(1): 19-25.

Tam, N.F.Y., A.M.Y. Chong and Y.S. Wong. 2002. Removal of tributyltin (TBT) by live and dead microalgal cells. **Mar. Pollut. Bull.** 45: 362-371.

Tan, H.L. 2003. The mobility of tributyltin in degrade sediments disposed on land. Department of Chemical Engineering, University of Queenland, Australia.

Thain, J.E. and M.J. Waldock. 1986. The impact of tributyltin (TBT) antifouling paints on molluscan fisheries. **Water Sci Technol.** 18: 193-202.

Tutschku, S., S. Mothes and K. Dittrich. 1994. Determination and speciation of organoyin compounds by gas chromatography-microwave induced plasma-atomic emission spectroscopy. **J. Chrom. A.** 683: 269-276.

Upathem, E.S., M. Koura, M.D. Ahmed and A.H. Awad. 1980. Focal control of Schistosoma haematobium-transmitting snails, *Bulinus* (Ph.) *abyssicus*, using controlled release tri-n-butyltin fluoride and copper sulphate, pp. 449-459. *In* R. baker, eds. **Release of Bioactive materials.** Acadamic Press, New York, USA.

USEPA (U.S. Environmental Protection Agency). 1985. Technical Support Doccument: Tributyltin. Office of Pesticide Programs, Washington DC., USA.

USEPA (U.S. Environmental Protection Agency). 2000. **Endocrine disruption screening program.** Available Source: http://www.epa.gov, September 6, 2009.

Wang, X., L. Ding, H. Zhang, J. Cheng, A. Yu, L. Liu, Z. Liu and Y. Li. 2006. Development of an analytical method for organotin compounds in fortified flour samples using microwave-assisted extraction and normal-phase HPLC with UV detection. **J. Chrom. B.** 843: 268-274.

Waite, M.E., K.E. Evans. J.E. Thain and M.J. Waldock. 1989. Organotin concentrations in the Rivers Bure and Yare, Norfolk Broads, England. **Appl Organomet Chem.** 3(5): 383-391.

Weimin, C., W. Zhengpeng, H. Xiaoting, Z. Xiaolian, X. Fang and C. Chuenguang. 2005. Photocatalytic degradation of phenol in aqueous nitrogen-doped TiO_2 suspensions with various light sources. **Appl. Catal., B.** 57: 223–231.

WHO (World Health Organisation). 2002. **The international Programme on Chemical safety (IPCS): Global assessment of the state-of-the-science of the endocrine disruptors.** Available Source: http://www.who.int/ipcs/pubrications/new_issues/endocrine_disruptors/en, September 6, 2010.

Wikipedia. 2009. Available Source: http://en.wikipedia.org, September 12, 2009.

Wong. P.T.S., Y.K. Chau, O. Kramar and G.A. Bengert. 1982. Structure-toxicity relationship of tin compounds on algae. **Can. J. Fish. Aquat. Sci.** 39: 483-488.

Wuertz, S. C.E. Miller, R.M. Prister and J.J. Cooney. 1991. Tributyltin-resistant bacteria from estuarine and freshwater sediments. **Appl. Environ. Microbiol.** 57(10): 2783-2789.

Zacharewski, T. 1998. Identification and assessment of endocrine disruptors: limitations of vivo in vitro assays. **Environmental Health Perspectives.** 106: 577-582.

APPENDICES

Appendix A

Calculation of crystallite sizes, phase identification using the Sherrer’s equation

The crystallite size was also calculated applying the Sherrer's equation as shown in equation 1

$$d = \frac{k\lambda}{\beta \cos\theta_B} \qquad \text{.....(1)}$$

where d is the crystallite size (nm)

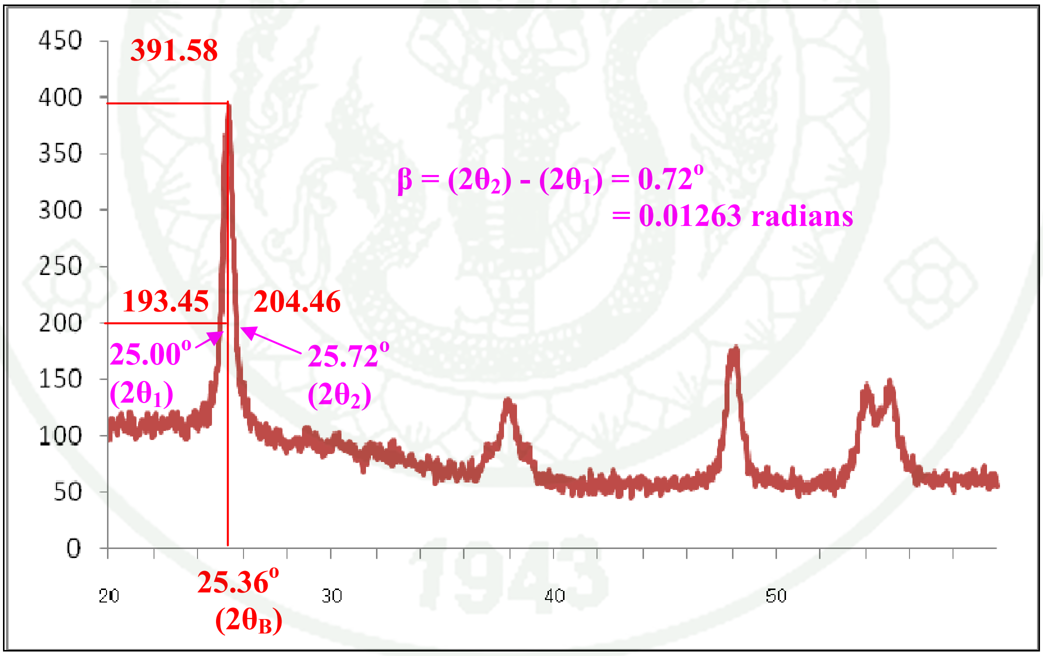
k is the constant whose value is approximately 0.9

λ is the wavelength of the X-ray radiation source (0.154 nm for Cu Kα)

β is the full width at half maximum intensity (FWHM) (radians)

θ_B is the Bragg angle at the position of the peak maximum

This is an example of finding all constants involved in the Sherrer's equation.



Appendix Figure A1 The XRD patterns of N-doped TiO_2 using titanium(IV) tetraisopropoxide as a titania precursor with calcination temperature of 400°C.

Note: All color-labelled numbers were average values from the XRD raw data; not be estimated by naked eyes.

Appendix B

Calculation of the unit cell volume from three lattice parameters

The unit cell volume was calculated from the product of three lattice parameters (a, b and c), which can be equated for the tetragonal system (a≠b=c) as follows;

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \qquad \text{.....(3)}$$

where d is a lattice spacing between the planes in the atomic lattice
h, k and l are the Miller indices
a, b and c are the lattice parameters

This is an example of finding all constants involved in the equation 3. Firstly, a *d*-spacing value was calculated from Bragg's equation as shown below.

$$2d\sin\theta_B = n\lambda \qquad \text{.....(4)}$$

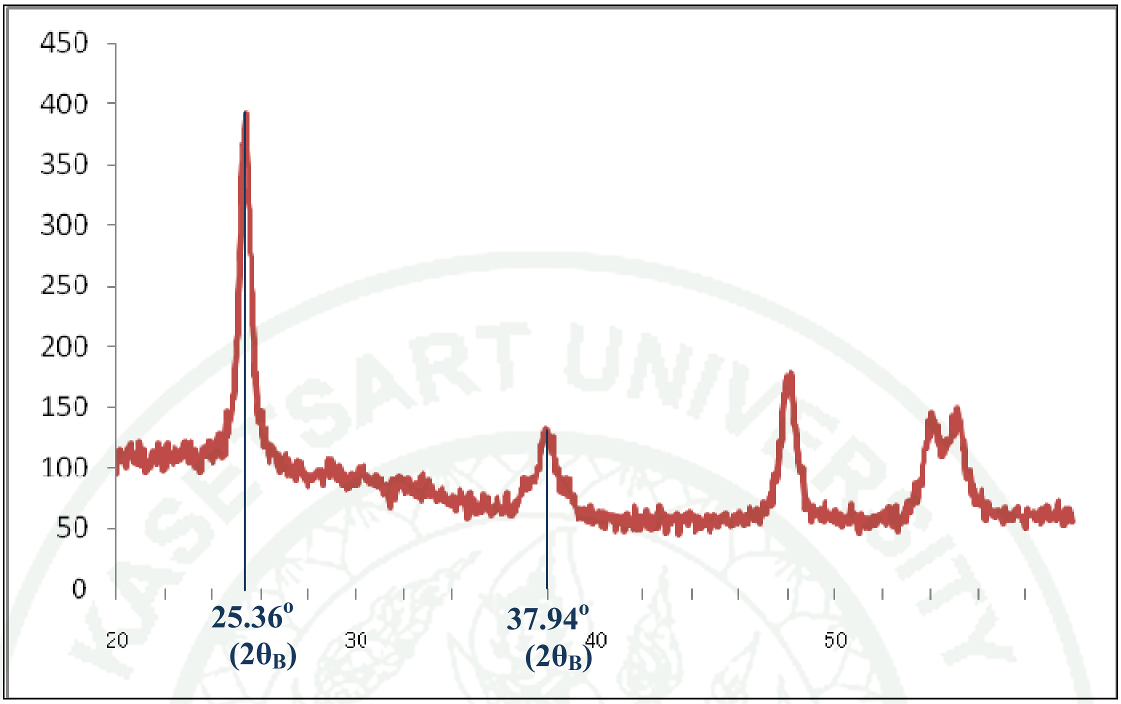
where θ_B is a Bragg's angle
n is an integer determined by the order given (n = 1)
λ is the wavelength of x-rays ($\lambda_{Cu\ K\alpha}$ = 0.154 nm)

In case of anatase XRD pattern as depicted in Figure B1, at $2\theta_B$ of 25.36° and 37.94° the *d*-spacing values were 0.3509 and 0.2373 nm, respectively. Secondly, the *d*-spacing values and the Miller indices were replaced into the equation 3.

For the (101) plane; $$\frac{1}{0.3509^2} = \frac{1^2+0^2}{a^2} + \frac{1^2}{c^2} \qquad \text{.....(5)}$$

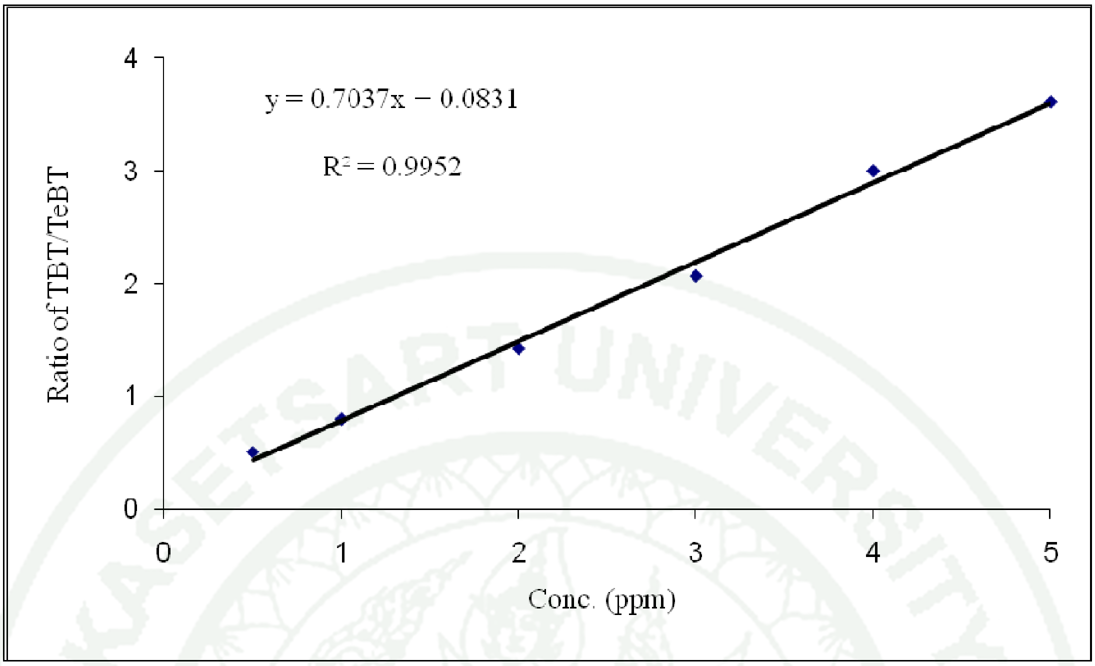
For the (004) plane; $$\frac{1}{0.2373^2} = \frac{0^2+0^2}{a^2} + \frac{4^2}{c^2} \qquad \text{.....(6)}$$

Last, from the equations 5 and 6, a and c lattice constants will be obtained; a = 0.3777 nm and c = 0.9492 nm. Hence, the unit cell volume is finally equal to 0.1354 nm^3.

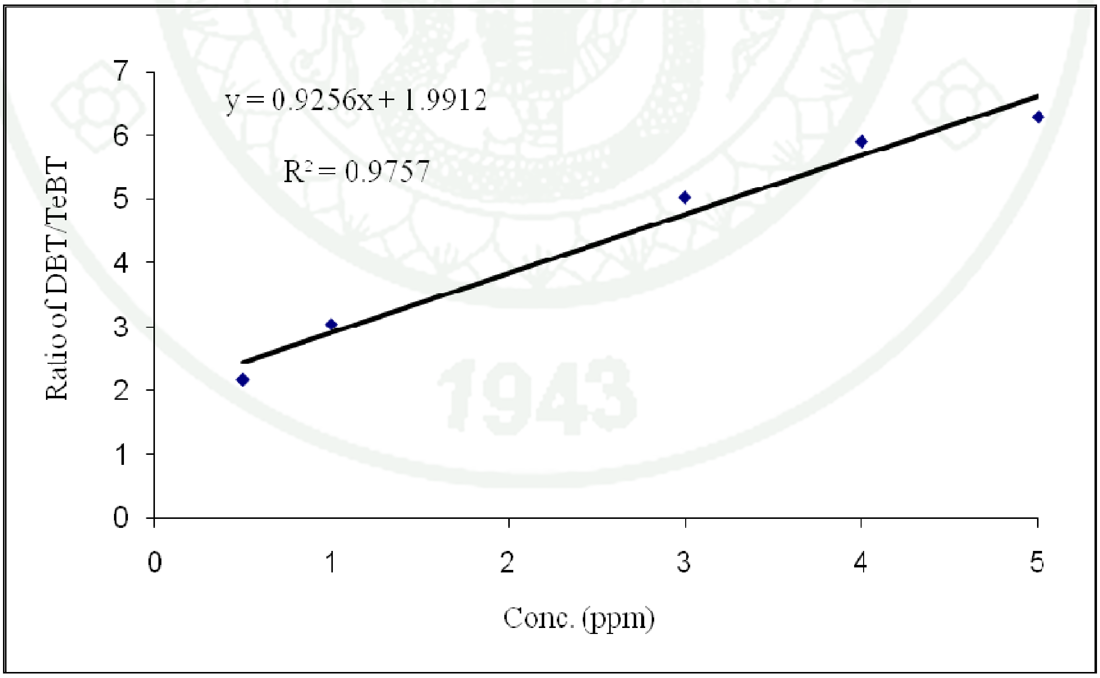


Appendix Figure B1 The XRD patterns of N-doped TiO_2 using titanium(IV) tetraisopropoxide as a titania precursor with calcination temperature of 400°C.

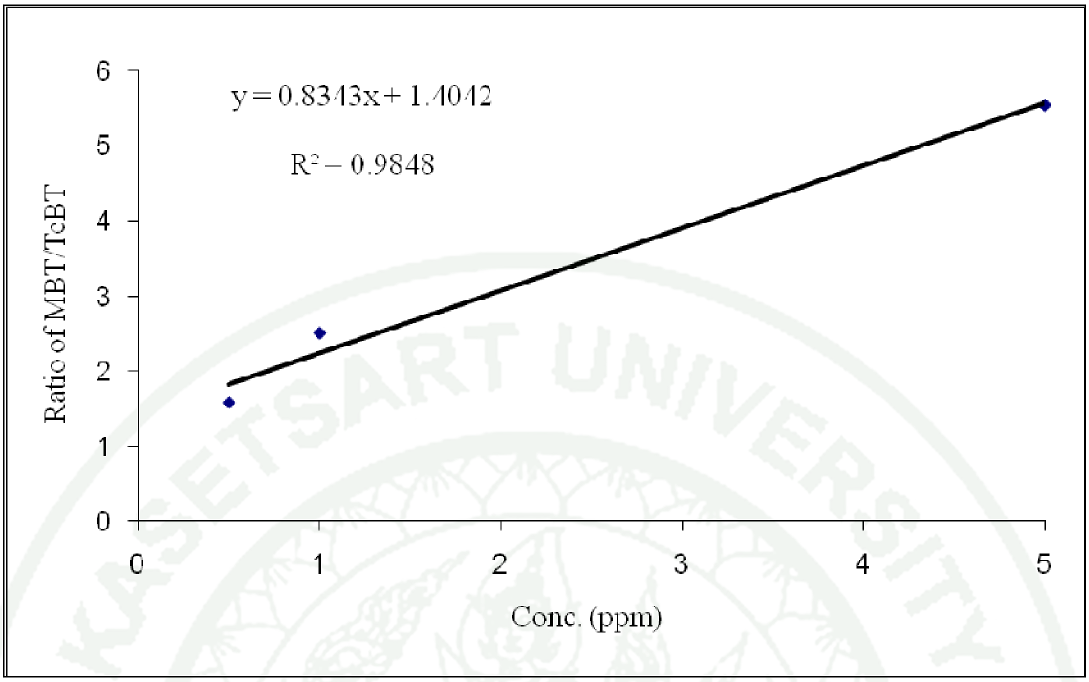
Appendix C
Linear calibration curves of three substrates and raw data of all photodegradation reactions



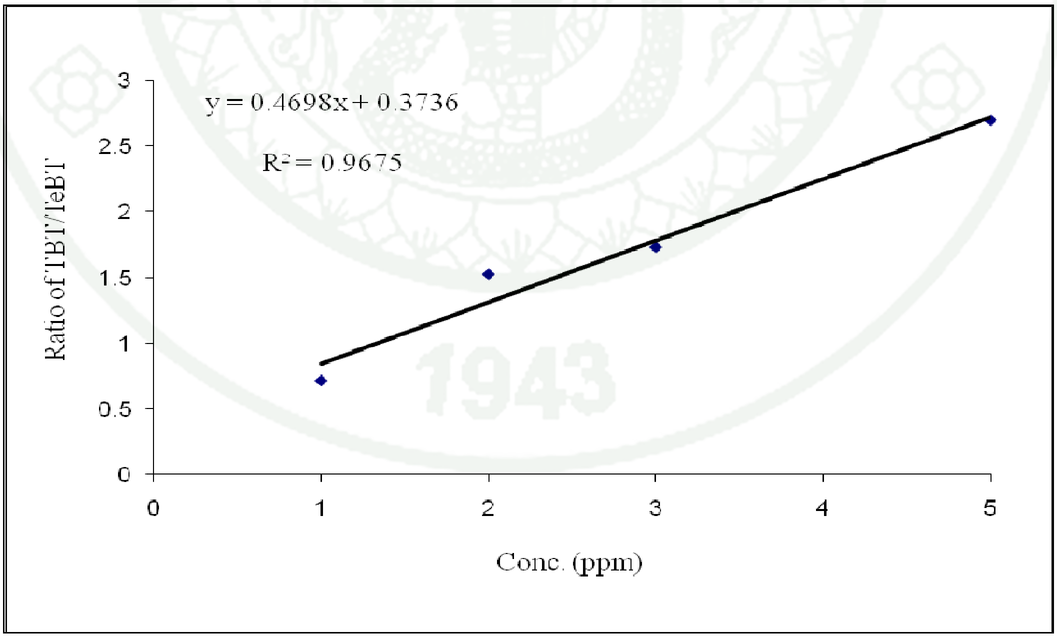
Appendix Figure C1 The linear calibration curve of tributyltin (TBT) performed by GC-FPD.



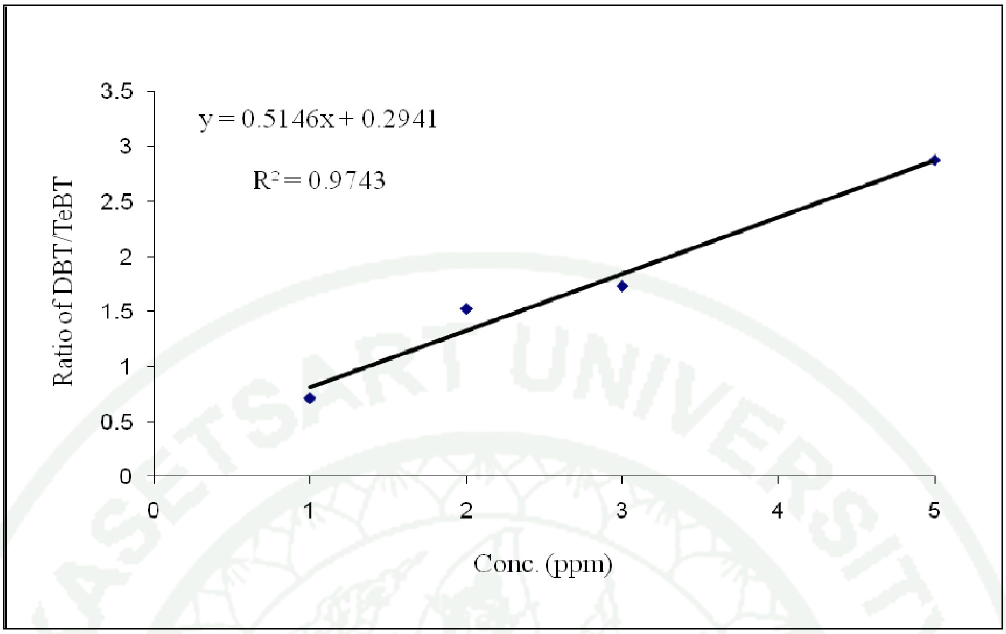
Appendix Figure C2 The linear calibration curve of dibutyltin (DBT) performed by GC-FPD.



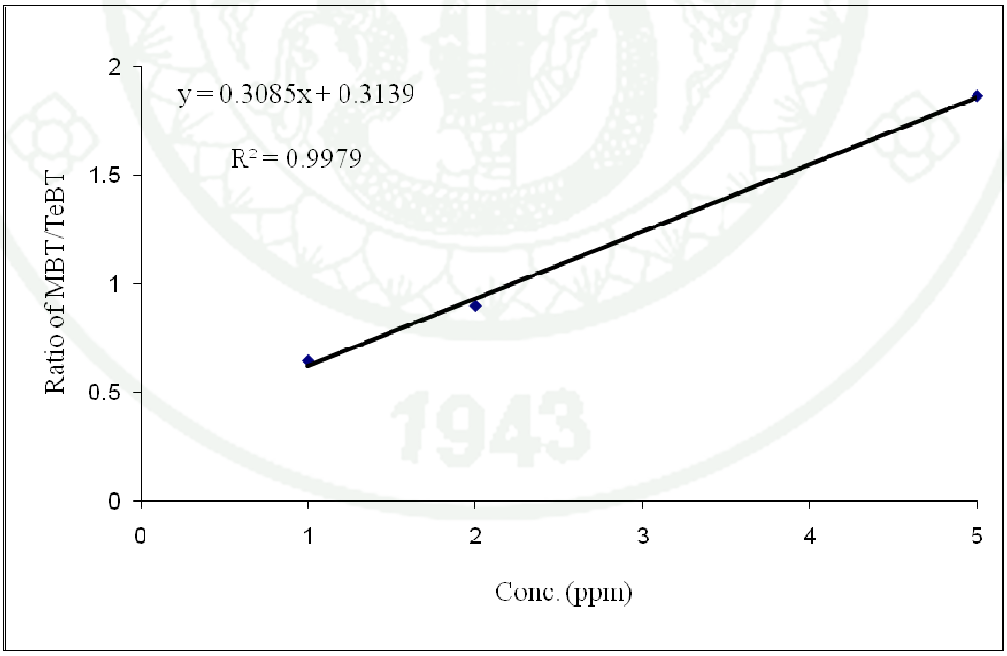
Appendix Figure C3 The linear calibration curve of dibutyltin (DBT) performed by GC-FPD.



Appendix Figure C4 The linear calibration curve of dibutyltin (TBT) performed by GC-MS.



Appendix Figure C5 The linear calibration curve of dibutyltin (DBT) performed by GC-MS.



Appendix Figure C6 The linear calibration curve of dibutyltin (MBT) performed by GC-MS.

Appendix Table C1 Raw data of the photodegradation reaction of tributyltin (TBT) by without catalyst under UV-light illumination performed by GC-FPD.

Degrading time (h)	Ratio of TBT/TeBT			Concentration[a] (ppm)			Relative concentration (C/C_o)				
	Ratio_1	Ratio_2	Ratio_3	C_1	C_2	C_3	C_1/C_o	C_2/C_o	C_3/C_o	$(C/C_o)_{ave}$	$\text{Std}_{(C/Co)}$
before lamp on (C_0)	2.3740	2.2973	2.3119	3.2555	3.1466	3.1672	0.9881	0.9314	0.9650	0.9615	0.02849
1	2.3467	2.1454	2.2338	3.2167	2.9307	3.0562					
before lamp on (C_0)	2.6900	2.5179	2.2748	3.7045	3.4600	3.1145	0.9566	0.9310	0.9566	0.9481	0.01479
2	2.3785	2.3499	2.1797	3.2619	3.2213	2.9794					
before lamp on (C_0)	2.4378	2.5035	2.1078	3.3461	3.4395	2.8772	0.9551	0.6760	1.1195	0.9169	0.2242
3	2.3320	1.7194	2.3497	3.1959	2.3253	3.2209					
before lamp on (C_0)	1.4902	1.5677	1.6000	1.9996	2.1097	2.1556	1.1203	0.8813	0.9493	0.9836	0.1231
4	1.6594	1.3914	1.5231	2.2401	1.8592	2.0463					
before lamp on (C_0)	1.6952	1.5442	1.4981	2.2909	2.0763	2.0108	1.0166	0.9298	1.0581	1.0015	0.06546
5	1.7219	1.4416	1.5803	2.3289	1.9305	2.1276					

[a] concentrations were converted by using linear calibration as shown above.

Appendix Table C2 Raw data of the photodegradation reaction of tributyltin (TBT) by P25-TiO_2 under UV-light illumination performed by GC-FPD.

Degrading time (h)	Ratio of TBT/TeBT			Concentration[a] (ppm)			Relative concentration (C/C_o)				
	$Ratio_1$	$Ratio_2$	$Ratio_3$	C_1	C_2	C_3	C_1/C_o	C_2/C_o	C_3/C_o	$(C/C_o)_{ave}$	$Std_{(C/Co)}$
before lamp on (C_0)	1.9707	1.8832	1.8971	2.6824	2.5581	2.5778	0.7526	0.8834	0.9272	0.8544	0.09084
1	1.5037	1.6734	1.7649	2.0187	2.2599	2.3900					
before lamp on (C_0)	2.5582	2.7117	2.1954	3.5173	3.7354	3.0017	0.5723	0.6659	0.5107	0.5830	0.07815
2	1.4997	1.8336	1.1619	2.0131	2.4875	1.5331					
before lamp on (C_0)	1.7728	1.9452	2.0249	2.4012	2.6461	2.7595	0.6845	0.4362	1.1195	0.5632	0.1243
3	1.2398	0.8954	1.1876	1.6437	1.1543	1.5695					
before lamp on (C_0)	2.6882	3.0123	2.6890	3.7020	4.1626	3.7031	0.3654	0.3221	0.3374	0.3416	0.02199
4	1.0351	1.0265	0.9624	1.3528	1.3407	1.2495					
before lamp on (C_0)	2.7408	2.5065	2.5471	3.7767	3.4438	3.5015	0.1975	0.1608	0.1580	0.1721	0.02203
5	0.6079	0.4727	0.4724	0.7458	0.5536	0.5533					

[a] concentrations were converted by using linear calibration as shown above.

Appendix Table C3 Raw data of the photodegradation reaction of tributyltin (TBT) by undoped TiO_2 under UV-light illumination performed by GC-FPD.

Degrading time (h)	Ratio of TBT/TeBT			Concentration[a] (ppm)			Relative concentration (C/C_o)				
	$Ratio_1$	$Ratio_2$	$Ratio_3$	C_1	C_2	C_3	C_1/C_o	C_2/C_o	C_3/C_o	$(C/C_o)_{ave}$	$Std_{(C/Co)}$
before lamp on (C_0)	1.4415	1.5650	1.4447	1.9304	2.1058	1.9350	1.0043	0.9140	1.0316	0.9833	0.06155
1	1.4474	1.4376	1.4878	1.9387	1.9248	1.9962					
before lamp on (C_0)	0.6443	0.6426	0.6263	0.7975	0.7950	0.7719	1.1247	1.0267	1.1078	1.0864	0.05239
2	0.7143	0.6575	0.6849	0.8970	0.8163	0.8552					
before lamp on (C_0)	1.4600	1.4942	1.4419	1.9567	2.0053	1.9310	1.0044	0.9521	0.9877	0.9814	0.02669
3	1.4660	1.4267	1.4252	1.9652	1.9093	1.9073					
before lamp on (C_0)	1.0657	0.9982	0.9901	1.3963	1.3004	1.2889	0.9461	1.1235	1.1241	1.0646	0.1026
4	1.0127	1.1113	1.1027	1.3210	1.4611	1.4489					
before lamp on (C_0)	0.5202	0.5411	0.5390	0.6211	0.6509	0.6478	0.8488	0.8465	0.8735	0.8563	0.01500
5	0.4541	0.4708	0.4813	0.5272	0.5510	0.5659					

[a] concentrations were converted by using linear calibration as shown above.

Appendix Table C4 Raw data of the photodegradation reaction of tributyltin (TBT) by N-doped TiO_2 under UV-light illumination performed by GC-FPD.

Degrading time (h)	Ratio of TBT/TeBT			Concentration[a] (ppm)			Relative concentration (C/C_o)				
	$Ratio_1$	$Ratio_2$	$Ratio_3$	C_1	C_2	C_3	C_1/C_o	C_2/C_o	C_3/C_o	$(C/C_o)_{ave}$	Std $_{(C/Co)}$
before lamp on (C_0)	0.7175	0.6715	0.6816	0.9016	0.8361	0.8505	1.0962	1.0824	1.1396	1.1061	0.02985
1	0.7786	0.7199	0.7652	0.9883	0.9050	0.9692					
before lamp on (C_0)	1.5016	1.5437	1.5143	2.0158	2.0756	2.0339	1.0566	1.0497	1.0014	1.0359	0.03009
2	1.5820	1.6162	1.5163	2.1300	2.1787	2.0367					
before lamp on (C_0)	1.7512	1.3680	1.3884	2.3705	1.8259	1.8549	0.7754	0.9607	0.9283	0.8881	0.09896
3	1.3766	1.3175	1.2948	1.8381	1.7541	1.7219					
before lamp on (C_0)	1.3398	1.3348	1.2848	1.7858	1.7788	1.7077	0.5648	0.5426	0.5980	0.5685	0.02790
4	0.7928	0.7623	0.8018	1.0085	0.9652	1.0213					
before lamp on (C_0)	1.6767	1.5840	1.5178	2.2646	2.1329	2.0388	0.4065	0.4772	0.4791	0.4543	0.04134
5	0.7310	0.7993	0.7704	0.9207	1.0178	0.9767					

[a] concentrations were converted by using linear calibration as shown above.

Appendix Table C5 Raw data of the photodegradation reaction of tributyltin (TBT) by without catalyst under visible light illumination performed by GC-FPD.

Degrading time (h)	Ratio of TBT/TeBT			Concentration[a] (ppm)			Relative concentration (C/C_o)				
	$Ratio_1$	$Ratio_2$	$Ratio_3$	C_1	C_2	C_3	C_1/C_o	C_2/C_o	C_3/C_o	$(C/C_o)_{ave}$	Std $_{(C/Co)}$
before lamp on (C_0)	1.3884	1.4596	1.5015	1.8550	1.9561	2.0157	1.0970	1.0854	0.9272	1.0365	0.09485
1	1.5151	1.5771	1.3983	2.0349	2.1231	1.8689					
before lamp on (C_0)	1.5588	1.5771	1.6100	2.0970	2.1231	2.1699	0.9310	1.0704	0.9301	0.9774	0.08049
2	1.5379	1.6823	1.5046	2.0673	2.2725	2.0201					
before lamp on (C_0)	1.5796	1.5007	1.4457	2.1267	2.0144	1.9363	0.9055	1.0569	1.0964	1.0196	0.1008
3	1.4382	1.5813	1.5771	1.9257	2.1291	2.1231					
before lamp on (C_0)	1.6212	1.4904	1.5715	2.1857	1.9999	2.1150	0.8937	1.0967	0.9941	0.9948	0.1015
4	1.4577	1.6265	1.5627	1.9533	2.1932	2.1026					
before lamp on (C_0)	1.6744	1.6265	1.6334	2.2613	2.1932	2.2031	0.9681	1.0108	0.8750	0.9513	0.06944
5	1.6237	1.6431	1.4396	2.1892	2.2168	1.9277					

[a] concentrations were converted by using linear calibration as shown above.

Appendix Table C6 Raw data of the photodegradation reaction of tributyltin (TBT) by P25-TiO_2 under visible light illumination performed by GC-FPD.

Degrading time (h)	Ratio of TBT/TeBT			Concentration[a] (ppm)			Relative concentration (C/C_o)				
	$Ratio_1$	$Ratio_2$	$Ratio_3$	C_1	C_2	C_3	C_1/C_o	C_2/C_o	C_3/C_o	$(C/C_o)_{ave}$	$Std_{(C/Co)}$
before lamp on (C_0)	1.3495	1.4126	1.3764	1.7996	1.8894	1.8378	1.0489	1.0531	1.2002	1.1007	0.08615
1	1.4115	1.4832	1.6353	1.8877	1.9897	2.2058					
before lamp on (C_0)	1.4821	1.4468	1.3920	1.9881	1.9379	1.8601	1.0978	1.0426	1.1802	1.1069	0.06925
2	1.6190	1.5049	1.6279	2.1825	2.0205	2.1953					
before lamp on (C_0)	1.3271	1.3549	1.1561	1.7679	1.8074	1.5247	0.9778	0.9491	1.1972	1.0414	0.1357
3	1.4382	1.5813	1.5771	1.9257	2.1291	2.1231					
before lamp on (C_0)	1.2487	1.3139	1.2951	1.6563	1.7491	1.7223	1.1375	0.9352	0.9592	1.0106	0.1105
4	1.4089	1.2342	1.2457	1.8840	1.6357	1.6521					
before lamp on (C_0)	1.2896	1.3025	1.2384	1.7146	1.7328	1.6417	1.0189	1.0600	1.0833	1.0541	0.03259
5	1.3125	1.3756	1.3346	1.7470	1.8367	1.7784					

[a] concentrations were converted by using linear calibration as shown above.

Appendix Table C7 Raw data of the photodegradation reaction of tributyltin (TBT) by undoped TiO_2 under visible light illumination performed by GC-FPD.

Degrading time (h)	Ratio of TBT/TeBT			Concentration[a] (ppm)			Relative concentration (C/C_o)				
	$Ratio_1$	$Ratio_2$	$Ratio_3$	C_1	C_2	C_3	C_1/C_o	C_2/C_o	C_3/C_o	$(C/C_o)_{ave}$	$Std_{(C/Co)}$
before lamp on (C_0)	0.9502	0.9556	1.2925	1.2323	1.2399	1.7187	1.3034	1.2307	0.7931	1.1091	0.2760
1	1.2133	1.1569	1.0423	1.6061	1.5259	1.3631					
before lamp on (C_0)	1.2111	1.1253	1.1553	1.6029	1.4810	1.5237	0.9023	0.9892	0.9409	0.9441	0.04356
2	1.1009	1.1140	1.0919	1.4463	1.4650	1.4336					
before lamp on (C_0)	0.7816	0.8663	0.8441	0.9926	1.1130	1.0814	1.1033	0.9568	0.8677	0.9759	0.1190
3	0.8537	0.8324	0.7434	1.0951	1.0648	0.9383					
before lamp on (C_0)	0.7435	0.8369	0.7683	0.9384	1.0711	0.9737	1.1158	0.9893	1.0954	1.0668	0.06790
4	0.8199	0.8288	0.8336	1.0471	1.0597	1.0665					
before lamp on (C_0)	0.7755	0.7429	0.7565	0.9839	0.9377	0.9569	1.0661	1.0711	1.0434	1.0602	0.01471
5	0.8212	0.7898	0.7858	1.0489	1.0043	0.9985					

[a] concentrations were converted by using linear calibration as shown above.

Appendix Table C8 Raw data of the photodegradation reaction of tributyltin (TBT) by N-doped TiO_2 under visible light illumination performed by GC-FPD.

Degrading time (h)	Ratio of TBT/TeBT			Concentration[a] (ppm)			Relative concentration (C/C_o)				
	$Ratio_1$	$Ratio_2$	$Ratio_3$	C_1	C_2	C_3	C_1/C_o	C_2/C_o	C_3/C_o	$(C/C_o)_{ave}$	Std $_{(C/Co)}$
before lamp on (C_0)	1.2466	1.1665	1.2467	1.6535	1.5396	1.6536	1.0499	1.1437	1.0942	1.0959	0.04690
1	1.3047	1.3222	1.3563	1.7360	1.7608	1.8093					
before lamp on (C_0)	1.3290	1.3734	1.3286	1.7704	1.8336	1.7699	1.0423	0.9121	0.9462	0.9669	0.06752
2	1.3817	1.2600	1.2615	1.8453	1.6724	1.6746					
before lamp on (C_0)	1.4055	1.5843	1.4033	1.8792	2.1333	1.8761	0.7230	0.6455	0.6982	0.6889	0.03956
3	1.0392	1.0522	1.0049	1.3587	1.3772	1.3099					
before lamp on (C_0)	1.3512	1.3133	1.3636	1.8020	1.7482	1.8196	0.6782	0.7287	0.6271	0.6780	0.05077
4	0.9431	0.9795	0.8861	1.2221	1.2738	1.1412					
before lamp on (C_0)	1.3271	1.4038	1.4073	1.7678	1.8768	1.8818	0.6568	0.5763	0.5937	0.6089	0.04237
5	0.9001	0.8442	0.8692	1.1611	1.0816	1.1171					

[a] concentrations were converted by using linear calibration as shown above.

Appendix Table C9 Raw data of the photodegradation reaction of dibutyltin (DBT) by N-doped TiO_2 under visible light illumination performed by GC-MS.

Degrading time (h)	Ratio of TBT/TeBT			Concentration^a (ppm)			Relative concentration (C/C_o)				
	$Ratio_1$	$Ratio_2$	$Ratio_3$	C_1	C_2	C_3	C_1/C_o	C_2/C_o	C_3/C_o	$(C/C_o)_{ave}$	$Std_{(C/Co)}$
before lamp on (C_0)	4.1030	4.0502	4.1731	7.4017	7.2991	7.5379	0.9514	0.7497	0.8064	0.8358	0.1040
1	3.9179	3.1101	3.4223	7.0419	5.4722	6.0788					
before lamp on (C_0)	4.0735	4.6719	3.9825	7.3443	8.5071	7.1675	0.8250	0.7186	0.9445	0.8294	0.1130
2	3.4122	3.4401	3.7777	6.0592	6.1134	6.7695					
before lamp on (C_0)	6.3242	6.2240	6.3999	11.7181	11.5233	11.8651	0.5911	0.5855	0.5863	0.5876	0.00303
3	3.8583	3.7659	3.8736	6.9262	6.7466	6.9559					
before lamp on (C_0)	3.9254	4.2587	4.7141	7.0565	7.7042	8.5892	0.3267	0.2929	0.2985	0.3060	0.01813
4	1.4804	1.4552	1.6133	2.3052	2.2563	2.5636					
before lamp on (C_0)	5.5545	5.1576	5.1688	10.2222	9.4511	9.4729	0.2255	0.2387	0.2706	0.2450	0.02319
5	1.4804	1.4552	1.6133	2.3052	2.2563	2.5636					

^{a}concentrations were converted by using linear calibration as shown above.

Appendix Table C10 Raw data of the photodegradation reaction of monobutyltin (MBT) by N-doped TiO_2 under visible light illumination performed by GC-MS.

Degrading time (h)	Ratio of TBT/TeBT			Concentration[a] (ppm)			Relative concentration (C/C_o)				
	$Ratio_1$	$Ratio_2$	$Ratio_3$	C_1	C_2	C_3	C_1/C_o	C_2/C_o	C_3/C_o	$(C/C_o)_{ave}$	Std $_{(C/Co)}$
before lamp on (C_0)	2.8597	2.9559	2.9427	8.2521	8.5641	8.5211	0.9471	0.8358	0.8362	0.8730	0.06413
1	2.7250	2.5221	2.5121	7.8155	7.1580	7.1255					
before lamp on (C_0)	2.7776	3.0451	2.7311	7.9862	8.8533	7.8353	0.4587	0.3925	0.6685	0.5065	0.1441
2	1.4439	1.3859	1.9297	3.6630	3.4749	5.2375					
before lamp on (C_0)	1.5206	1.5931	1.4228	3.9114	4.1465	3.5946	0.4155	0.3544	0.2870	0.3523	0.06429
3	0.8153	0.7672	0.6321	1.6252	1.4694	1.0316					
before lamp on (C_0)	1.9447	2.0622	1.9381	5.2862	5.6671	5.2647	0.2193	0.2350	0.2132	0.2225	0.01126
4	0.6716	0.7248	0.6602	1.1594	1.3321	1.1226					
before lamp on (C_0)	5.5545	5.1576	5.1688	10.2222	9.4511	9.4729	0.1008	0.1020	0.2864	0.1631	0.1068
5	1.4804	1.4552	1.6133	2.3052	2.2563	2.5636					

[a] concentrations were converted by using linear calibration as shown above.

Appendix Table C11 Raw data of the photodegradation reaction of tributyltin (TBT) by without catalyst under natural light illumination performed by GC-FPD.

Degrading time (h)	Ratio of TBT/TeBT			Concentration[a] (ppm)			Relative concentration (C/C_o)				
	$Ratio_1$	$Ratio_2$	$Ratio_3$	C_1	C_2	C_3	C_1/C_o	C_2/C_o	C_3/C_o	$(C/C_o)_{ave}$	Std $_{(C/Co)}$
before illumination	1.8646	1.8646	1.8646	3.7996	3.7996	3.7996	1	1	1	1	0.0000
1	1.4768	1.6390	1.4268	3.0386	3.3569	2.9405	0.7997	0.8835	0.7739	0.8190	0.05729
2	1.6865	1.4960	1.4151	3.4501	3.0764	2.9176	0.7679	0.8097	0.7679	0.7818	0.02413
3	1.4995	1.4115	1.4591	3.0832	2.9106	3.0040	0.8115	0.7660	0.7906	0.7894	0.02274
4	1.5442	1.3798	1.5501	3.1709	2.8483	3.1824	0.8345	0.7496	0.8376	0.8072	0.04992
5	1.4402	1.2826	1.5433	2.9668	2.6576	3.1692	0.7808	0.6994	0.8341	07715	0.06781

[a] concentrations were converted by using linear calibration as shown above.

Appendix Table C12 Raw data of the photodegradation reaction of tributyltin (TBT) by P25-TiO_2 under natural light illumination performed by GC-FPD.

Degrading time (h)	Ratio of TBT/TeBT			Concentration[a] (ppm)			Relative concentration (C/C_o)				
	$Ratio_1$	$Ratio_2$	$Ratio_3$	C_1	C_2	C_3	C_1/C_o	C_2/C_o	C_3/C_o	$(C/C_o)_{ave}$	Std $_{(C/Co)}$
before illumination	1.6023	1.6023	1.6023	3.3202	3.3202	3.3202	1	1	1	1	0.0000
1	0.9860	1.0010	0.8436	2.0755	2.1049	1.7961	0.6251	0.6340	0.5410	0.6000	0.05134
2	0.6267	1.0205	0.9039	1.3706	2.1433	1.9144	0.4128	0.6455	0.5766	0.5450	0.1195
3	0.6781	0.5314	0.6832	1.4713	1.1836	1.4814	0.4431	0.3565	0.4462	0.4153	0.05094
4	0.4456	0.6807	0.5495	1.0151	1.4765	1.2189	0.3057	0.4447	0.3671	0.3725	0.06964
5	0.2898	0.4933	0.6448	0.7095	1.1088	1.4061	0.2137	0.3340	0.4235	0.3237	0.1053

[a] concentrations were converted by using linear calibration as shown above.

Appendix Table C13 Raw data of the photodegradation reaction of tributyltin (TBT) by undoped TiO_2 under natural light illumination performed by GC-FPD.

Degrading time (h)	Ratio of TBT/TeBT			Concentration[a] (ppm)			Relative concentration (C/C_o)				
	$Ratio_1$	$Ratio_2$	$Ratio_3$	C_1	C_2	C_3	C_1/C_o	C_2/C_o	C_3/C_o	$(C/C_o)_{ave}$	Std $_{(C/Co)}$
before illumination	1.4225	1.4225	1.4225	2.9321	2.9321	2.9321	1	1	1	1	0.0000
1	1.0739	1.2264	0.8682	2.2480	2.5473	1.8444	0.7667	0.8687	0.6290	0.7548	0.1203
2	0.8051	1.0823	0.8990	1.7205	2.2646	1.9049	0.5868	0.7723	0.6497	0.6696	0.09436
3	1.0092	0.8683	0.7319	2.1211	1.8446	1.5768	0.7234	0.6291	0.5378	0.6301	0.09281
4	0.8051	0.9083	0.9517	1.7205	1.9230	2.0083	0.5868	0.6558	0.6849	0.6425	0.05041
5	0.8427	0.6570	0.6773	1.7943	1.4300	1.4698	0.6119	0.4877	0.5013	0.5336	0.06814

[a] concentrations were converted by using linear calibration as shown above.

Appendix Table C14 Raw data of the photodegradation reaction of tributyltin (TBT) by N-doped TiO_2 under natural light illumination performed by GC-FPD.

Degrading time (h)	Ratio of TBT/TeBT			Concentration[a] (ppm)			Relative concentration (C/C_o)				
	$Ratio_1$	$Ratio_2$	$Ratio_3$	C_1	C_2	C_3	C_1/C_o	C_2/C_o	C_3/C_o	$(C/C_o)_{ave}$	Std $_{(C/Co)}$
before illumination	1.9968	1.9968	1.9968	4.0591	4.0591	4.0591	1	1	1	1	0.0000
1	0.8264	0.7067	0.7559	1.7624	1.5275	1.6240	0.4342	0.3763	0.4001	0.4035	0.02908
2	0.6373	0.6098	0.7098	1.3913	1.3374	1.5336	0.3428	0.3295	0.3778	0.3500	0.02497
3	0.6276	0.5538	0.5244	1.3722	1.2274	1.1697	0.3380	0.3024	0.2882	0.3095	0.02570
4	0.3751	0.4656	0.3780	0.8767	1.0543	0.8825	0.2106	0.2597	0.2174	0.2310	0.02485
5	0.2026	0.3710	0.3102	0.5383	0.8687	0.7493	0.1326	0.2140	0.1846	0.1771	0.04121

[a] concentrations were converted by using linear calibration as shown above.

Appendix Table C15 Raw data of the photodegradation reaction of monobutyltin (MBT) by N-doped TiO_2 under natural light illumination performed by GC-MS.

Degrading time (h)	Ratio of TBT/TeBT			Concentration[a] (ppm)			Relative concentration (C/C_o)				
	$Ratio_1$	$Ratio_2$	$Ratio_3$	C_1	C_2	C_3	C_1/C_o	C_2/C_o	C_3/C_o	$(C/C_o)_{ave}$	Std $_{(C/Co)}$
before illumination	2.0478	2.0478	2.0478	5.6205	5.6205	5.6205	1	1	1	1	0.0000
1	0.8876	0.9252	1.0504	1.8595	1.9816	2.3874	0.3308	0.3526	0.4248	0.3694	0.04916
2	0.8164	0.6144	0.7291	1.6289	0.9739	1.3458	0.2898	0.1733	0.2394	0.2342	0.05845
3	0.7845	0.7830	0.7747	1.5254	1.5204	1.4938	0.2714	0.2705	0.2658	0.2692	0.00302
4	0.5824	0.4762	0.5208	0.6707	0.8705	0.5261	0.1549	0.0936	0.1193	0.1126	0.03076
5	-	-	-	-	-	-	-	-	-	-	-

[a] concentrations were converted by using linear calibration as shown above.

Appendix Table C16 Raw data of the photodegradation reaction of mix solutions (MBT, DBT and TBT) by N-doped TiO_2 under visible light illumination performed by GC-MS.

OTCs	time (h)	Ratio of TBT/TeBT			Concentration[a] (ppm)			Relative concentration (C/C_o)				
		$Ratio_1$	$Ratio_2$	$Ratio_3$	C_1	C_2	C_3	C_1/C_o	C_2/C_o	C_3/C_o	$(C/C_o)_{ave}$	$Std_{(C/Co)}$
TBT	Lamp off	1.5148	1.5434	1.7223	2.4291	2.4900	2.8708	0.8793	0.9701	0.9517	0.9337	0.04801
	1	1.3770	1.5084	1.6571	2.1358	2.4155	2.7321					
	Lamp off	1.6937	1.5533	1.7658	2.8100	2.5110	2.9635	1.1259	1.1090	1.0198	1.0849	0.1915
	2	1.8599	1.6819	1.7935	3.1637	2.7847	3.0223					
	Lamp off	2.4753	1.9120	1.5926	4.4736	3.2745	2.5948	0.4460	0.6410	0.8625	0.6499	0.1218
	3	1.3111	1.3597	1.4251	1.9954	2.0990	2.2381					
	Lamp off	1.3241	1.4024	1.2881	2.0233	2.1898	1.9465	0.3816	0.4323	0.4326	0.4115	0.1244
	4	0.3244	0.3262	0.3156	19.8933	20.000	19.357					
DBT	Lamp off	2.0828	2.0628	2.3417	3.4759	3.4371	3.9790	1.0473	1.0751	0.8880	1.0035	0.1010
	1	2.1673	2.1958	2.1123	3.6401	3.6954	3.5333					

[a] concentrations were converted by using linear calibration as shown above.

Appendix Table C16 (Continue)

OTCs	time (h)	Ratio of TBT/TeBT			Concentration[a] (ppm)			Relative concentration (C/C_o)				
		$Ratio_1$	$Ratio_2$	$Ratio_3$	C_1	C_2	C_3	C_1/C_o	C_2/C_o	C_3/C_o	$(C/C_o)_{ave}$	$Std_{(C/Co)}$
DBT	Lamp off	2.3071	2.2906	2.5608	3.9119	3.8797	4.4048	1.2369	0.9669	0.8982	1.0340	0.3827
	2	2.7841	2.2245	2.3300	4.8387	3.7513	3.9563					
	Lamp off	3.5222	2.3639	2.1547	6.2729	4.0221	3.6156	0.6389	0.9218	1.0667	0.8758	0.1503
	3	2.3566	2.2019	2.2788	4.0080	3.7074	3.8567					
	Lamp off	3.4415	3.4634	3.3214	6.1162	6.1587	5.8829	0.4468	0.5019	0.5503	0.4996	0.2596
	4	1.7003	1.8846	1.9600	2.7326	3.0908	3.2372					
MBT	Lamp off	1.5611	1.3553	1.5618	4.0428	3.3755	4.0451	0.8112	0.8482	0.6577	0.7723	0.1010
	1	1.3256	1.1971	1.1346	3.2795	2.8630	2.6604					
	Lamp off	1.5852	1.4569	1.6866	4.1208	3.7050	4.4497	0.9180	0.8202	0.8016	0.8446	0.3827
	2	1.4810	1.2514	1.4142	3.7830	3.0390	3.5667					

[a] concentrations were converted by using linear calibration as shown above.

Appendix Table C16 (Continue)

OTCs	time (h)	Ratio of TBT/TeBT			Concentration[a] (ppm)			Relative concentration (C/C_o)				
		$Ratio_1$	$Ratio_2$	$Ratio_3$	C_1	C_2	C_3	C_1/C_o	C_2/C_o	C_3/C_o	$(C/C_o)_{ave}$	Std $_{(C/Co)}$
MBT	Lamp off	1.7751	1.7163	1.3402	4.7366	4.5458	3.3268	0.5283	0.4154	0.7217	0.5551	0.3290
	3	1.0858	0.8965	1.0546	2.5021	1.8884	2.4009					
	Lamp off	2.1542	2.2499	2.0204	5.9653	6.2755	5.5315	0.5655	0.5605	0.6035	0.5765	0.09501
	4	1.3545	1.3991	1.3438	3.3732	3.5177	3.3385					

[a] concentrations were converted by using linear calibration as shown above.

Appendix Table C17 Raw data of the photodegradation reaction of mix solutions (MBT, DBT and TBT) by N-doped TiO_2 under visible light illumination performed by GC-MS.

OTCs	time (h)	Ratio of TBT/TeBT			Concentration[a] (ppm)			Relative concentration (C/C_o)				
		Ratio$_1$	Ratio$_2$	Ratio$_3$	C_1	C_2	C_3	C_1/C_o	C_2/C_o	C_3/C_o	$(C/C_o)_{ave}$	Std $_{(C/Co)}$
TBT	Lamp off	2.3199	1.9638	2.0529	4.1429	3.3849	3.5745	1	1	1	1	0.0000
	1	1.5242	1.3130	1.2655	2.4491	1.9995	1.8985	0.5912	0.5907	0.5311	0.5710	0.03453
	2	2.2605	1.7730	1.9250	4.0163	2.9787	3.3023	0.9695	0.8800	0.9238	0.9244	0.04474
	3	1.5496	1.5567	1.6442	2.5032	2.5182	2.7045	0.6042	0.7439	0.7566	0.7016	0.08457
	4	1.4949	1.5953	1.6920	2.3868	2.6006	2.8062	0.5761	0.7683	0.7851	0.7098	0.1161
DBT	Lamp off	2.9193	2.2259	2.6306	5.1014	3.7539	4.5405	1	1	1	1	0.0000
	1	1.0087	0.8652	0.8597	1.3887	1.1098	1.0992	0.2722	0.2956	0.2421	0.2700	0.02684
	2	0.6053	0.7049	0.7200	0.6047	0.7982	0.8276	0.1185	0.2126	0.1823	0.1711	0.04803
	3	-	-	-	-	-	-	-	-	-	-	-
	4	-	-	-	-	-	-	-	-	-	-	-

[a] concentrations were converted by using linear calibration as shown above.

Appendix Table C17 (Continue)

OTCs	time (h)	Ratio of TBT/TeBT			Concentration[a] (ppm)			Relative concentration (C/C_o)				
		$Ratio_1$	$Ratio_2$	$Ratio_3$	C_1	C_2	C_3	C_1/C_o	C_2/C_o	C_3/C_o	$(C/C_o)_{ave}$	Std $_{(C/Co)}$
MBT	Lamp off	0.3323	0.3357	0.3182	0.3697	0.5806	9.5152	1	1	1	1	0.0000
	1	0.7500	0.7129	0.6438	1.4138	1.2933	1.0694	0.2956	0.3586	0.2299	0.2947	0.06433
	2	1.3588	1.3341	1.1759	3.3871	3.3068	2.7942	0.7082	0.9168	0.6008	0.7419	0.1607
	3	0.9517	0.8806	0.9408	2.0675	1.8368	2.0320	0.4323	0.5093	0.4369	0.4595	0.04318
	4	0.8982	0.9337	0.9484	1.8941	2.0090	2.0566	0.3961	0.5570	0.4422	0.4651	0.08288

[a] concentrations were converted by using linear calibration as shown above.

Appendix D

Calculation of rate constants

The procedure used to find rate constants was adapted from previous research by Fang *et al.* (2007). They assumed that the degradation of methylene blue in the presence of photocatalysts was the first-order kinetic reaction because they plotted a graph between $\ln C_0/C$ and degrading time (h). Then, they obtained the relative coefficient (R^2) was close to 1 and the slope of the graph could be considered as the rate constant of the photodegradation reaction. Therefore, this work properly modified their method to find the rate constants.

For the first-order rate law (at t = 0, concentration of C is $[C]_0$);

$$Rate = \frac{d[A]_t}{[A]_0} = -kt$$

The integrated rate law is thus;

$$[A]_t = [A]_0 e^{-kt}$$

The rate law is applied in order to plot liner graph by taking natural logarithm

$$\ln[A]_t = \ln[A]_0 + \ln e^{-kt}$$

$$\ln[A]_0 - \ln[A]_t = kt$$

$$\ln\frac{[A]_0}{[A]_t} = kt$$

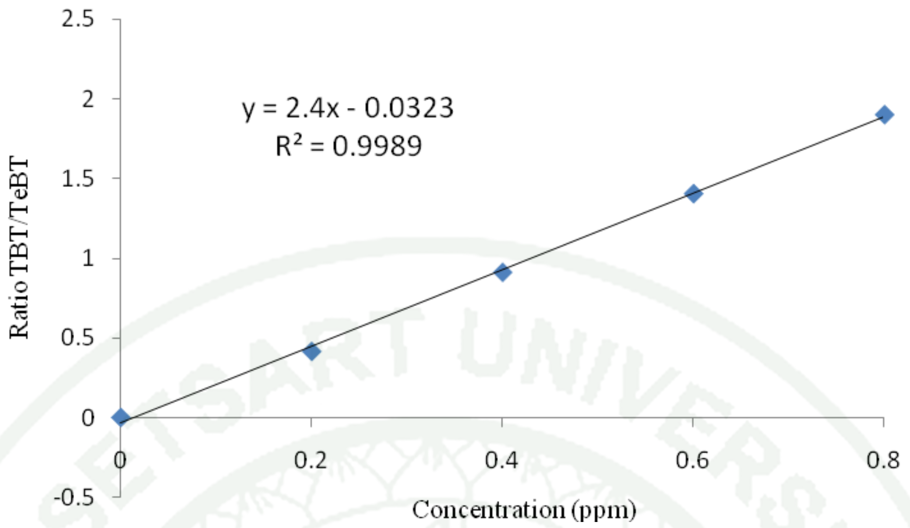
In experiment, the C_0 and C was used instead of $[A]_0$ and $[A]_t$, respectively;

$$\ln \frac{C_0}{C} = kt$$

Therefore, the liner graph was plotted between $\ln C_0/C$ and t, the rate constant was obtained from slope of graph.

Appendix E

Calculation of concentration of organotin compounds in water sample collected from Lam Chabang Harbour Gulf of Thailand



Appendix Figure E1 The linear calibration curve of TBT.

From the linear calibration curve of TBT

$$y = 2.4001x - 0.0323$$

Where x is concentrationof TBT

y is ratio of area of TBT/TeBT

The peak area of TBT which was contaminated in sea water from Lam Chabang Gulf of Thailand was 4.120098.

So $$4.120098 = 2.4001x - 0.0323$$

$$x = \frac{4.120098 + 0.0323}{2.4001}$$

$$x = 0.586 \text{ mg/L}$$

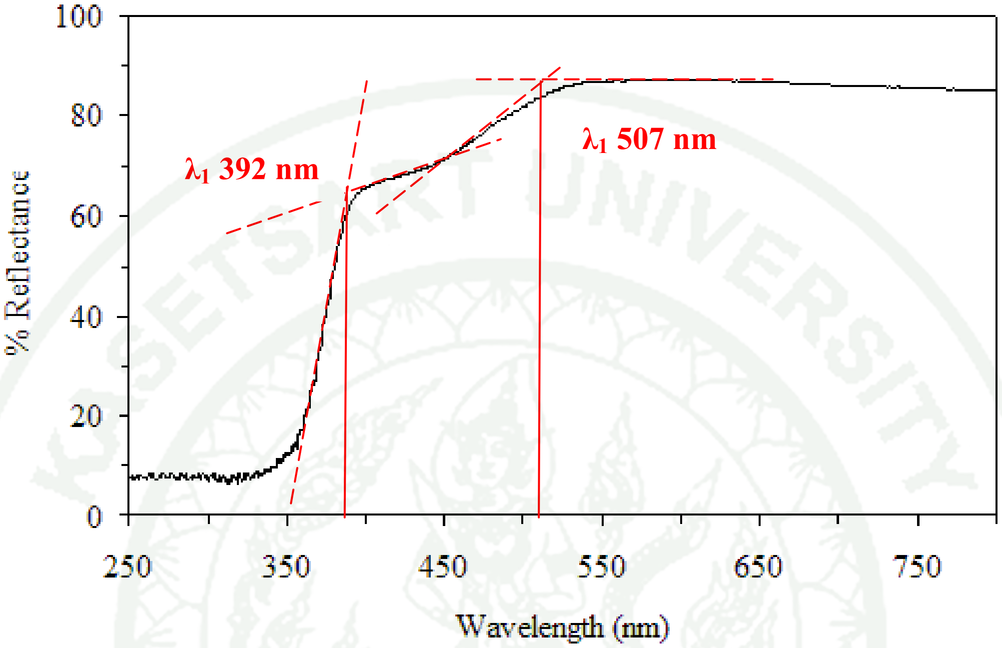
The concentration of TBT which was contaminated in sea water from Lam Chabang Gulf of Thailand was 0.586 mg/L in 1 mL of sample. So for 400 mL of sample;

$$\frac{0.586}{400} = 0.00146 \text{ mg/L or } 1.46\ \mu\text{g/L}$$

Appendix F

The procedure for the determination of the absorption edge of UV-Vis/DR results

The procedure that was used to find the absorption edge of each UV-Vis /DR spectrum conformed to previous research by Feng *et al.* (2007) as follows;



Appendix Figure F1 The UV-Vis/DR spectrum of N-doped TiO_2 using titanium(IV) tetraisopropoxide mixed with NH_3 and calcined at 400 °C.

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