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**Enhanced oxidation of brominated phenols  
using iron(III)-porphyrin catalysts  
immobilized on functionalized supports**

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# **Chapter 1**

## ***General Introduction***

Since industrial revolution, fossil fuels and chemicals are applied in industrial process, which well-affect the life of human beings, improve the life quality and change the life styles. Nowadays, almost every aspect of our daily life has been benefited from the revolution of chemical products and related industries, such as medical, farming, and transporting. Meanwhile, we suffer from environmental problems such as the air and water pollutions, which are caused by industrial processes and waste in daily life. Among those environmental issues, water pollution is very severe and should be addressed as soon as possible, which mainly results from inorganic contamination such as the cadmium and methylmercury pollution in Japan last century; and organic contamination, e.g., tap water pollution accident by benzene of oil in China recently. The water pollution accidents make us take seriously not only on production processes but also waste management. For developing a sustainable society, water treatment for removing the toxic compounds in industrial wastewater and landfill leachates is definitely necessary.

### **1.1. Brominated phenols and their derivatives in flame retardants.**

Brominated phenols are widely used chemicals in many fields. There are several kinds of brominated phenols have been developed and synthesized for different purposes. Fig. 1.1 shows the chemical structure of the most popular used brominated phenols. The main application of brominated phenols is reactive or additive flame retardants in a large range of resins and polyester polymers.

Flame retardants are chemicals added to polymeric materials, both natural and synthetic, to enhance flame-retardance properties. There are three main families of chemical flame retardants: halogenated products, organophosphorus products and

inorganic flame retardants. Within the halogenated flame retardants, bromine and chlorine compounds are the only halogen compounds having commercial significance as flame-retardant chemicals.

The brominated flame retardants (BFRs) are much more numerous than the chlorinated types because of their higher efficacy [1]. The main BFRs are the polybrominated (i) neutral aromatic, (ii) neutral cycloaliphatic, (iii) phenolic, including neutral derivatives, (iv) aromatic carboxylic acid esters and (v) tris-alkyl phosphate compounds [1–3]. Brominated phenols that have been classified as flame retardants include 2,4-dibromophenol (2,4-DBP), 2,4,6-tribromophenol (TrBP), pentabromophenol (PBP), TBBPA and TBBPS. The physicochemical properties of those brominated phenols are shown in Table 1.1. TrBP, PBP, TBBPS and TBBPA are precursors of non-phenolic derivatives also being applied as BFRs, i.e. TrBP allyl ether (TrBP-AE), PBP allyl ether (PBP-AE), TrBP 2,3-dibromopropyl ether (TrBP-DBPE), TBBPS bis(2,3-dibromopropyl ether) (TBBPS-BDBPE) and TBBPA bismethyl ether (TBBPA-bME).

Among those brominated phenols, TBBPA is the highest-volume brominated flame retardant in the world representing about 60% of the total BFR market [4]. TBBPA is produced in various countries, including the USA, Israel, Japan and China. The total amount of TBBPA produced was estimated to be over 120,000 tonnes per year [5] and 150,000 tonnes per year [6]. The global demand for TBBPA is reported to have increased from 50,000 tonnes per year in 1992 to 145,000 tonnes per year in 1998, with an average growth of 19 % per year [7].

The primary use of TBBPA is as a reactive intermediate in the production of flame-retarded epoxy resins used in printed circuit boards [8]. Some 90% of the total

use of TBBPA is as a reactive intermediate in the manufacture of epoxy and polycarbonate resins. A secondary use for TBBPA is as an additive flame retardant in acrylonitrile butadiene styrene (ABS) systems, high impact polystyrene (HIPS) and phenolic resins. Additive use accounts for approximately 10% of the total use of TBBPA [4]. TBBPA is also used in the manufacture of derivatives which also being applied as BFRs in niche applications and the total amount of TBBPA derivatives used is less than the amount of TBBPA used (approximately 25% on a weight basis) [8].

TrBP is the most widely produced brominated phenol [9]. The production volume of TrBP was estimated at approximately 3600 tonnes in China, Japan in 2003 and 4500 to 23,000 tonnes in the US in 2006 [10]. In the EU, TrBP is considered a High Production Volume Chemical (HPVC), a substance produced or imported in quantities in excess of 1000 tonnes per year [11]. 2,4-DBP is produced as a flame retardant and/or as an intermediate for other flame retardants [12] but much lower volumes than TrBP, 4-BP and PBP. 2,4-DBP, TrBP and PBP are used as reactive flame retardants in epoxy resins, phenolic resins. TrBP is a common intermediate for such products as end-stop for brominated epoxy resin made from tetrabromobisphenol A (probably the largest application), tribromophenyl allyl ether, and 1,2-bis(2,4,6-tribromophenoxyethane) [13]. PBP is a precursor of PBP-AE. Furthermore, TrBP is also registered as a wood preservative in South America; for example, the current pesticide register for Chile reveals that three products based on the sodium tribromophenol salt are approved for use as a fungicide treatment (two manufacturers in Chile and one in Brazil).

Due to widely use of bromophenols, those compounds are not only found in dust, indoor air, flue gas, river, sediment and landfill leachates, but also found in the environment in biological matrices such as fish and birds [10,14]. Its can enter the

environment as a result of releases at production sites but probably more importantly via leakage from products where it has been introduced as an additive flame retardant [15–17]. These compounds are persistent, bioaccumulative, and have been distributed in wildlife [18,19]. It was also detected in human milk and serum in previous reports [20]. Recent studies have shown that these bromophenols can cause carcinogenic, thyrotoxic, estrogenic, and neurotoxic effects in experimental animals and humans [21–23]. Therefore, novel technique for treatment of wastewater, which contains those compounds, is very important.

## **1.2. Technique for the removal of bromophenols in aqueous solution**

To removal of organic pollutants in water, many technologies have been developed. Basically, the methods are on the basis of physical, chemical and biological processes. Sorption represents a typical physical process to remove the organic pollutants, which use the high surface area solids such as activated carbon and clay minerals [24]. Chemical processes are related to chemical reactions for the detoxication of organic pollutant by photodegradation and chemical oxidation. Biodegradation is a method, which based on biological process. In this section, the methods for removing brominated phenol by sorption, biodegradation, photodegradation and chemical oxidative degradation are introduced.

### **1.2.1. Sorption of brominated phenols by adsorbents**

Sorption as a simple, efficient, and economic method to remove organic compounds have applied in water purification systems. This method offers advantages such as widely available adsorbents, easily adsorption process, low energy cost, environmental friendly and easily regenerative process. For removing the bromophenol

in contaminated water system, several materials were developed and examined in bromophenol removal.

The sorption characteristics of TBBPA on graphene oxide had been investigated by Zhang et al. [25]. The TBBPA sorption was increased with an increase in initial concentration of TBBPA. However, the presence of anions and HA reduced the TBBPA sorption. Both  $\pi$ - $\pi$  interaction and hydrogen bonding might be responsible for the sorption of TBBPA on graphene oxide. To enhance the reusability and give the convenient recovery of the used adsorbent, a  $\text{Fe}_3\text{O}_4$ /Graphene oxide nanoparticle was synthesized as an adsorbent to remove TBBPA. The kinetics of adsorption was found to fit the pseudo-second-order model perfectly. The adsorption isotherm well fitted the Langmuir model, and the theoretical maximum of adsorption capacity calculated by the Langmuir model was  $27.26 \text{ mg g}^{-1}$ . The  $\text{Fe}_3\text{O}_4$ /Graphene oxide can be regenerated in 0.2 M NaOH solution [26].

Carbon nanotubes (CNTs), originally discovered by Iijima [27], have widespread applications as environmental sorbents [28,29]. CNTs are mainly divided into two types depending on the layers involved in them: single walled (SWCNTs) and multiwalled carbon nanotubes (MWCNTs). The high potential of MWCNTs for the removal of TBBPA from aqueous solution was demonstrated and the sorption mechanisms, thermodynamics of TBBPA on MWCNTs from aqueous solutions were investigated by Fafous et al. [30]. The equilibrium between TBBPA and MWCNTs was approximately achieved in 60 min with 96% removal of TBBPA. The Langmuir model exhibited a slightly better fit to the sorption data than the Freundlich model. The sorption kinetics was found to follow pseudo-second-order model expression. However, separating CNTs from the aqueous phase is very difficult because of their very small size. To overcome

such problems, amino-functionalized magnetite and magnetic materials such as cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ) were combined with MWCNTs [31,32]. Those composites performed better than MWCNTs or MNPs for the adsorption properties of TBBPA. After adsorption, the composites could be conveniently separated from the media by an external magnetic field and regenerated in NaOH aqueous [31,32].

Recently, dummy molecularly imprinted polymers (DMIPs), which utilize the structural analogues of the target molecules as the template molecules, have been applied as adsorbents with higher selectivity. Dummy molecularly imprinted polymer (DMIP) for TBBPA was prepared with a sol-gel process on the surface of micro-nano silica particles and TBBPA was chosen as the dummy template to avoid TBBPA bleeding. The DMIP for TBBPA had a large adsorption capacity ( $230 \text{ mmol g}^{-1}$ ), which was about 6 times as much as that of the non-imprinted polymer, fast binding kinetics (20 min) and high selectivity for TBBPA [33]. Yin et al. [34] reported DMIPs on silica gel particles for highly selective recognition of TBBPA were prepared by a sol-gel process, in which diphenolic acid (DPA) and bisphenol A (BPA) were selected as dummy template molecules. The maximum static adsorption capacities for TBBPA of the DPA- molecularly imprinted polymers (DPA-MIPs), BPA-molecularly imprinted polymers (BPA-MIPs) and non-imprinted polymers were 45, 38 and  $22 \text{ mg g}^{-1}$  respectively. The results indicated DPA-MIPs had more high affinity binding sites for TBBPA, which demonstrated that the strong interactions between the template and the functional monomer were favorable to form high affinity binding sites and improve the selectivity of polymers.

### **1.2.2. Biodegradation**

Biodegradation is the chemical decomposition of materials by bacteria or other

biological means. Although often conflicted, biodegradable is distinct in meaning from “compostable”. While biodegradable simply means to be consumed by microorganisms and return to compounds found in nature, “compostable” makes the specific demand that the object break down in a compost pile. Biodegradation is nature’s way of recycling wastes, or breaking down organic matter into nutrients that can be used by other organisms. Biodegradation could be a cost-effective and environmental-friendly way to remove the bromophenol from contaminated water and soil.

The anaerobic biodegradation of monobrominated phenols by microorganisms enriched from marine and estuarine sediments was determined in the presence of electron acceptors (Fe(III),  $\text{SO}_4^{2-}$ , or  $\text{HCO}_3^-$ ). 2-Bromophenol was debrominated to phenol, with the subsequent utilization of phenol under all three reducing conditions while debromination of 3-bromophenol was also observed under sulfidogenic and methanogenic conditions but not under iron-reducing conditions. Higher debromination rates under methanogenic conditions than under sulfate-reducing or iron-reducing condition were observed. The production of phenol as a transient intermediate demonstrates that reductive dehalogenation is the initial step in the biodegradation of bromophenols under iron-and sulfate-reducing conditions [35]. The dehalogenation activity of sponge-associated microorganisms with 2-BP, 3-BP, 4-BP, 2,6-DBP and TrBP under methanogenic and sulfidogenic conditions was reported. Debromination of TrBP and 2,6-DBP to 2-BP was more rapid than the debromination of the monobrominated phenols. Sponge-associated microorganisms enriched on organobromine compounds had distinct 16S rDNA TRFLP patterns and were most closely related to the  $\delta$  subgroup of the proteobacteria [36].

Biotransformation of TBBPA was examined in anoxic estuarine sediments. Complete debromination of TBBPA to bisphenol A with no further degradation of bisphenol A, was observed under both methanogenic and sulfate-reducing conditions [37]. Biodegradation of brominated phenols by cultures and laccase of *Trametes versicolor* was reported by Sahoo et al., and a significant degradation of brominated phenols by laccase was achieved only in the presence of 2,2'-azinobis-(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) structural characterization of major products, suggesting the reaction between bromophenol and ABTS radicals [38].

Beside the reductive debromination of bromophenols by microorganisms, some bromophenol degrading bacteria were isolated and examined for the biodegradation of bromophenols. The *Rhodococcus opacus* GM-14 was examined to biodegrade the mixtures of halogenated phenols. The *Rhodococcus opacus* GM-14 grew well on the 2-BP and 4-BP. The 2-BP and 4-BP were completely consumed and Br<sup>-</sup> was released [39]. The *Achromobacter piechaudii*, was isolated from a contaminated desert soil, designated as strain TBPZ was able to metabolize TrBP and chlorophenols. The degradation of halogenated phenols accompanied with the stoichiometric release of bromide or chloride. Growth and degradation of bromophenol were enhanced in the presence of yeast extract [40].

The bacterium, designated strain TB01, was identified as an *Ochrobactrum* species that utilizes TrBP as sole carbon and energy source was isolated from soil contaminated with brominated pollutants. TrBP was converted to phenol through sequential reductive debromination reactions via 2,4-DBP and 2-BP by this strain [41]. In addition, the aerobic heterotrophic bacteria present in psychrophilic lakes have the ability to degrade

TrBP [42].

The efficiency of *Arthrobacter chlorophenolicus* A6 on the biodegradation of phenolic compounds was demonstrated by Unell et al., the ability on 4-BP degradation was investigated in packed bed reactor and complete removal of 4-BP was achieved [43–45].

### **1.2.3. Novel techniques for the degradation of bromophenol**

Degradation is on the basis of chemical processes, which become one of the most important methods to removal of organic pollutants. There are several technologies that have been developed for degradation of bromophenols.

#### **1.2.3.1. Photo-degradation**

Photocatalytic oxidation is an environmental-friendly technique in pollution control, which has been considered as an efficient tool for degrading a large number of persistent organic compounds under mild conditions. According to the light source, the photocatalytic oxidation can divide to the UV light-driven photocatalytic oxidation and the visible light-driven photocatalytic oxidation.

Photochemical transformations of TBBPA and related phenol, such as 2-BP, 2-CP, 3,4-DCP and bisphenol at UV irradiation of aqueous solutions was reported by Eriksson et al. [46]. For improving the degradation efficiency of TBBPA, the titanomagnetite was synthesized and applied to the heterogeneous UV/Fenton degradation of TBBPA. In the system with  $0.125 \text{ g L}^{-1}$  of  $\text{Fe}_{2.02}\text{Ti}_{0.98}\text{O}_4$  and  $10 \text{ mmol L}^{-1}$  of  $\text{H}_2\text{O}_2$ , almost complete degradation of TBBPA ( $20 \text{ mg L}^{-1}$ ) was accomplished within 240 min of UV irradiation at pH 6.5. TBBPA possibly underwent the sequential debromination to form TriBBPA, DiBBPA, Mono-BBPA and BPA, and  $\beta$ -scission to generate seven brominated

compounds. All of these products were finally completely removed from reaction mixture [47]. Nanoarchitectural BiOBr microspheres was synthesized and adopted to decompose TBBPA [48]. The decomposition of TBBPA was effectively enhanced by BiOBr compared with P25 TiO<sub>2</sub> and the TBBPA was almost totally eliminated after 15 min in the UV-vis/BiOBr system. Magnetite catalysts doped by five common transition metals (Ti, Cr, Mn, Co and Ni) were prepared and investigated in the UV/Fenton degradation of TBBPA. The improvement extent increased in the following order: Co < Mn < Ti approximate to Ni < Cr [49]. Recently, Gao et al. [50] reported that hematite (Fe<sub>2</sub>O<sub>3</sub>) or goethite (FeOOH) doped ZnIn<sub>2</sub>S<sub>4</sub> showed excellent photocatalytic activity in debromination of TrBP. After a 2-h photocatalytic reaction, 88% and 80% debromination were observed with Fe<sub>2</sub>O<sub>3</sub>-ZnIn<sub>2</sub>S<sub>4</sub> and FeOOH-ZnIn<sub>2</sub>S<sub>4</sub> respectively.

Because UV light only accounts for a small portion (~5%) of the sun spectrum in comparison to the visible region (~45%), the photocatalyst with response in visible region has attracted much attention. A series of heterostructured metallic silver/bismuth niobate (Ag/Bi<sub>5</sub>Nb<sub>3</sub>O<sub>15</sub>) hybrid materials with a single-crystalline orthorhombic layered structure and photoresponse in both the UV and visible light region were prepared. The photocatalytic activity was evaluated by the degradation of an aqueous TBBPA under visible light irradiation (400 nm <  $\lambda$  < 680 nm and 420 nm <  $\lambda$  < 680 nm). The highest TBBPA degradation efficiency was obtained at neutral conditions (pH 5–7) [51].

#### **1.2.3.2. Chemical oxidation of bromophenols**

Due to the widely use of bromophenols in industry and the health risk of those compounds, the removal and degradation of bromophenols in leachates are of great importance. The biodegradation kinetic of bromophenol is slow and the photocatalytic degradation of bromophenol was sensitive to the diffraction, reflection of solvent, and

concomitant such as suspensions. The chemical oxidative degradation is considered the practical, economical, low request for equipments and efficient method to degrade bromophenol in wastewater.

Traditionally, using strong oxidants can oxidize the organic pollutants. The birnessite ( $\delta\text{-MnO}_2$ ) had been examined for the oxidative degradation of TBBPA, and 90% of TBBPA was removed for 60 min at pH 4.5 [52]. Without the catalyst, a strong oxidizing agent,  $\text{KMnO}_4$ , was applied to degrade chlorophenol in the presence of HS, and a chlorophenol was efficiently degraded in the presence of 5 molar equivalent of  $\text{KMnO}_4$  [53]. Because the large use of  $\text{KMnO}_4$  may cause the second water pollution of manganese, the practical use of  $\text{KMnO}_4$  should be limited.

Except for  $\text{KMnO}_4$ ,  $\text{KHSO}_5$ ,  $\text{H}_2\text{O}_2$  and dioxygen were regarded as environmental friendly oxidants due to the reaction products of those oxidants are water and sulfate. Catalytic oxidation is the process that the catalyst can activate those oxidants to form radical species or other reactive species to degrade pollutants. It can dramatically enhance the degradation efficiency, accelerate the reaction rate and reduce the oxidant dosage. There are several catalytic systems have been developed and examined for the degradation of bromophenols.

$\text{CuFe}_2\text{O}_4$  magnetic nanoparticles (MNPs) was developed to catalyze peroxymonosulfate to generate sulfate radical to degrade TBBPA. 56% of TOC removal and a TBBPA debromination ratio of 67% was achieved with higher addition of peroxymonosulfate ( $1.5 \text{ mmol L}^{-1}$ ) [54]. Recently, the effects of reducing agents on the degradation of TrBP were investigated in a heterogeneous Fenton-like system using an iron-loaded natural zeolite (Fe-Z). The enhancement in the degradation and debromination of TrBP was achieved by addition of a reducing agent, such as ascorbic

acid (ASC) or hydroxylamine ( $\text{NH}_2\text{OH}$ ). It is noteworthy that the complete mineralization of TrBP was achieved at pH 5, when  $\text{NH}_2\text{OH}$  and  $\text{H}_2\text{O}_2$  were sequentially added to the reaction mixture [55]. To the best of our knowledge, this is the highest degradation efficiency of TrBP in reported methods.

#### 1.2.3.3. *Biomimetic catalysts*

Although the higher degradation efficiency of bromophenols has been reported in the metal oxides catalyzed systems, the disadvantages of metal oxides systems, such as harsh conditions, the use of large quantities of chemicals, leaching of heavy metal, and based on conditions without dissolved organic matter, major contaminants in landfill leachates, restrict the practice use of those catalysts. The cytochromes P450 constitute a large family of cysteinato-heme enzymes (over 500 members) present in all forms of lives (e.g., plants, bacteria, and mammals) and they play a key role in the oxidative transformation of endogenous and exogenous molecules [56]. Iron(III)-porphyrin and iron(III)-phthalocyanine can be regarded as model compounds that mimic the catalytic center in cytochrome P-450, which is involved oxidation processes of various organic substrates *in vivo* [57]. The use of iron(III)-porphyrins and iron(III)-phthalocyanine in the oxidative degradation of halogenated phenols, such as chlorophenols [58–63] and TBBPA [64–66], has been examined in homogeneous systems. Chlorophenols and TBBPA were quickly degraded in the Iron(III)-porphyrin/ $\text{KHSO}_5$ , Iron(III)-phthalocyanine/ $\text{KHSO}_5$  and Iron(III)-porphyrin/ $\text{H}_2\text{O}_2$  systems. The complete degradation of chlorophenol and TBBPA was achieved within 30 min in the presence of HS or absence of HS with 2.5 molar equivalent of  $\text{KHSO}_5$ . The chemical structures of iron(III)-porphyrins and iron(III)-phthalocyanine catalysts are shown in Fig. 1.2. Comparing with TBBPA and chlorophenols, only a few reports focus on the application

of iron(III)-porphyrin on the degradation of polybrominated phenols [67–69] and the debromination of TrBP was more difficult than 2,4,6-trichlorophenol [69].

Although the higher degradation efficiency of chlorophenol and TBBPA were obtained in homogenous catalytic systems, oxidative degradations suffers from disadvantages like the deactivation because of self-degradation of iron(III)-porphyrins, [70–72] and recyclability unavailable. Preparation and application of the heterogenous iron(III)-porphyrin catalysts in the oxidation reaction have been reported. The iron(III)-porphyrin catalysts are supported on solids, such as graphene [73], SiO<sub>2</sub> [67,74–77], mesoporous silica [68], polymers [77] and ion-exchange resins [78,79]. The immobilization of iron(III)-porphyrin not only suppress self-degradation, enhance the recyclability but also evolve new catalytic functions by supports such as size selectivity.

Iron(III)-tetrakis(*p*-hydroxyphenyl)porphyrin (FeTHP), was introduced into a humic acid via a formaldehyde or urea-formaldehyde polycondensation reaction to stabilize the catalyst. The prepared supramolecular catalysts were then attached to Dowex-22, an anion-exchange resin. The catalytic activities of the supported catalysts was evaluated in the oxidation of 2,6-DBP [78]. FeTMPyP and FeTPPS were supported on cation- (FeTMPyP/CER) and anion-exchange (FeTPPS/AER) resins respectively were reported by Miyamoto et al. [79]. Their catalytic activity and durability for degradation of TBBPA were examined in the absence and presence of humic acid. The FeTMPyP/CER catalyst was highly durable, catalyzing the degradation of over 90% of the TBBPA and no bleaching was observed in the FeTMPyP/CER catalyst after ten recyclings.

Although the reusability of iron-porphyrins was enhanced and self-degradation was suppressed by immobilization, the catalytic activities (TOF and mineralization) have not

been so increased because of mass transfer limitation, catalysts leaching from the solid support, coverage of substrates and/or byproducts and competitive inhibition by concomitants, such as HAs, in leachates [67,68,75]. Thus the novel immobilized strategy to overcome those problems is very important.

### **1.3. Influence of humic substances on the bromophenol transformation and degradation**

Humic substances (HSs) are ubiquitous in the environment, occurring in all soils, waters, and sediments of the ecosphere [80]. HSs are produced by the decomposition of plant and animal tissues to low-molecular-weight compounds and the polymerization to yield dark colored polymers. Based on solubility in acid and alkalis, HSs can be classified to (1) Humic acid (HA) (Fig. 1.3), which is soluble in alkali and insoluble in acid; (2) Fulvic acid (FA), which is soluble in alkali and in acid; and (3) humin, which is insoluble in both alkali and acid. For soil HSs, the major acidic functional groups in HAs and FAs are carboxylic acid and phenolic OH groups [80]. Alcoholic OH and carbonyl (quinonoid and ketonic C=O) groups are also well represented. The total acidity, and especially the COOH content, and alcoholic OH group content of FAs are appreciably higher than those of HAs.

#### **1.3.1. Interaction of HSs with bromophenols.**

HSs may interact with organic pollutants in several ways, including adsorption and partitioning, solubilization, hydrolysis catalysis, and photosensitization. These processes have important implications in the fate, performances and behavior of organic pollutants,

affecting to their biodegradation and detoxification, bioavailability, accumulation, mobilization and transport [80]. Adsorption represents probably the important mode of interaction of organic pollutants with HSs, which can occur through physical-chemical binding by specific mechanisms and forces with varying degrees of strengths [81]. These include ionic, hydrogen, and covalent binding, charge-transfer or electron-donor acceptor mechanisms, dipole-dipole and Van der Waals forces, ligand exchange, cation and water bridging, and non-specific, hydrophobic or partitioning processes [82]. Hydrophobic sites in HS include aliphatic side chains or lipid portions and aromatic lignin-derived moieties with high carbon content and bearing a small number of polar groups. Hydrophobic adsorption on the surface or trapping within internal pores of the HS macromolecular sieve has been proposed as an important nonspecific mechanism for retention of organic pollutant that interact weakly with water [81,82]. The sorption of bromophenol to HS was reported by Ohlenbusch et al. and the sorption to HS decreased when pH of solution was increased [83]. Zhang et al. reported that sorption and removal of TBBPA from solution by graphene oxide was largely inhibited in the presence of HS. The TBBPA adsorption decreased from 40.7 to 14.1 mg g<sup>-1</sup> when HS concentration increased from 0 to 30.0 mg g<sup>-1</sup> due to the competition of TBBPA adsorption by HS. The competition of HA with TBBPA for sorption sites tended to reduce the TBBPA sorption on graphene oxide [25]. In addition, the actual water-solubility of certain organic pollutants can significantly be modified by adsorption onto HS. At a given concentration of dissolved HS, the solubility of bromophenol was enhanced in the presence of HS [16,17].

### ***1.3.2. Influence of HSs on the degradation of bromophenol***

Soil organic matter, including HSs, is considered to be the major electron donor (reductant) in soils, and a major factor in determining and controlling the soil redox potential [84]. Phenolic moieties in HS, which include mono- and poly-hydroxylated benzene units, have antioxidant properties, and it can therefore be expected to affect the concentrations and lifetimes of reactive oxidants in soils and aquatic systems [85,86]. By quenching reactive oxidants, phenolic moieties may protect other functional groups in HSs from the oxidation and therefore play an important role in the stability of HS in the environment. In surface waters, dissolved HSs may decrease indirect photolysis of organic pollutants both by quenching reactive oxygen species and by donating electrons to radical intermediates formed during pollutant degradation, thereby reducing them back to parent compound [87,88]. In water treatment facilities, electron donation by HSs increases the amount of chemical oxidants that are required for water disinfection and pollutant removal [89,90]. In the Fenton ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ) treatment of industrial wastewater, the removal of organic compounds, such as phenol, 2,4-dimethylphenol, benzene, toluene, *o*-, *m*-, *p*-xylene, and dichloromethane, were significantly inhibited in the presence of HSs [91]. The photodegradation percentage of BDE-209 decreased substantially in the presence of HSs [92]. In a previous report, the degradation efficiency of chlorophenol was found to decrease in the presence of  $8 \text{ mg-C L}^{-1}$  HS due to competition for the oxidant [93], and the oxidative degradation of TBBPA became more different in the presence of HS [65]. The proposed interaction process of HS with bromophenol in catalytic system is shown in Fig. 1.4. For heterogeneous catalytic systems, HSs can not only serve as competitors for oxidants but also as an adsorbate, where the catalytic centers are covered [94]. The degradation of TrBP and TBBPA by supported iron-porphyrin catalyst was largely inhibited by the presence of HS

[67,75,79]. Thus, the influence of HSs on the catalytic degradation of bromophenol is essential data for the practical use of catalysts and how to reduce the adverse effect of HS on the catalytic system is important issue.

#### **1.4. Strategies for the design of new biomimetic catalyst**

In the present study, the iron-porphyrin was used as biomimetic catalyst to degrade brominated phenols in landfill leachates. To suppress the deactivation of iron(III)-porphyrin due to the self-degradation and dimerization, and to enhance the reaction selectivity in the presence of HSs, the iron(III)-porphyrin was immobilized on the functionalized SiO<sub>2</sub>, mesoporous silica and magnetite to degrade TrBP, TBBPA and PBP in the presence of HSs.

The outline of the present study is summarized as below:

Chapter 1: This chapter shows a general introduction of the present study. The application of bromophenols, previous technique for treatment of bromophenols, and the influence of humic substances on the bromophenol degradation were described. In addition, the advantages and disadvantages of iron(III)-porphyrin catalysts for the catalytic oxidation of bromophenols were explained, based on the previous reports. Subsequently, my strategy to overcome the problems for iron(III)-porphyrin catalysts was discussed.

Chapter 2: To suppress the self-degradation of iron(III)-porphyrin, iron(III)-5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin (FeTCPP) was immobilized on a functionalized silica gel (SiO<sub>2</sub>-FeTCPP) to catalytic degradation of TrBP. The influences of pH on the TrBP degradation percent, debromination and degradation products were examined. For the practical use of catalyst, the reusability and the

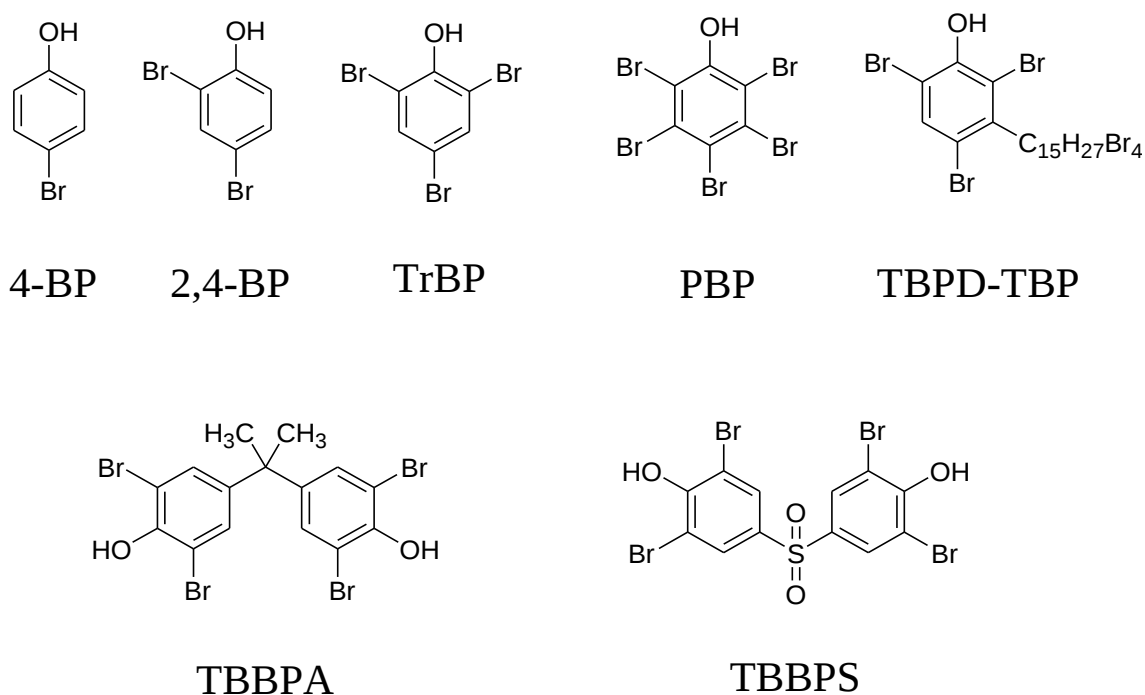
influence of HS was investigated.

Chapter 3: To enhance the performance of iron(III)-porphyrin catalyst in the presence of HS, the iron(III)-tetrakis(*p*-sulfonatephenyl)porphyrin (FeTPPS) was axial immobilized on imidazole functionalized silica (FeTPPS/IPS). The prepared catalyst with the larger negative surface charge effectively excluded HS from the vicinity of catalytic sites. The FeTPPS/IPS was applied on the catalytic degradation of TBBPA in the presence and absence of HS.

Chapter 4: To suppress the inhibition of HSs for the oxidative degradation, a mesoporous molecular sieve SBA-15 supported FeTPyP (FeTPyP-SBA-15) was synthesized and applied to the degradation of PBP using  $\text{KHSO}_5$  as an oxygen donor. The FeTPyP-SBA-15 had a high selectivity for the catalytic degradation of PBP and the orderly porous structure of FeTPyP played a key role in decreasing the adverse effect of the HS.

Chapter 5: To overcome the disadvantages in the lower catalytic activities of heterogeneous catalysts, the “liquid phase” methodologies are introduced into the solid catalysts to “restore” homogeneous catalytic conditions. For this purpose and facilitating separation of the used catalyst, FeTPPS was introduced to the ionic liquid coated  $\text{Fe}_3\text{O}_4$  by ion-pair formation via electrostatic interaction. The prepared  $\text{Fe}_3\text{O}_4$ -IL-FeTPPS was examined to the catalytic oxidation of TrBP.

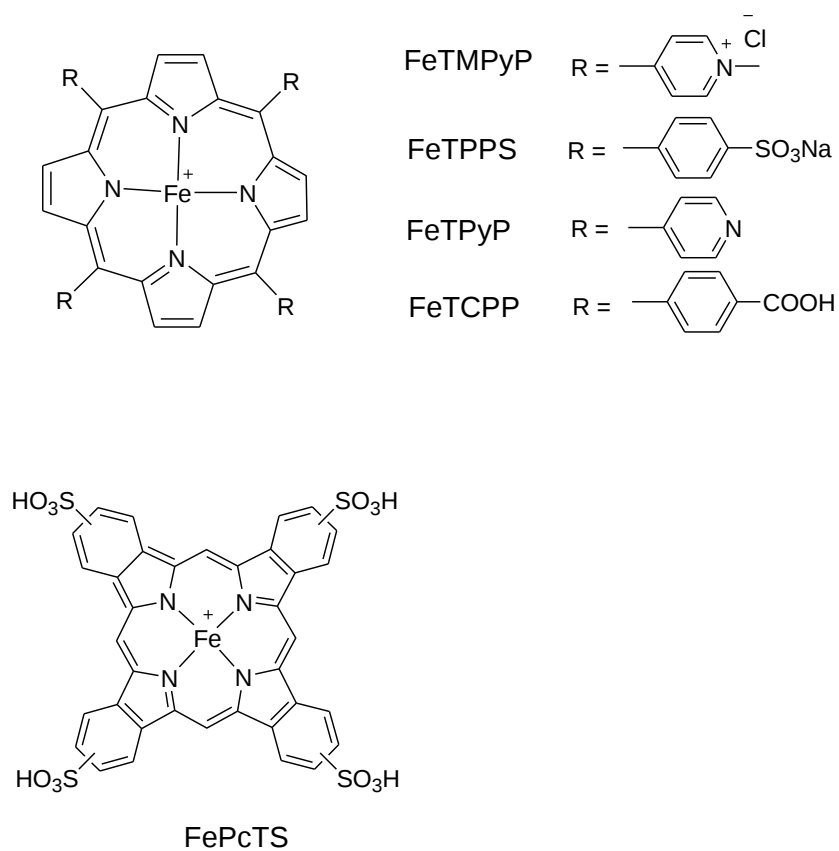
Chapter 6: The conclusion of the present study is described in this chapter.



**Fig. 1.1.** Chemical structures of bromophenols. 4-Bromophenol (4-BP), 2,4-dibromophenol (2,4-DBP), 2,4,6-Tribromophenol (TrBP), pentabromophenol (PBP), 3-(tetrabromopentadecyl)-2,4,5-tribromophenol (TBPD-TrBP), tetrabromobisphenol A (TBBPA) and tetrabromobisphenol S (TBBPS).

Table 1.1. Physicochemical properties of bromophenols.

| Bromophenols | CAS No.  | MW    | Melting point<br>(°C) | Boiling point<br>(°C) | $pK_a$                           | $\log K_{ow}$ | Water solubility at 25 °C<br>(mg L <sup>-1</sup> ) |
|--------------|----------|-------|-----------------------|-----------------------|----------------------------------|---------------|----------------------------------------------------|
| 4-BP         | 106-41-2 | 173.0 | 64                    | 238                   | 9.17                             | 2.62          | 17400                                              |
| 2,4-DBP      | 615-58-7 | 251.9 | 38                    | 238                   | 7.86                             | 3.47          | 2080                                               |
| TrBP         | 118-79-6 | 330.8 | 89                    | 290                   | 6.34                             | 4.40          | 56.61                                              |
| PBP          | 608-71-9 | 488.6 | 230                   | Sublimes              | 4.43                             | 5.22          | 0.1                                                |
| TBBPA        | 79-94-7  | 543.9 | 178                   | 316                   | $pK_{a1}, 7.5$<br>$pK_{a2}, 8.5$ | 4.5           | 4.16                                               |



**Fig. 1.2.** Chemical structures of biomimetic catalysts, iron(III)-porphyrins and iron(III)-phthalocyanines. Fe(III)-tetrakis(1-methyl-4-pyridyl)porphyrin (FeTMPyP), Fe(III)-tetrakis(4-sulfonatophenyl)porphyrin (FeTPPS), Fe(III)-tetrakis(4-pyridyl)porphyrin (FeTPyP), Fe(III)-tetrakis(4-carboxyphenyl)porphyrin (FeTCPP) and Fe(III)-phthalocyanine-tetrasulfonic acid (FePcTS)

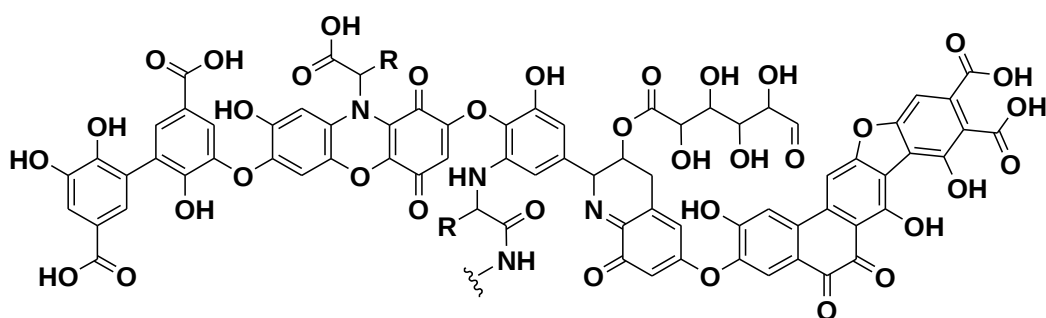


Fig. 1.3. Model structure of HA in the forest soil [95].

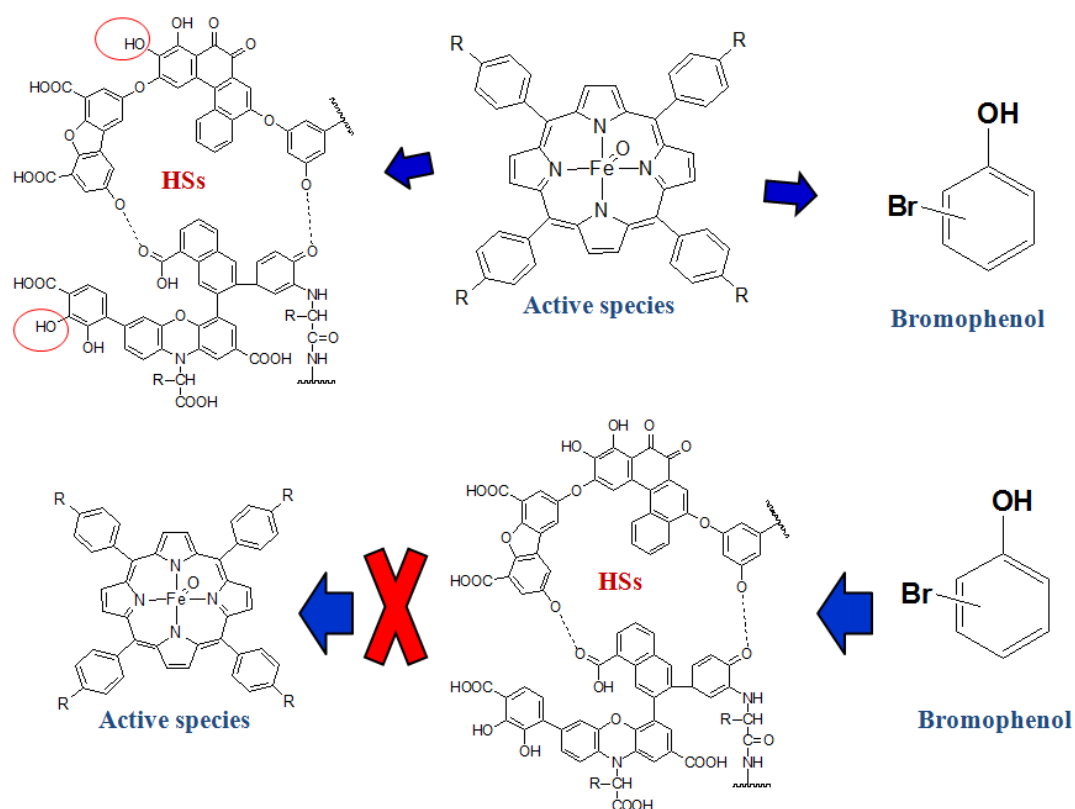


Fig. 1.4. The proposed interactions of HSs with bromophenol in the catalytic systems [96].

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# Chapter 2

*Potassium monopersulfate oxidation of  
2,4,6-tribromophenol catalyzed by a SiO<sub>2</sub>-supported  
iron(III)-5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin*

## 2.1. Introduction

As mentioned in Chapter 1, 2,4,6-Tribromophenol (TrBP) is widely used in the production of fungicides [1], brominated flame retardants (BFRs), and as an intermediate in the production of BFRs [2]. It has also been reported that TrBP adversely affects endocrine and reproductive systems, because it can competitive binding to transport proteins and interfere with the thyroid hormone system by virtue [3]. TrBP is found in wastes from electrical devices including BFRs and leaches into the surrounding environment [4]. Thus, the removal and degradation of TrBP in leachates are of great importance.

Iron(III)-porphyrin can be regarded as model compound that mimics the catalytic center in cytochrome P-450 [5]. The use of iron(III)-porphyrins in the oxidative degradation of halogenated phenols, such as chloro- and bromophenols, has been examined in homogeneous systems [6–14]. However, in the presence of peroxides such as H<sub>2</sub>O<sub>2</sub> and KHSO<sub>5</sub>, iron(III)-porphyrin catalysts can undergo decomposition, leading to catalyst deactivation [15,16]. Immobilized catalysts that are supported on solids, such as the Mn-porphyrin supported anion-exchanger, are not only effective in suppressing self-degradation but also allow for the catalyst recycling [17,18]. Although the Fe(III)-porphyrin supported anion-exchanger was used to degrade 2,6-dibromophenol, the adsorption of anionic 2,6-dibromophenol inhibited its oxidation reaction and resulted in lower reusability [19].

On the other hand, landfill leachates contain dissolved organic matter, such as humic substances (HSs), which exhibit a large negative electrostatic field [20]. Thus, the support with anionic surface charges such as SiO<sub>2</sub> is suitable, in terms of the TrBP oxidation in landfill leachates and the catalyst recycle. In this chapter, to stabilize an iron(III)-porphyrin catalyst during KHSO<sub>5</sub> oxidation and enhance the reusability of the catalyst, iron(III)-5,10,15,20-tetrakis (4-carboxyphenyl)porphyrin (FeTCPP) was covalently bound to

SiO<sub>2</sub> via the amide linkage and tested as a catalyst for the degradation of TrBP. In addition, the influence of HSs, major concomitants in landfill leachates, on the catalytic oxidation of TrBP were investigated using the SiO<sub>2</sub>-FeTCPP catalyst, to obtain basic data for practical use.

## 2.2. Materials and Methods

### 2.2.1. Materials

The soil humic acid (SHA) sample used in this study was extracted from Shinshinotsu peat soil, as described in a previous report [21]. Nordic Lake humic acid (NLHA) and Nordic Lake fulvic acid (NLFA) were obtained from the International Humic Substances Society. TrBP, 5,10,15,20-tetrakis (4-carboxyphenyl)-21*H*,23*H*-porphyrin, FeCl<sub>3</sub>, 3-aminopropyltriethoxysilane (APTES) and silica gel were purchased from Tokyo Chemical Industry. KHSO<sub>5</sub> was obtained as a triple salt, 2KHSO<sub>5</sub>·KHSO<sub>4</sub>·K<sub>2</sub>SO<sub>4</sub> (Merck). To determine the major byproduct, 2,6-dibromo-*p*-benzoquinone (2,6-DBQ) as a standard for GC/MS analysis was synthesized and characterized, as described in a previous report [19].

### 2.2.2. Synthesis of Silica Supported Fe(III)TCPP

Figure 2.1 shows the strategy employed for the synthesis of the catalyst. The silica gel supported Fe(III)TCPP catalyst was synthesized by a previously reported method, with minor modifications, as described below [22].

#### *Synthesis of amine-functionalized silica gel (SiO<sub>2</sub>-NH<sub>2</sub>)*

Silica gel (5 g, 300 mesh) was suspended in 50 mL of anhydrous toluene, followed by the addition of 8.6 mmol of APTES. The suspension was refluxed for 24 h under a nitrogen atmosphere. The resulting solid was collected on a filter and washed with ethanol overnight in a Soxhlet extractor. The amine functionalized SiO<sub>2</sub> was dried at 40 °C *in vacuo* for 10 h to remove the excess solvent. The elemental analysis data for the sample was: C 6.62%, H

1.67%, N 2.27%.

#### *Synthesis of silica gel supported H<sub>2</sub>TCPP (SiO<sub>2</sub>-H<sub>2</sub>TCPP)*

The 2 g of SiO<sub>2</sub>-NH<sub>2</sub> were suspended in 30 mL of anhydrous dioxane, followed by the addition of 26.8 mmol of *N,N'*-dicyclohexylcarbodiimide (DCC). After adding 0.13 mmol of H<sub>2</sub>TCPP, the mixture was allowed to reflux for 24 h. The resulting solid was isolated and washed with ethanol in a Soxhlet extractor overnight. The product of SiO<sub>2</sub>-H<sub>2</sub>TCPP was dried *in vacuo* at 40 °C for 10 h. The elemental analysis data for the sample was: C 9.14%, H 1.8%, N 2.25%.

#### *Synthesis of silica gel supported Fe(III)TCPP (SiO<sub>2</sub>-FeTCPP)*

SiO<sub>2</sub>-H<sub>2</sub>TCPP (1 g) was added to 30 mL of DMF, followed by the addition of 0.6 g of FeCl<sub>3</sub>. The mixture was refluxed for 6 h under a nitrogen atmosphere. The crude product was washed in a Soxhlet extractor with DMF and then methanol. To remove excess ferric ions, the resulting solid was washed with a 5% HCl solution and then washed with water until the pH reached to 7. The final product was washed with NaOH (0.1 mM), deionized water, and then dried *in vacuo*, to give the sodium salt of SiO<sub>2</sub>-FeTCPP catalyst. The elemental analysis data for the sample was: C 4.45%, H 1.11%, N 1.1%.

### **2.2.3. Characterizations of the Synthesized Catalyst**

Elemental analysis was performed on a Yanaco MT-6 type CHN corder. The catalyst loading amount in the immobilized catalyst was determined by a metal analysis using ICP-AES (ICPE9000, Shimadzu) after wet-decomposition procedures, as described in a previous report [23]. FT-IR spectra were recorded using an FT/IR 600 type spectrometer (Japan Spectroscopic Co. Ltd.) with KBr pellets. Diffuse Reflectance UV-vis spectra were obtained using a V-630 type spectrophotometer (Japan Spectroscopic Co. Ltd.). Zeta potentials were recorded using a Zetasizer Nano ZS90 (Malvern Instruments Ltd.).

#### 2.2.4. Test for TrBP Degradation

A 20 mL aliquot of 0.02 M citrate / phosphate buffer at pH 3-8 was placed in a 100-mL Erlenmeyer flask. A 400  $\mu$ L aliquot of 0.01 M TrBP in acetonitrile and 2 mg of the catalyst was then added to the buffer. Subsequently, aqueous solutions of 1000 mg L<sup>-1</sup> HS in 0.05 M NaOH solution and 250  $\mu$ L of 0.1 M aqueous potassium monopersulfate (KHSO<sub>5</sub>) were added, and the flask was then subjected to shaking at 25 °C in an incubator. After the reaction, the concentrations of the remained TrBP and the released Br<sup>-</sup> were determined by HPLC and ion chromatography (ICS-90, Dionex), respectively, as described in a previous study [14]. Byproducts produced as a result of the catalytic oxidation of TrBP were separated from the reaction mixture by extraction with *n*-hexane and were analyzed by GC/MS, as described in a previous report [14].

### 2.3. Results and Discussion

#### 2.3.1. Characterization of Catalyst

FT-IR spectra of silica, amino-modified silica, and immobilized FeTCPP are shown in Figure 2.2. The FT-IR spectrum of SiO<sub>2</sub>-NH<sub>2</sub> contained characteristic vibration bands at around 1096, 804, and 469 cm<sup>-1</sup>, corresponding to the stretching, bending, and out of plane deformation vibrations of Si-O-Si bonds, respectively. A strong absorption with a maximum at 1096 cm<sup>-1</sup> and a shoulder at 1221 cm<sup>-1</sup> was assigned to Si-C vibration. A broad absorption centered at 3447 cm<sup>-1</sup> was assigned to the N-H stretching vibration of NH<sub>2</sub> for the amino-functionalized silica and the O-H stretching vibration of Si-OH groups. The NH<sub>2</sub> bending vibration was observed at 1631 and 1641 cm<sup>-1</sup>. IR absorption in the 3000 – 2800 cm<sup>-1</sup> region was assigned to symmetrical and asymmetrical C-H stretching vibrations in the aminopropyl ligand of the amino-functionalized silica. In addition, small peaks, observed in range of 1300-1500 cm<sup>-1</sup>, are attributed to a C-H bending vibration. After immobilizing the

FeTCPP on the amino-functionalized silica (SiO<sub>2</sub>-FeTCPP in Fig. 2.2.), a small peak was observed in 1700 – 2000 cm<sup>-1</sup> due to C=O stretching vibrations. Aromatic C-H stretching was observed at 3015 cm<sup>-1</sup>. The weak absorbance in the 1400 – 1600 cm<sup>-1</sup> region is assigned to C=C, C=N ring stretching (skeletal bands) as well as the C-H stretching vibration in aminopropyl ligands. C-H out-of-plane bending was apparent by the occurrence of peaks at 750 and 740 cm<sup>-1</sup>.

The total content of amino groups in amino-functionalized silica was estimated from the CHN elemental analysis. The amount of aminopropyl groups in SiO<sub>2</sub>-NH<sub>2</sub> was estimated to be 1.62 mmol g<sup>-1</sup>. An ICP-AES analysis permitted the Fe content in immobilized FeTCPP catalyst to be determined (1.5 mg g<sup>-1</sup>). The loaded FeTCPP in SiO<sub>2</sub>-FeTCPP was therefore estimated to be 27 μmol g<sup>-1</sup>.

The change in the surface chemistry of the silica was characterized by zeta potential data, which is related to the surface charge (Fig. 2.3). Unmodified silica had a large negative zeta potential over a wide range of pH (pH from 2 to 12), reflecting a large negative charge due to the presence of deprotonated silanol groups. In comparison, the functionalized particles and the final catalyst, with their -NH<sub>2</sub>, -COOH, and -COONa groups, could have a net positive, neutral or negative charge, depending on the pH. The amine functionalized silica had a positive charge at pH values below 10 due to the protonation of the amino group. The magnitude of the zeta potential was increased in the low pH range, compared with the unfunctionalized silica. The isoelectric point (IEP) of H<sub>2</sub>TCPP modified silica shifted significantly to 8.58. When the pH was above 8.58, the particles had a large negative potential. When the pH was below 8.56, the particle had a positive potential but it was lower than that for the amine-functionalized silica. When the sodium salt of the SiO<sub>2</sub>-FeTCPP was used, the zeta potential decreased and the IEP shifted to a value below pH 3. Thus, the SiO<sub>2</sub>-FeTCPP catalyst is negatively charged in the pH range of 3 – 12.

### 2.3.2. Effect of pH on the TrBP Degradation

Figure 2.4 shows the kinetic curves for TrBP degradation at pH 7 for SiO<sub>2</sub> alone, SiO<sub>2</sub>-H<sub>2</sub>TCPP and SiO<sub>2</sub>-FeTCPP in the presence of SHA (25 mg L<sup>-1</sup>) and KHSO<sub>5</sub> (1250 μM). In the absence of solids (Fig. 2.4. closed circles ●), no TrBP degradation was detected within 4 h. Silica (SiO<sub>2</sub>), and SiO<sub>2</sub>-H<sub>2</sub>TCPP (Fig. 2.4. upward pointing triangles ▲ and downward pointing triangles ▼) did not show catalytic activity. In the presence of SiO<sub>2</sub>-FeTCPP, essentially, 100% of the TrBP was degraded within 4 h.

Figure 2.5a shows the influence of pH on the percentage of TrBP degradation with SHA after a 4 h reaction. The SiO<sub>2</sub>-FeTCPP showed high catalytic activity in the pH range from 3 to 8. In the absence of SHA, the percentage of TrBP degradation was virtually pH independent (Fig. 2.5a). However, in the presence of SHA, the percentage of TrBP degradation was influenced by the solution pH. At pH 3, 4 and 8, the percentage of TrBP degradation was significantly decreased, compared to the values in the absence of SHA. In contrast, at pH 5, 6 and 7, the percentage of TrBP degradation in the presence of SHA was nearly equal to the corresponding values in its absence. These results suggest that the inhibition of TrBP degradation was pH-dependent. It is known that pH governs the speciation distribution of HS and TrBP [24]. In addition, the sorption of SHA to the catalyst surfaces and the electron transfer process are pH-dependent. SHA is sparingly soluble in water at low pH, and it is possible that colloids formed become absorbed to the catalyst, which would inhibit contact between the substrate and catalyst. At higher pH, such as at pH 8, the phenolic hydroxyl groups in SHA are deprotonated to phenolate anions [25], which are readily oxidized in the presence of an oxidant and compete with TrBP for oxidant. Those properties may lead to a lower percentage of TrBP degradation in the presence of SHA at pH 3, 4 and 8.

Debromination was also observed during the oxidation reaction (Fig. 2.5b). After a 4 h reaction, the bromide concentration increased with an increase in pH and reached the highest

value at pH 8 in the absence of SHA. In the presence of SHA, after a 4 h reaction, the bromide concentration was higher than that in the absence of SHA, especially at pH 5-7. The kinetic curve of bromide concentration at pH 7 showed that the concentration of bromide initially increased and then gradually decreased in the absence of SHA (Fig. 2.5c). Because the standard oxidation-reduction potential of  $\text{HSO}_4^- / \text{HSO}_5^-$  ( $E^\circ = + 1.82$ ) [26] is higher than that for  $\text{Br}^- / \text{Br}_2$  ( $E^\circ = + 1.0873$ ) [27], the released  $\text{Br}^-$  can be oxidized to elemental bromine during the reaction. This may lead to the decrease in bromide concentration in the absence of SHA. In contrast, the bromide concentration increased with increasing reaction time in the presence of SHA. Even though the initial rate of debromination was reduced due to the presence of SHA, the bromide concentration increased steadily as the reaction progressed and finally became higher than that in the absence of SHA. These results suggest that SHA prevents the oxidation of bromide and reduces the activity of the oxidant. From the kinetic curve for debromination (Fig. 2.5d), the released bromide rapidly reached equilibrium at pH 4, and the released bromide was maintained at a low concentration. However, under neutral to alkaline conditions, the bromide concentration increased steadily during the oxidation reaction, indicating that the TrBP is gradually oxidized to debrominated compounds in the presence of SHA. Therefore, SHA may inhibit the oxidation of released  $\text{Br}^-$  by  $\text{KHSO}_5$ .

Another possible reason for the higher debromination rate in the presence of SHA may be due to the debromination via the oxidative coupling of phenoxy radicals in HA with aromatic carbons in TrBP and its intermediates [14]. To verify that Br is added to SHA as a result of oxidation, the SHA fraction after the reaction was separated and the Br content was determined. The Br content of this sample was found to be 8.7%, suggesting that reaction intermediates from TrBP were incorporated into SHA as a result of oxidation reactions.

### **2.3.3. By-products of TrBP Degradation**

To identify the by-products derived from TrBP, the reaction mixture was extracted with *n*-hexane after adding acetic anhydride as an acetylation reagent. GC/MS chromatograms of the reaction mixture at different pH values and the compounds assigned based on mass spectral data are shown in Fig. 2.6a and Fig. 2.6d, respectively. At pH 4, even though the percent of TrBP degradation reached 99% in the absence of SHA, the reaction system still retained a large amount of 2,6-DBQ (3 in Fig. 2.6d). In the presence of SHA, after a 4 h reaction, TrBP was not completely degraded. Namely, 2,6-DBQ, 4,6-dibromo-catechol (4 in Fig. 2.6d) and its dimer (7 in Fig. 2.6d) were formed. However, even though only 90% the TrBP was degraded in the presence of SHA at pH 8, no brominated products were detected, except for trace amounts of 2,6-DBQ. At pH 7, after a 4 h reaction, over 99% of the TrBP was degraded in both the presence and absence of SHA. Figure 2.6b shows GC/MS chromatograms for different reaction periods at pH 7 in the presence of SHA. 2,6-DBQ was the major intermediate product produced during the catalytic oxidation of TrBP. Trace amounts of 2,6-DBQ were detected at a reaction time of 0.5 h. When the reaction time was increased, the amount of 2,6-DBQ initially increased first and then decreased. With the reaction time extended to 4 h, the degradation of TrBP appeared to be complete. Figure 2.6c shows kinetic data for the formation and degradation of 2,6-DBQ in the presence of SHA. The highest concentration of 2,6-DBQ was achieved at a reaction time of 2 h.

#### **2.3.4. Influence of HS Types and Concentrations on the TrBP Degradation**

The structural features of the HSs were significantly altered based on their origins and the conditions used for their preparation. Since the influence of HSs on the degradation of TrBP was various with the different HSs types and origins, the information related to the influence of HS type on the TrBP degradation was investigated for such a system can be put to practical use. The range of pH for raw leachates from landfills was reported to be within

5.4 – 12.5 [20]. Therefore, the influence of HS concentration on the degradation of TrBP was investigated at pH 7.

SHA was obtained from peat that was formed under anaerobic conditions, similar to landfills, while this sample was of soil origin. To investigate the influence of HSs which is aquatic origins like leachates, a Nordic Lake humic acid and Nordic Lake fulvic acid (NLHA and NLFA) were examined. The significant differences in the structural features for these HSs were the content of carboxylic groups, which contribute to their anionic charge: SHA 3.6 meq g<sup>-1</sup> C; NLHA 9.1 meq g<sup>-1</sup> C; NLFA 11.2 meq g<sup>-1</sup> C [28].

Figure 2.7 shows the influence of HS type and their concentration on the kinetics of TrBP degradation. The pseudo-first-order rate constant ( $k_{obs}$ ) decreased with an increase in the HS concentration showing the inhibition of oxidation reactions. Although the degree of inhibition was not significantly varied at 100 and 200 mg L<sup>-1</sup> of HSs, differences by HS type were observed for concentrations of HS below 50 mg L<sup>-1</sup>. The lowest inhibition was observed in the presence of NLFA. NLFA had the highest carboxylic group content of the three samples; the zeta potential profile depicted in Fig. 2.3 showed that this catalyst had a negative zeta potential at pH 7, indicative of a large negative charge on the catalyst surface. Thus, NLFA would be readily repelled from the catalyst surface via electrostatic repulsion compared with NLHA and SHA. This might result in the suppression of competitive oxidation and the adsorption of HS to catalytic sites. In addition, it was reported that the affinity of hydrophobic pollutants is lower in HS that contain larger amounts of polar groups, such as carboxylic acids [28,29]. Thus, the hydrophobic interaction of TrBP with NLFA may be weaker than those with other HSs. Thus, the lower inhibition in the case of NLFA can be attributed to its higher negative charge, which would reduce interactions between the catalyst surface and the substrate, TrBP.

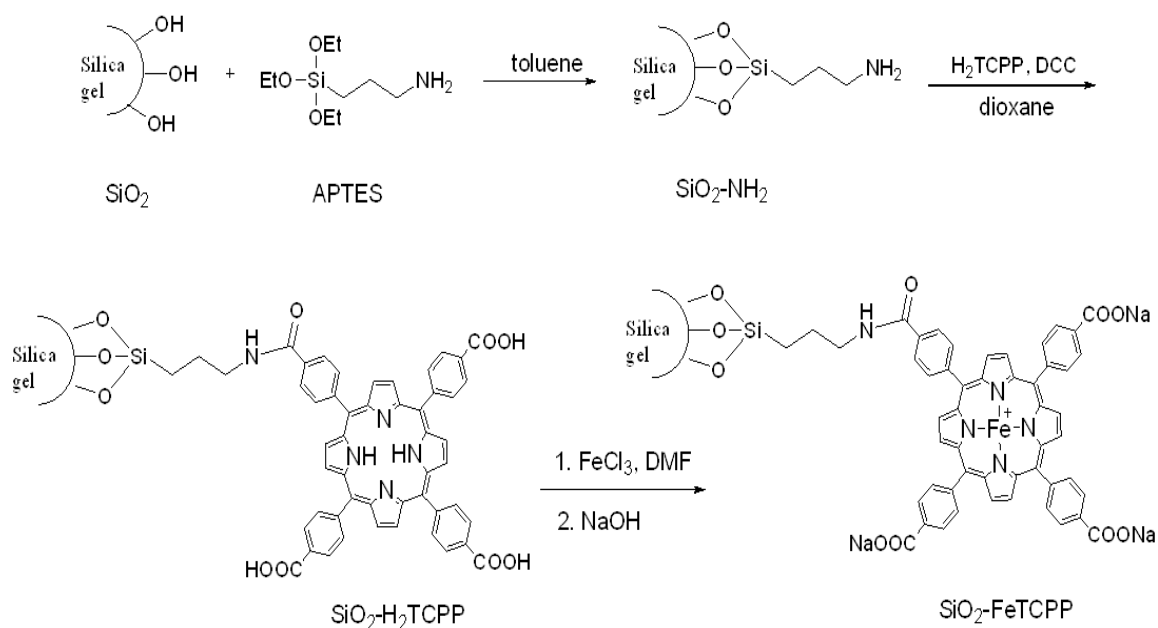
### 2.3.5. Reusability

When the homogeneous catalytic system (i.e., FeTCPP + KHSO<sub>5</sub>) was applied to TrBP degradation at pH 7, the reaction mixture was bleached and the catalyst was deactivated immediately (data not shown). This is consistent with the results for homogenous systems using Fe(III)-tetrakis(*p*-sulfonatophenyl) porphyrin [15, 22]. The reusability of SiO<sub>2</sub>-FeTCPP was examined, in terms of its use in water treatment. After each reaction, the catalyst was filtered and then washed with deionized water and ethanol. After ten cycles, more than 80% of TrBP was degraded even in the presence of SHA and long-time incubating for 24 h (Fig. 2.8). Figure 2.9 shows diffuse reflectance UV-vis spectra for both the fresh catalyst and that after its use for five cycles. The fresh catalyst showed three peaks at 409 nm, 572 nm and 614 nm. After five cycles, all of the peaks remained, but became smoother. The loading amount of reused SiO<sub>2</sub>-FeTCPP was determined by ICP-AES. After first cycle, the catalyst loading amount was decreased to 8.8  $\mu\text{mol g}^{-1}$  and after five cycles, the catalysts loading amount was 3.4  $\mu\text{mol g}^{-1}$ . Those data indicated that the structure of FeTCPP was not totally destroyed during the oxidative degradation reaction. The results of recycle test demonstrate that a relatively higher catalytic activity for the SiO<sub>2</sub>-FeTCPP catalyst is retained after ten cycles.

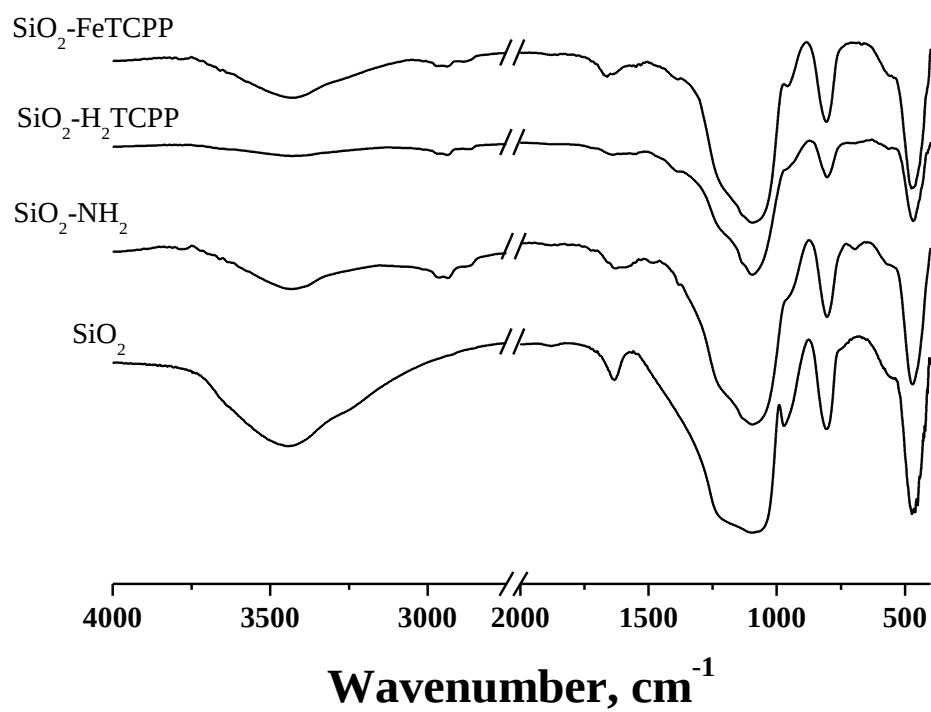
## 2.4. Conclusion

A supported Fe(III)-porphyrin catalyst, SiO<sub>2</sub>-FeTCPP, was effective for the degradation of TrBP over a wide pH range, which includes the pH values characteristic for landfill leachates. The prepared catalyst showed a higher reusability, even in the presence of contaminants, such as HSs. The presence of HS, a major constituent in landfill leachates, inhibited the catalytic oxidation by SiO<sub>2</sub>-FeTCPP at pH 7 that was the optimal value for TrBP degradation. However, debromination was enhanced in the presence of HS, compared to its absence, because HS prevented the further oxidation of Br<sup>-</sup> by KHSO<sub>5</sub>. HS with higher levels

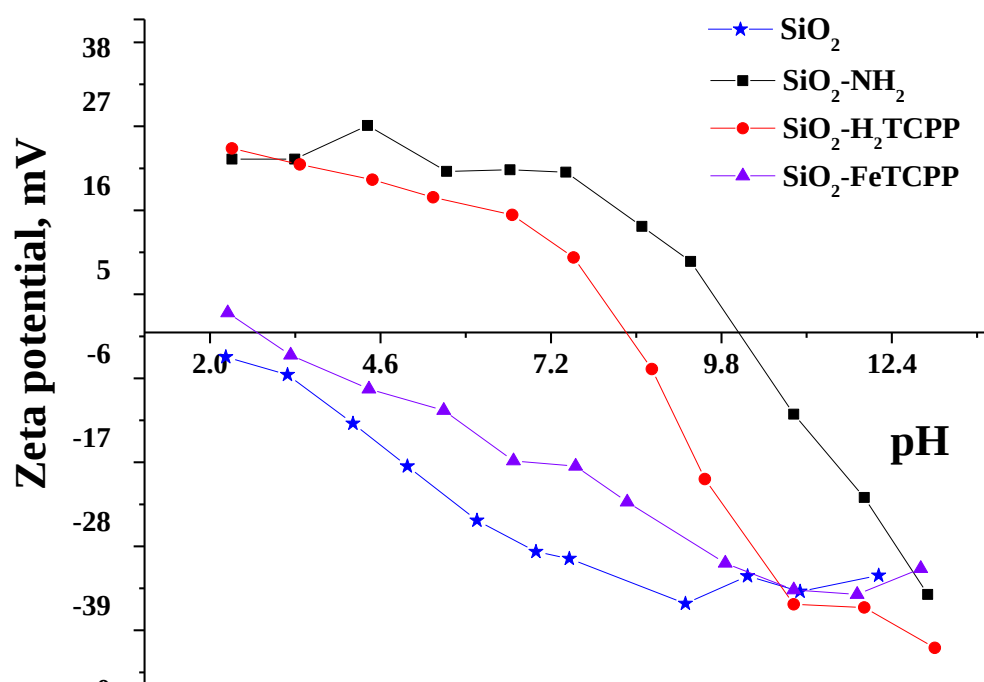
of carboxylic acid groups, such as fulvic acid, resulted in a somewhat lower level of inhibition compared to humic acid. However, more than 90% of TrBP was finally degraded at HS concentrations below 50 mg L<sup>-1</sup>.



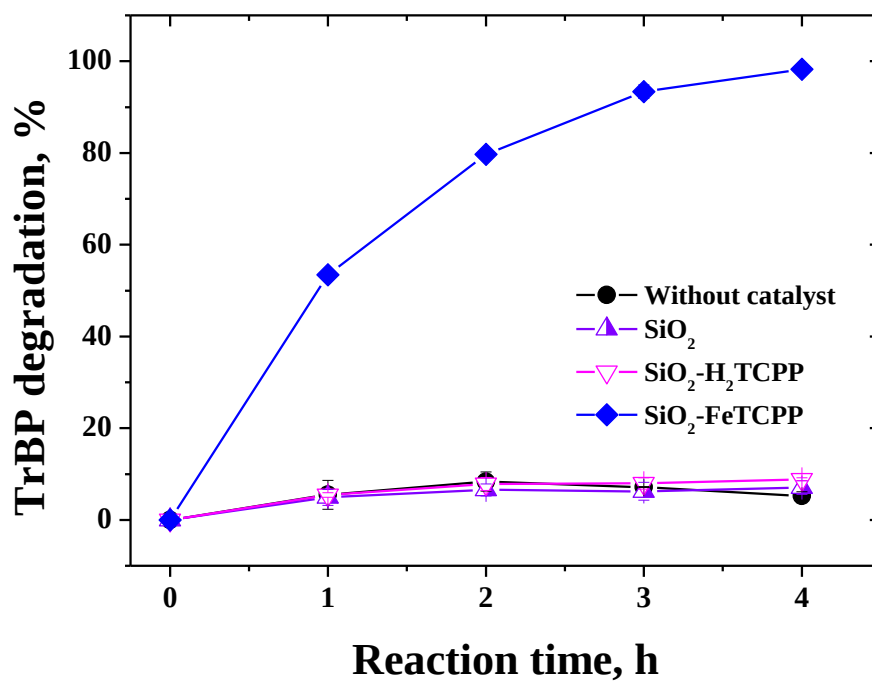
**Fig. 2.1.** Synthesis of silica gel supported Fe(III)TCPP catalyst.



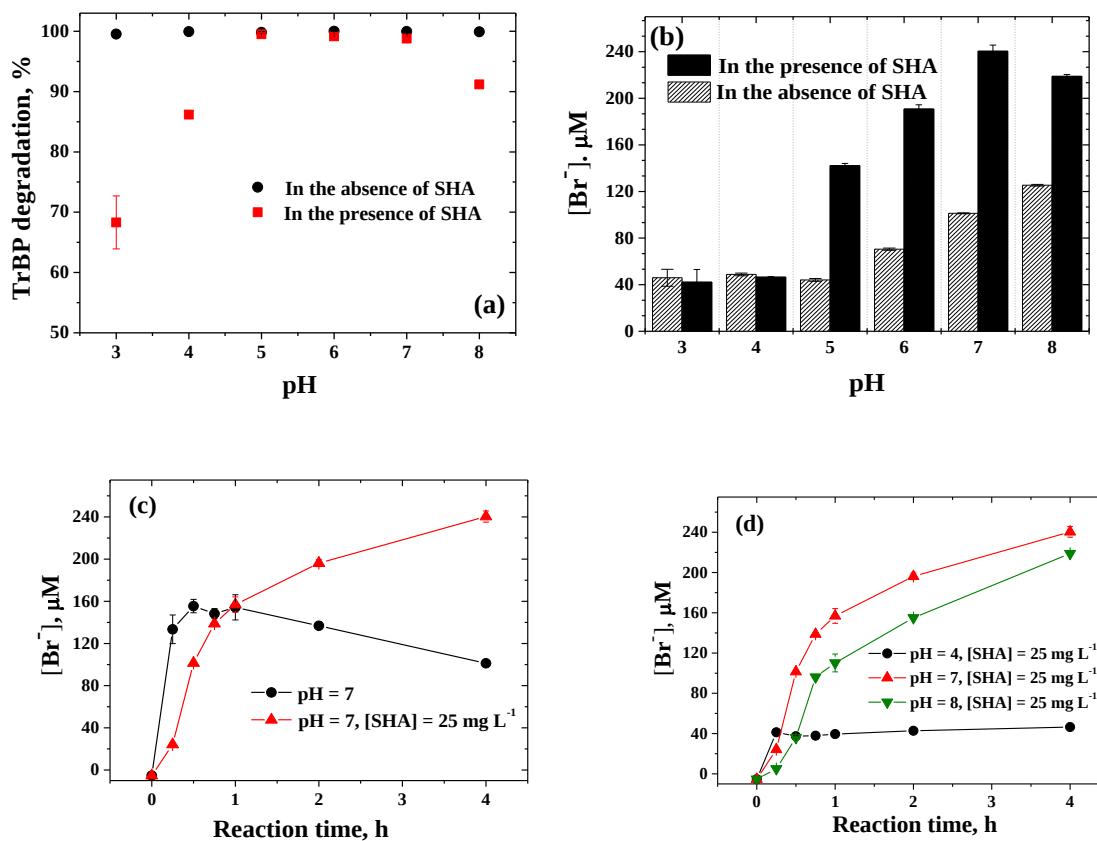
**Fig. 2.2.** FT-IR spectra of silica,  $\text{SiO}_2$ -NH<sub>2</sub>,  $\text{SiO}_2$ -H<sub>2</sub>TCPP and  $\text{SiO}_2$ -FeTCPP.



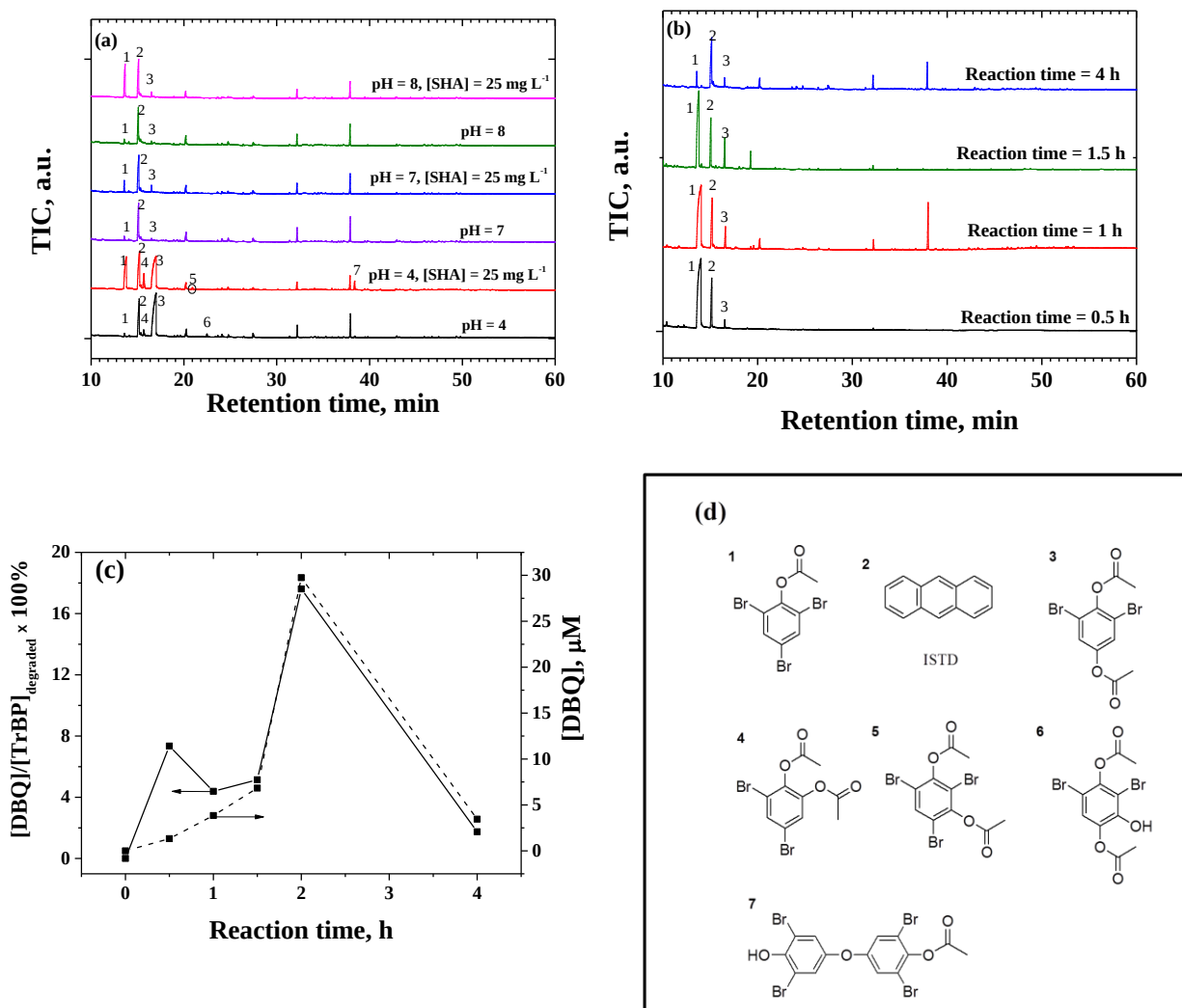
**Fig. 2.3.** The effect of Zeta potential versus pH for silica,  $\text{SiO}_2\text{-NH}_2$ ,  $\text{SiO}_2\text{-H}_2\text{TCPP}$  and  $\text{SiO}_2\text{-FeTCPP}$ .



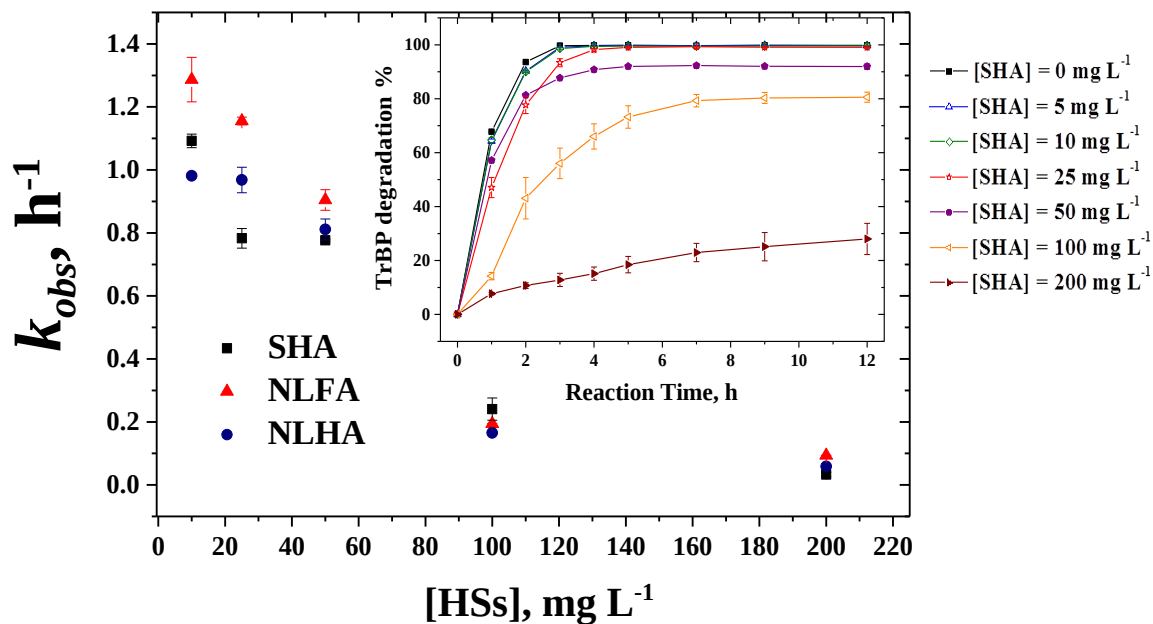
**Fig. 2.4.** Effect of catalyst on the TrBP degradation. The reaction conditions were as follows:  $[\text{TrBP}]_0$ , 200  $\mu\text{M}$ ; [catalyst], 2.7  $\mu\text{M}$  (100  $\text{mg L}^{-1}$ );  $[\text{KHSO}_5]$ , 1250  $\mu\text{M}$ ;  $[\text{SHA}]$ , 25  $\text{mg L}^{-1}$ .



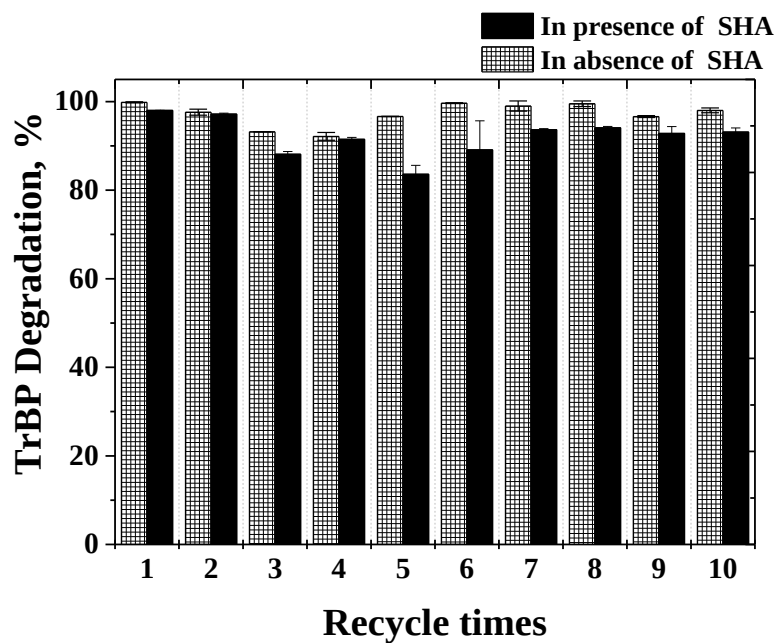
**Fig. 2.5.** Influence of pH on the percent TrBP degradation and debromination. The reaction conditions were as follows:  $[\text{TrBP}]_0$ , 200  $\mu\text{M}$ ; [catalyst], 2.7  $\mu\text{M}$ ;  $[\text{KHSO}_5]$ , 1250  $\mu\text{M}$ ; [SHA], 25  $\text{mg L}^{-1}$ ; reaction time, 4 hours.



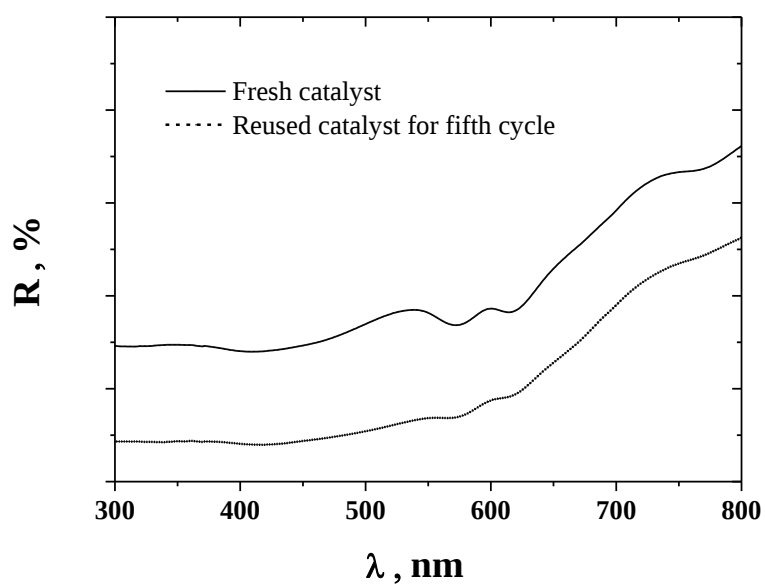
**Fig. 2.6.** (a) GC/MS chromatograms of a *n*-hexane extract of the different pH reaction mixture. The reaction conditions were as follows: [TrBP]<sub>0</sub>, 200 μM; [catalysts], 2.7 μM; [KHSO<sub>5</sub>], 1250 μM; reaction time, 4 hours, (b) GC/MS chromatograms of a *n*-hexane extract of the reaction mixture. The reaction conditions were as follows: pH = 7, [TrBP]<sub>0</sub>, 200 μM; [catalyst], 2.7 μM; [KHSO<sub>5</sub>], 1250 μM, (c) Kinetics of formation of byproduct 2,6-DBQ. The reaction conditions were as follows: [TrBP]<sub>0</sub>, 200 μM; [catalyst], 2.7 μM; [KHSO<sub>5</sub>], 1250 μM; [SHA], 25 mg L<sup>-1</sup>, and (d) The identified byproducts from mass spectra.



**Fig. 2.7.** Influence of HS concentration and type on the pseudo-first-order rate constant for TrBP degradation. The insert shows the influence of SHA concentration on the kinetics of TrBP degradation. The reaction conditions were as follows:  $[\text{TrBP}]_0$ , 200  $\mu\text{M}$ ;  $[\text{catalyst}]$ , 2.7  $\mu\text{M}$ ;  $[\text{KHSO}_5]$ , 1250  $\mu\text{M}$ ; pH = 7.



**Fig. 2.8.** Reusability of the catalyst. The reaction conditions were as follows:  $[\text{TrBP}]_0$ , 200  $\mu\text{M}$ ; [catalyst], 2.7  $\mu\text{M}$ ;  $[\text{KHSO}_5]$ , 1250  $\mu\text{M}$ ; [SHA], 25  $\text{mg L}^{-1}$ ; reaction time, 24 h; pH = 7.



**Fig. 2.9.** Diffuse Reflectance UV-vis spectra for the fresh catalyst and the  $\text{SiO}_2\text{-FeTCPP}$  after use for five cycles.

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# Chapter 3

*Oxidative debromination and degradation of  
tetrabromobisphenol A by a functionalized  
silica-supported  
iron(III)-tetrakis(p-sulfonatophenyl)porphyrin catalyst*

### 3.1. Introduction

In a previous studies, our research group examined the degradation of TBBPA using a homogeneous iron(III)-porphyrin catalytic system [1,2]. The findings indicated that the oxidation was not efficient and no debromination was observed because the catalyst underwent self-degradation and inhibition by contaminating HA [2]. As mentioned in chapter 2, the iron(III)-porphyrin catalyst was covalently supported on the functionalized silica, and the stability and reusability were enhanced. However, HAs were not fully eliminated from the vicinity of catalytic sites and inhibited the catalytic oxidation of TrBP.

Because HAs contain larger amount negative surface charge, the positively charged surface of supports such as anion-exchange resin can also adsorb anionic HA, which results in a decrease in degradation performance. However, nitrogen atoms that are included in the functional groups of the anion-exchange resins can serve as a ligand for coordination with iron(III). If the iron(III) in the anionic porphyrin could be tightly attached to the nitrogen atom on the support by coordination, the surface potentials of the solid catalysts would be changed to negative after complexation. In addition, the presence of axial ligand like imidazol can enhance the catalytic activity [3]. Using such a type of the solid catalyst, the adsorption of anionic concomitants, such as HAs, would be suppressed, thus producing a stabile form of iron(III)-porphyrin catalyst on the support. In addition, the catalytic activity may be increased.

Tetrabromobisphenol A (TBBPA), a widely used brominated flame retardant (BFR), is used in the treatment of paper, textiles, plastics, electronic equipment, upholstered furniture and chiefly in epoxy resins that are used in circuit board laminates

[4]. The leaching of BFRs, as well as TBBPA, from wastes derived from such materials in landfills is facilitated in the presence of HA, which is a major component in landfill leachates [5,6]. Many studies have shown that TBBPA can induce cytotoxicity and hepatotoxicity, and it has the potential to disrupt estrogen signaling [7], therefore, the development of effective methods for removing TBBPA from landfill leachates is an important issue. Methods have been reported for oxidative degradation of TBBPA (e.g., birnessite oxidation [8], photo-oxidation [9] and permanganate oxidation [10]), but most involve the cleavage of the  $\beta$ -carbon in TBBPA, and not debromination. In addition, the influence of other contaminants, such as HAs, on TBBPA oxidation has not been investigated in detail, even though it is well known that HAs are major components of landfill leachates.

In this chapter, an anionic iron(III)-tetrakis(*p*-sulfonatephenyl)porphyrin (FeTPPS) immobilized on silica modified with an imidazole via the axial coordination was examined as a catalyst for the enhanced degradation and debromination of TBBPA in the presence of HA. In addition, the influence of HA on the rate of TBBPA degradation, debromination and reusability were investigated.

## 3.2. Materials and Methods

### 3.2.1. Materials

The SHA was used as model HA sample in this study, which was extracted from Shinshinotsu peat soil, as described in a previous report [11]. Tetrabromobisphenol A (TBBPA), 3-isocyanatopropyltrimethoxysilane and *N*-(3-aminopropyl)imidazole, were purchased from Tokyo Chemical Industry (Tokyo, Japan). FeTPPS was synthesized

according to the reported procedure [12].  $\text{KHSO}_5$  was obtained as a triple salt,  $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$  (Merck, Darmstadt, Germany).

### 3.2.2. Synthesis of Silica Supported FeTPPS Catalyst

Scheme 3.1 shows the strategy used in the synthesis of the catalyst. The silica gel supported Fe(III)TPPS catalyst was synthesized by a previously reported method [13], with minor modifications. In a 2-neck flask, (3-isocyanatopropyl)triethoxysilane (1.3 mL) and *N*-(3-aminopropyl) imidazole (700  $\mu\text{L}$ ) were added to dioxane (20 mL) to synthesize 3-(1-imidazolyl)propylcarbonyl-3'-aminopropyl-triethoxysilane. The mixture was stirred for 12 h at 70  $^{\circ}\text{C}$ . Subsequently, 1.5 g of silica gel (10–40 mesh, Wako Pure Chemicals, Osaka, Japan) was added, and the mixture was stirred at 80  $^{\circ}\text{C}$  for 12 h. The resulting solid was collected on a filter and consecutively washed with 0.5 M HCl,  $\text{H}_2\text{O}$ , 0.1M NaOH and finally washed with  $\text{H}_2\text{O}$ . The 3-(1-imidazolyl)propylcarbonyl-3'-aminopropylsilica (IPS) was then carefully dried overnight in vacuum oven at 50  $^{\circ}\text{C}$ . In a 100 mL flask, IPS (0.5 g) was added to FeTPPS solution (3.0 mM, 15 mL). The mixture was shaken at 25  $^{\circ}\text{C}$ , 150 rpm under 24 h in the dark. After the reaction, the FeTPPS/IPS was collected and washed with 1 M NaCl solution, ultra-pure water, and dried under vacuum.

### 3.2.3. Characterization of the Synthesized Catalyst

The catalyst loading amount was estimated using UV-visible absorption spectroscopy. UV-visible absorption spectroscopy and Diffuse Reflectance UV-vis spectra were obtained using a V-630 type spectrophotometer (Japan Spectroscopic Co. Ltd., city, Japan). FT-IR spectra were recorded using an FT/IR 600 type spectrometer

(Japan Spectroscopic Co. Ltd.) with KBr pellets. The specific surface areas of the samples were obtained from N<sub>2</sub> sorption isotherm at 77 K using a Beckman Coulter SA3100 (Brea, California, USA). Zeta potentials were recorded using a Zetasizer Nano ZS90 (Malvern Instruments Ltd., Worcestershire, UK)

### 3.2.4. Assay for TBBPA Degradation

A 10 mL aliquot of a 0.02 M citrate/phosphate buffer at pH 4–8 was placed in a 100-mL Erlenmeyer flask. An aliquot (50 µL) of 0.01 M TBBPA in acetonitrile and the FeTPPS/IPS (3 mg) were then added to the buffer. Subsequently, aqueous solutions of 1000 mg L<sup>-1</sup> SHA in 0.05 M NaOH solution and 0.1 M aqueous potassium monopersulfate (KHSO<sub>5</sub>, 100 µL) were added, and the flask was then allowed to shake at 25 °C in an incubator. After the reaction, the concentrations of the remained TBBPA were measured by an HPLC with a UV detector. The separation of TBBPA in the reaction mixture was accomplished with a COSMOSIL 5C<sub>18</sub>-AR-II column (4.6 mmø × 250 mm). The mobile phase consisted of a mixture of methanol and 0.08% of H<sub>3</sub>PO<sub>4</sub> aqueous (78/22, v/v). The flow rate of the eluent and the detection wavelength were set to 1.0 mL min<sup>-1</sup> and at 220 nm, respectively. The released Br<sup>-</sup> was analyzed by ion chromatography (ICS-90 type, Dionex). The mobile phase was an aqueous mixture of 2.7 mM Na<sub>2</sub>CO<sub>3</sub> and 0.3 mM NaHCO<sub>3</sub>, and the flow rate of the eluent was set at 1.5 mL min<sup>-1</sup>. The degradation percent of TBBPA was calculated by the following equation:

$$\text{TBBPA degradation (\%)} = \frac{[\text{TBBPA}]_0 - [\text{TBBPA}]_t}{[\text{TBBPA}]_0} \times 100$$

where [TBBPA]<sub>0</sub> and [TBBPA]<sub>t</sub> represent the TBBPA concentrations remained in the

reaction mixture before and after a  $t$ -h reaction period, respectively. The pseudo first-order rate constant,  $k_{\text{obs}}$  ( $\text{h}^{-1}$ ), was estimated by non-linear least square regression analysis of the dataset for reaction time (h) and  $[\text{TBBPA}]_t/[\text{TBBPA}]_0$  to below equation:

$$\frac{[\text{TBBPA}]_t}{[\text{TBBPA}]_0} = \exp(-k_{\text{obs}}t)$$

The turnover number for TBBPA degradation and debromination was calculated by dividing the concentration of degraded TBBPA ( $\Delta[\text{TBBPA}] = [\text{TBBPA}]_0 - [\text{TBBPA}]_t$ ) or released  $\text{Br}^-$  by the catalyst concentration.

For the analysis of oxidation products, 1 M aqueous ascorbic acid (1 mL) was added, and pH of the solution was adjusted to 11–11.5 by adding aqueous  $\text{K}_2\text{CO}_3$  (600 g  $\text{L}^{-1}$ ). Subsequently, acetic anhydride (5 mL) was added dropwise to the solution, and a 1 mM anthracene solution in hexane (0.5 mL) was added as an internal standard (ISTD) for the GC/MS analysis. This mixture was doubly extracted with  $n$ -hexane (10 mL), and the extract was then dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After filtration, the extract was evaporated under a stream of dry  $\text{N}_2$ , and the residue was dissolved in  $n$ -hexane (0.25 mL). An aliquot of the extract (1  $\mu\text{L}$ ) was introduced into a GC-17A/QP5050 GC/MS system (Shimadzu, Kyoto, Japan). A Quadrex methyl silicon capillary column (0.25 mm id  $\times$  25 m) was employed in the separation. The temperature ramp was as follows: 65  $^\circ\text{C}$  for 1.5 min, 65–120  $^\circ\text{C}$  at 35  $^\circ\text{C min}^{-1}$ , 120–300  $^\circ\text{C}$  at 4  $^\circ\text{C min}^{-1}$  and a 300  $^\circ\text{C}$  held for 10 min.

### 3.3. Results and Discussion

### 3.3.1. Characterization of FeTPPS/IPS

The amount of FeTPPS molecules bound to the surface of the 3-(1-imidazolyl)propylcarbamoyl-3'-aminopropylsilica (IPS) was estimated by the change in absorbance at 394 nm of the Soret band in UV-visible absorption spectra. The relative absorption at a wavelength of 394 nm (corresponding to the Soret band of FeTPPS) between a stock solution of FeTPPS and the solution obtained after removing the FeTPPS/IPS was used to determine the concentration of FeTPPS molecules bound to the IPS. The findings indicated that 32.7  $\mu\text{mol}$  of FeTPPS was immobilized on 1 g of IPS.

FT-IR spectra of silica, IPS and FeTPPS/IPS are shown in Figure 3.1. The FT-IR spectrum of IPS contained characteristic vibration bands in the 2800–3000  $\text{cm}^{-1}$  region, corresponding to symmetrical and asymmetrical C-H stretching vibrations. The absorbance in the 1400–1600  $\text{cm}^{-1}$  region is assigned to C=C, C=N ring stretching (skeletal bands) as well as the C=O stretching vibration which was observed in the FT-IR spectra of IPS and FeTPPS/IPS.

The change in the surface chemistry of the catalyst was characterized by zeta potential analysis, which is related to the surface charge (Figure 3.2.). The unmodified silica had a negative zeta potential in the pH range of 3 to 9, which reflected a large negative surface charge due to the presence of deprotonated silanol groups. The FeTPPS/IPS catalyst had a negative zeta potential at pH values above 7.1. The FeTPPS/IPS catalyst had a positive zeta potential below pH 7.1, which can be attributed to the protonation of uncomplexed imidazole group in IPS. The zeta potential verse pH curve ( $\bullet$  in Figure 3.2.) for the reused catalyst was similar with fresh catalyst ( $\blacksquare$  in Figure 3.2.). However, the magnitude of the zeta potential was increased in the pH range

from 3 to 9, compared with the fresh catalyst. In addition, the point of zero charge (PZC) was shifted from pH 7.1 to 7.5 as a result of recycling. This may be due to the release and degradation of some FeTPPS during the oxidation reaction.

### **3.3.2. Influence of pH on the Degradation of TBBPA**

Since the pH was not only related to the redox potential of the oxidant but also to species distribution of TBBPA and other concomitants in aqueous solutions, the influence of pH on the degradation of TBBPA was investigated. In the absence of SHA, the degradation of TBBPA was not dependent on the pH of the solution. However, in the presence of SHA, the reaction was clearly pH dependent, and the presence of SHA also affected the degradation reaction. As shown in Figure 3.3a, in the presence of SHA, the percentage of degraded TBBPA increased with increasing pH and the highest degradation performance was observed at pH 8, where more than 95% the TBBPA was degraded in the presence of SHA, indicating that the oxidative degradation of TBBPA is inhibited by SHA. This inhibition was enhanced in the lower pH range and became weaker at higher pH. The zeta potential of the FeTPPS/IPS indicated that the catalyst had negative surface charge at pH values above 7.1 and a positive surface charge at pH values below 7.1. Because SHA has a large amount of negative surface charge [14], it can easily be adsorbed on the FeTPPS/IPS surface at a pH below 7.1. The interaction of TBBPA with catalytic sites could be blocked due to the adsorption of SHA at a pH lower than 7. The surface charge of the catalyst changed to negative at pH values higher than 7.1. In this pH range, the SHA appears to be excluded from the catalyst surface by electrostatic repulsion. Therefore, the inhibition by SHA became weaker in a high pH range. Debromination was observed during the oxidation reaction in the pH range from

pH 4 to 8 (Figure 3.3b). Although, in a previous study, no debromination was observed in the case of a homogeneous system [2],  $\text{Br}^-$  was clearly detected in the reaction mixture in the FeTPPS/IPS catalytic system. The low pH condition was beneficial for debromination, especially in the absence of SHA, and the highest debromination value was found at pH 4. The highest rate of debromination was also observed at pH 4 in the presence of SHA. However, compared with SHA free conditions, the extent of debromination decreased in the presence of SHA due to the drastic decrease in the rate of degradation of TBBPA. At pH 6 and 7, debromination was enhanced by SHA, even the degradation of TBBPA was inhibited by SHA. At pH 8, although the rate of debromination decreased slightly in the presence of SHA, the percent TBBPA degradation was the highest in the pH range from 3 to 8 in the presence or absence of SHA. In addition, the typical pH range for the leachates is reported to be 6.7–12 [5,6]. Therefore, the influences of SHA and catalyst concentration on the degradation of TBBPA were examined at pH 8.

To identify the oxidation products produced in the reactions, *n*-hexane extracts of reaction mixtures were analyzed by GC/MS for the 1.5-h and 5-h reaction periods. Figure 3.4 shows one of the chromatograms for an *n*-hexane extract of reaction mixtures at pH 8 in the presence of SHA. For the 1.5 h reaction period, the peak at 17.8 min of retention time was detected as a major oxidation product (Figure 3.4a). This peak was assigned as 4-(2-hydroxyisopropyl)-2,6-dibromophenol (2HIP-2,6DBP) acetate from the mass spectrum:  $m/z$  [relative intensity, fragment identify], 352 [2.65,  $\text{M}^+$ ], 310 [30.8,  $(\text{M}-\text{CH}_2\text{CO})^+$ ], 295 [100,  $(\text{M}-\text{CH}_3\text{CH}_2\text{CO})^+$ ], 252 [48.3,  $\text{C}_6\text{H}_4\text{OBr}_2^+$ ]. However, 2HIP-2,6DBP decreased for the 5 h reaction period, and the peak at 53.0 min of the retention time significantly increased (Figure 3.4b). This peak was assigned as the

trimer of 2,6-dibromophenol and the mass spectral identification was as follows:  $m/z$  [relative intensity, fragment identify], 836 [71.0,  $M^+$ ], 794 [100,  $(M-CH_2CO)^+$ ], 779 [44.2,  $(M-CH_3CH_2CO)^+$ ], 756 [48.3,  $(M-Br)^+$ ], 293 [14.8,  $C_6H_2(CH_3CO_2)Br_2^+$ ], 267 [28.8,  $C_6H_2O(OH)Br_2^+$ ]. The retention time and mass spectrum of 2HIP-2,6DBP acetate in the reaction mixtures were in good agreement with those for the acetate of the standard sample. In previous reports of TBBPA oxidation [8,9], while 2HIP-2,6DBP was found as one of the main byproducts, 2,6-dibromo-*p*-benzoquinone (2,6DBQ) was also detected as a main byproduct. However, no 2,6DBQ was found in the homogeneous FeTPPS-KHSO<sub>5</sub> catalytic system [2], even at pH 4 and 6 as well as at pH 8 for any of the reaction periods. The patterns of oxidation products were also not varied by solution pH (for at pH 4 and 6) for the heterogeneous FeTPPS/IPS-KHSO<sub>5</sub> catalytic system.

### **3.3.3. Influence of Catalyst Concentration on the TBBPA Degradation and Debromination**

Figure 3.5 shows the influence of catalyst concentration on the degradation of and debromination of TBBPA, in which the  $\Delta[TBBPA]$  represents the concentration of degraded TBBPA. A 0.7–3.4% decrease in the concentration of TBBPA was found in the presence of the FeTPPS/IPS (10–34  $\mu M$ ) without KHSO<sub>5</sub>. These results suggest that the contribution of TBBPA adsorption to the solid catalyst is minor in the case of  $\Delta[TBBPA]$ . The  $\Delta[TBBPA]$  steeply increased up to a concentration of 3.5  $\mu M$  of the FeTPPS/IPS catalyst, and then gradually increased at concentrations up to 34  $\mu M$  (Figure 3.5a). In the absence of the solid catalyst, a small amount of TBBPA degradation (3  $\mu M$ ) and  $Br^-$  release (4  $\mu M$ ) was observed for a 35 min reaction period. For the debromination (Figure 3.5b), the concentration of the released  $Br^-$  reached a

plateau of 3.5–17  $\mu\text{M}$  of the FeTPPS/IPS catalyst, but decreased at 34  $\mu\text{M}$ . These results indicate that the presence of the catalyst enhances the degradation of TBBPA. The decrease in debromination at a FeTPPS/IPS concentration of 34  $\mu\text{M}$  may be due to the enhanced oxidation of  $\text{Br}^-$  at higher catalyst concentrations. The turn over number for TBBPA degradation and debromination, as estimated for 3.5  $\mu\text{M}$  of the FeTPPS/IPS catalyst, was  $7.3 \pm 0.3$  and  $5.1 \pm 0.1$ , respectively.

#### **3.3.4. Influence of HA Concentration**

HA is present at levels of 20–200  $\text{mg-C L}^{-1}$  levels in landfill leachates [6], and HA can affect the distribution and oxidation reactions of organic pollutants. The influence of HA concentration was examined to assess the practical use of the FeTPPS/IPS catalyst and SHA was used as a model sample of HA. The pseudo-first-order rate constant ( $k_{\text{obs}}$ ) of TBBPA decreased with increasing concentration of SHA. When the SHA concentration increased from 2.8 to 14  $\text{mg-C L}^{-1}$ , the  $k_{\text{obs}}$  dramatically decreased from 1.6 to 0.3  $\text{h}^{-1}$ . With a further increase in the concentration of SHA, the  $k_{\text{obs}}$  decreased further. From the insert in Figure 3.6, a drop-off in the initial degradation rate was observed with a small (2.8  $\text{mg-C L}^{-1}$ ) mount of SHA. However, when the reaction time was prolonged, the percent degradation TBBPA rapidly reached values higher than 95% within 5 h in the case of an SHA concentration lower than 14  $\text{mg-C L}^{-1}$ . Over 95% the TBBPA was degraded within 9 h for SHA concentrations of up to 29  $\text{mg-C L}^{-1}$ . Even in the presence of high concentrations of SHA, 58–87  $\text{mg-C L}^{-1}$ , over 75% of the TBBPA was degraded within 12 h.

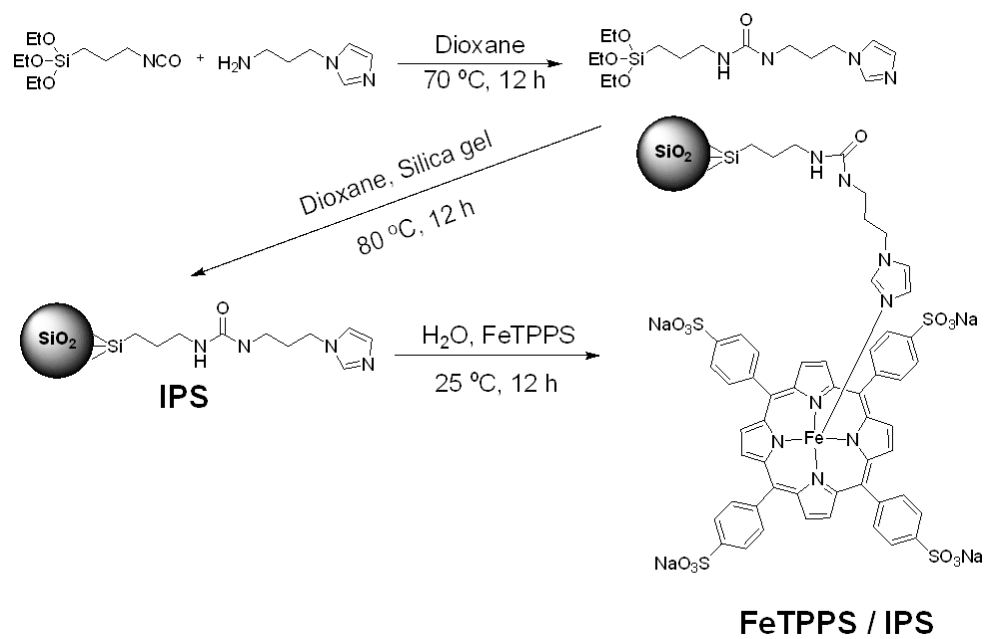
#### **3.3.5. Reusability of FeTPPS/IPS**

In terms of using FeTPPS/IPS for water treatment, catalyst reusability is an important factor from the economical point of view. After each reaction, the catalyst was isolated on a filter, and then washed with deionized water and acetone. The catalyst had a high degree of durability as demonstrated by the recyclability test shown in Figure 3.7a. Over 95% of the TBBPA was degraded in the presence or absence of SHA after five recyclings and more than 85% of the TBBPA was degraded after ten recyclings.

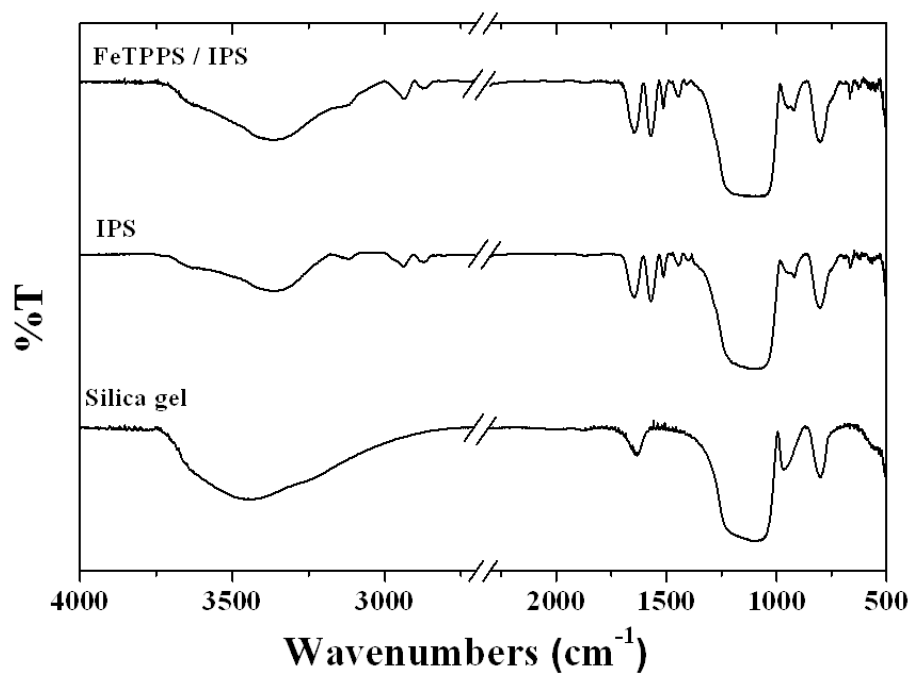
The reused catalyst exhibited a good catalytic activity up to ten catalytic runs with only a small loss in degradation efficiency. The debromination was around 0.4 ( $[\text{Br}^-]/\Delta[\text{TBBPA}]$ ) during the recyclability test (Figure 3.7b). However, the zeta potential of the FeTPPS/IPS increased slightly after five recyclings, as shown in Figure 2. At pH 8, the zeta potential of the reused catalyst was  $-6$  mV and the fresh catalyst was  $-30$  mV, indicating that the negative surface charge of the catalyst had decreased after the recyclability test. The HA would be predicted to be easily absorbed on the reused catalyst surface due to the change in surface charge, which would have an adverse impact on the degradation of TBBPA in the presence of HA. Therefore, with increasing catalyst reuse, the inhibition by SHA became a larger issue (Figure 3.7a). The surface area of the reused catalyst ( $194 \pm 10 \text{ m}^2 \text{ g}^{-1}$ ) was similar to that for the fresh catalyst ( $215 \pm 6 \text{ m}^2 \text{ g}^{-1}$ ). In addition, Figure 3.8 shows Diffuse Reflectance UV-vis spectra for the fresh catalyst and after being used for five cycles. The fresh catalyst showed two peaks at 409 nm and 550 nm. After five recyclings, all of the peaks remained, indicating that the structure of the FeTPPS remained intact during the oxidative degradation reaction. These results show that the higher catalytic activity of FeTPPS/IPS catalyst was retained after several recyclings.

### **3.4. Conclusion**

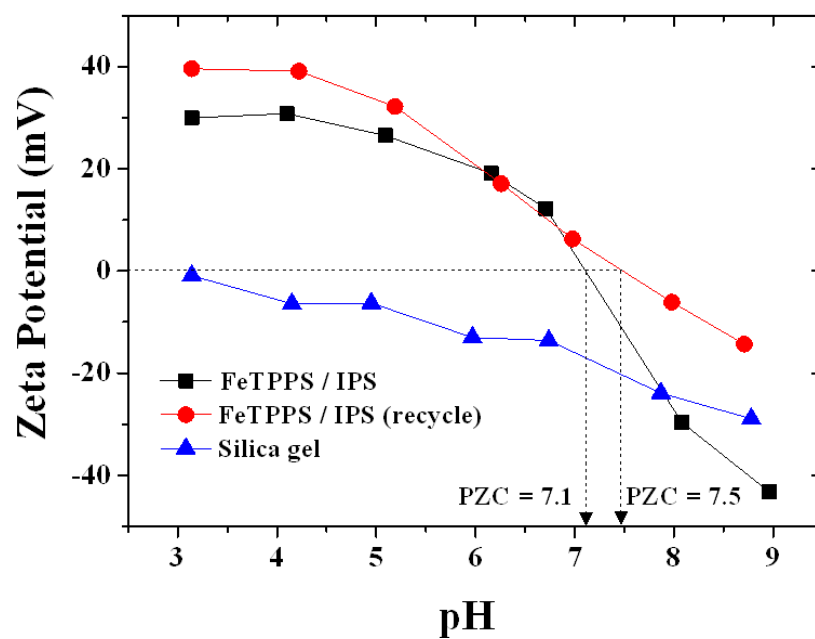
A FeTPPS/IPS catalyst was synthesized and its use in the degradation and debromination of TBBPA in the absence and presence of HA, a major component of leachates, was examined. This catalytic system was pH independent in the absence of SHA and the highest catalytic activity was found to be at pH 8 in the presence of SHA. Although the presence of SHA retarded the degradation of TBBPA, over 95% of the TBBPA was degraded in the case of SHA 28 mg-C L<sup>-1</sup>. In addition, FeTPPS/IPS exhibited good catalytic activity for up to ten recyclings. As a green and efficient catalyst, FeTPPS/IPS has promise for use in the field of pollution control.



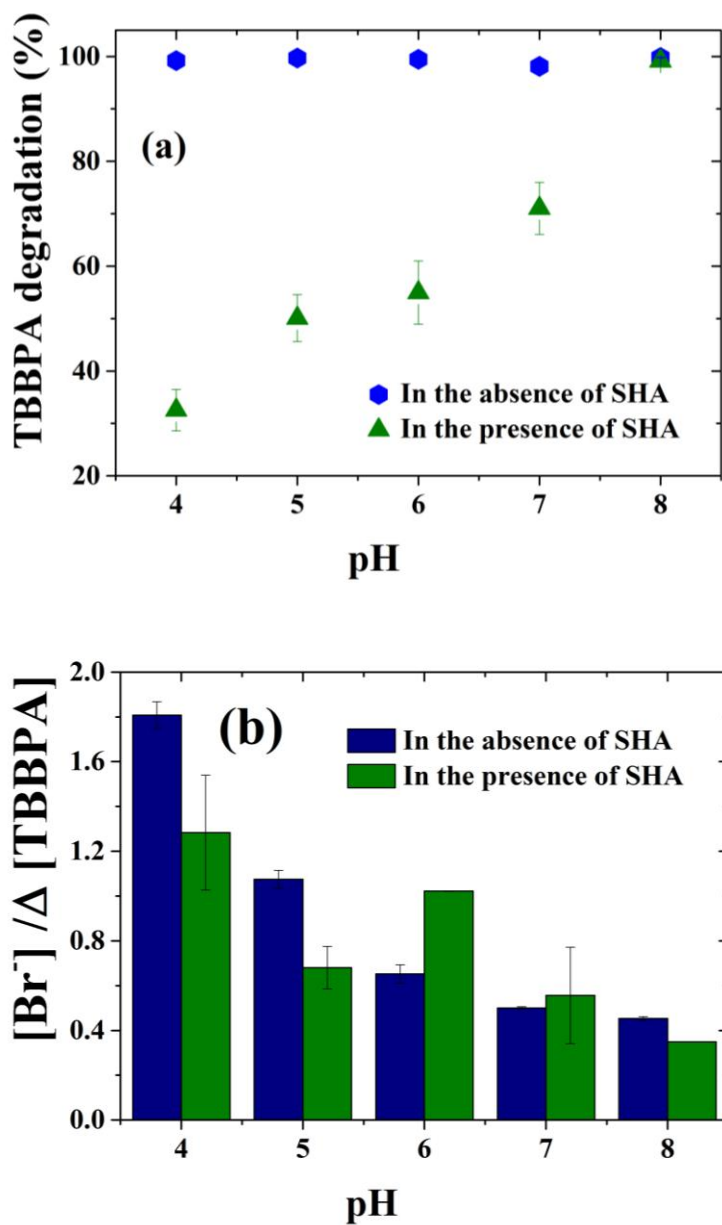
**Scheme 1.** Synthesis of IPS and FeTPPS/IPS.



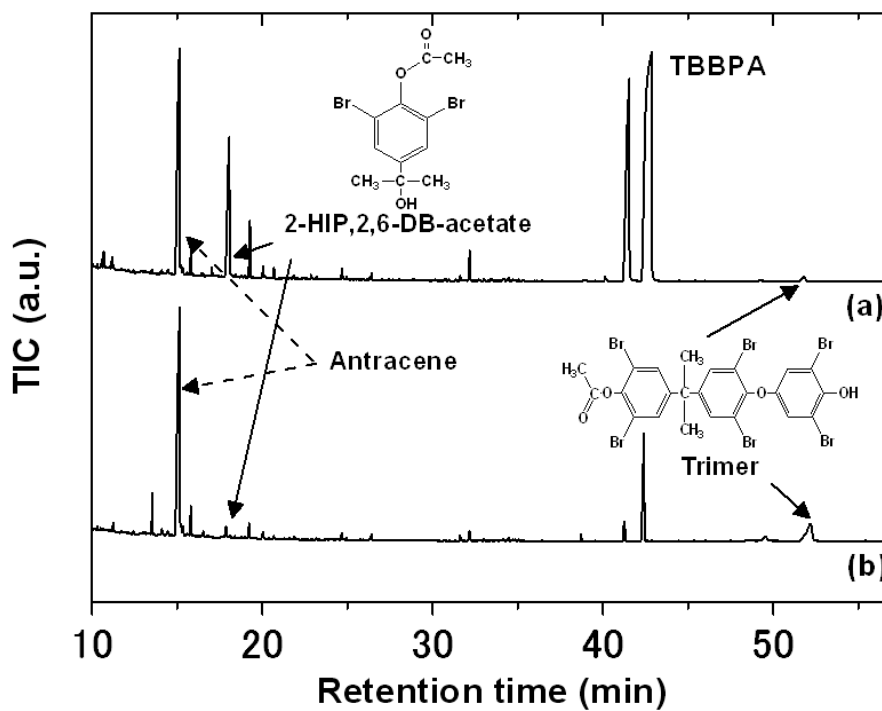
**Fig. 3.1.** FT-IR spectra of silica gel, IPS and FeTPPS / IPS with KBr pellet.



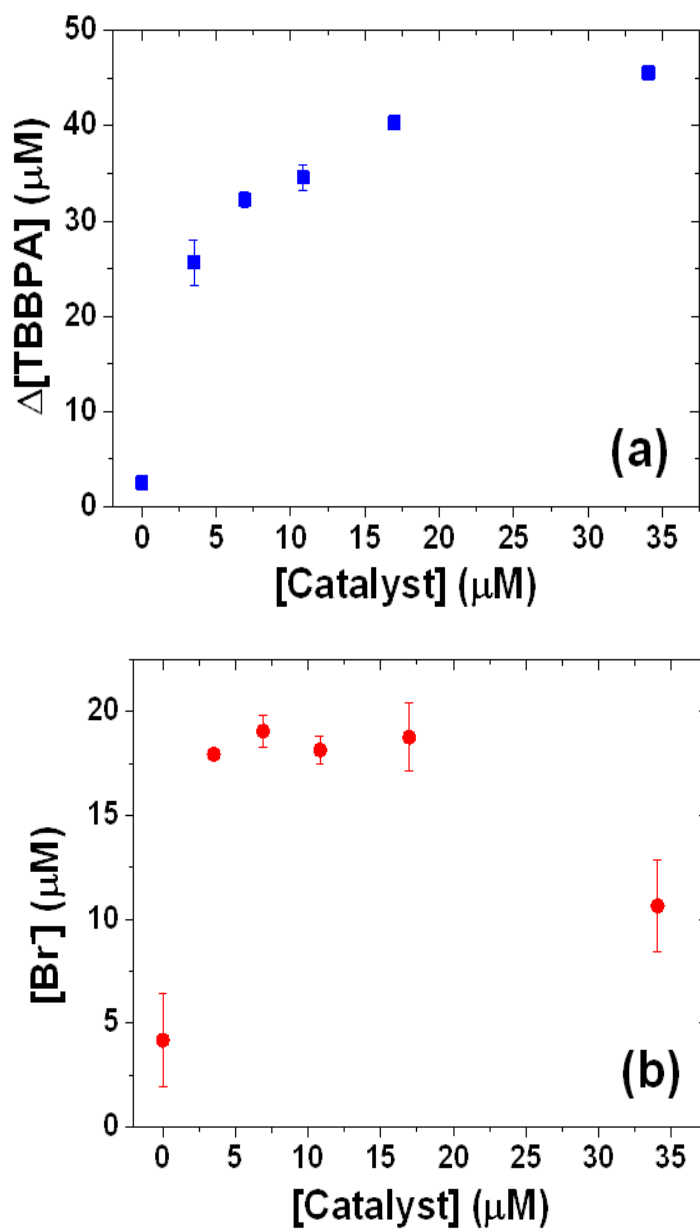
**Fig. 3.2.** The pH dependence on the Zeta potential for silica, FeTPPS/IPS and the FeTPPS/IPS that was reused 5 times.



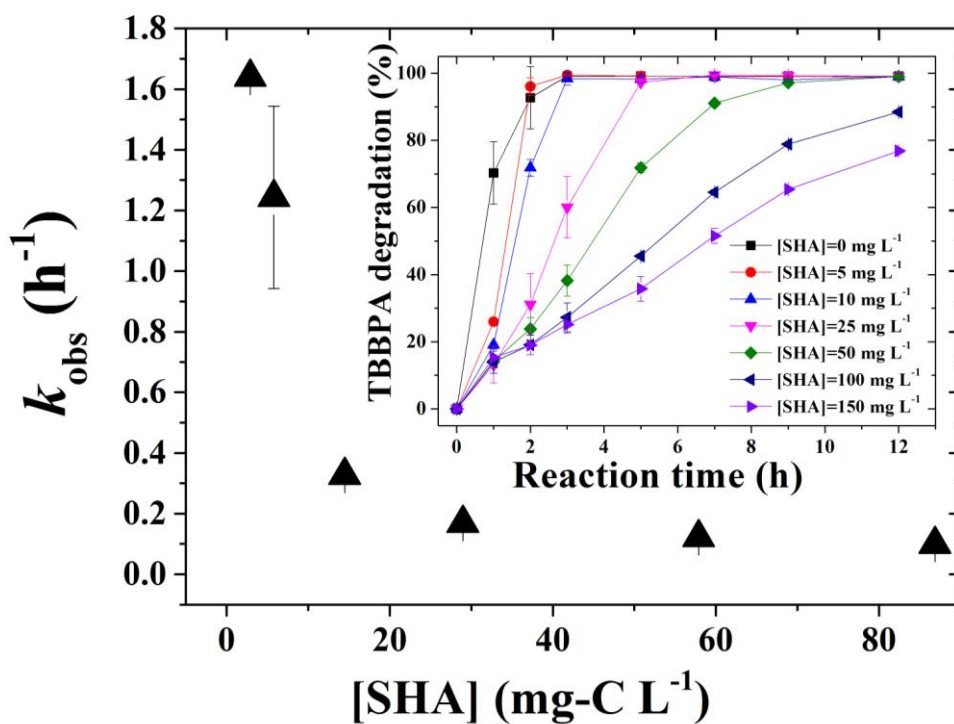
**Fig. 3.3.** (a) Influence of pH on percentage TBBPA degradation (b) Influence of pH on debromination. The reaction conditions were as follow:  $[TBBPA]_0$ , 50  $\mu M$ ;  $[FeTPPS/IPS]$ , 10  $\mu M$  (0.3 g L<sup>-1</sup>);  $[KHSO_5]$ , 1.0 mM;  $[SHA]$ , 25 mg L<sup>-1</sup>; temperature, 25 °C; reaction time, 4 h.



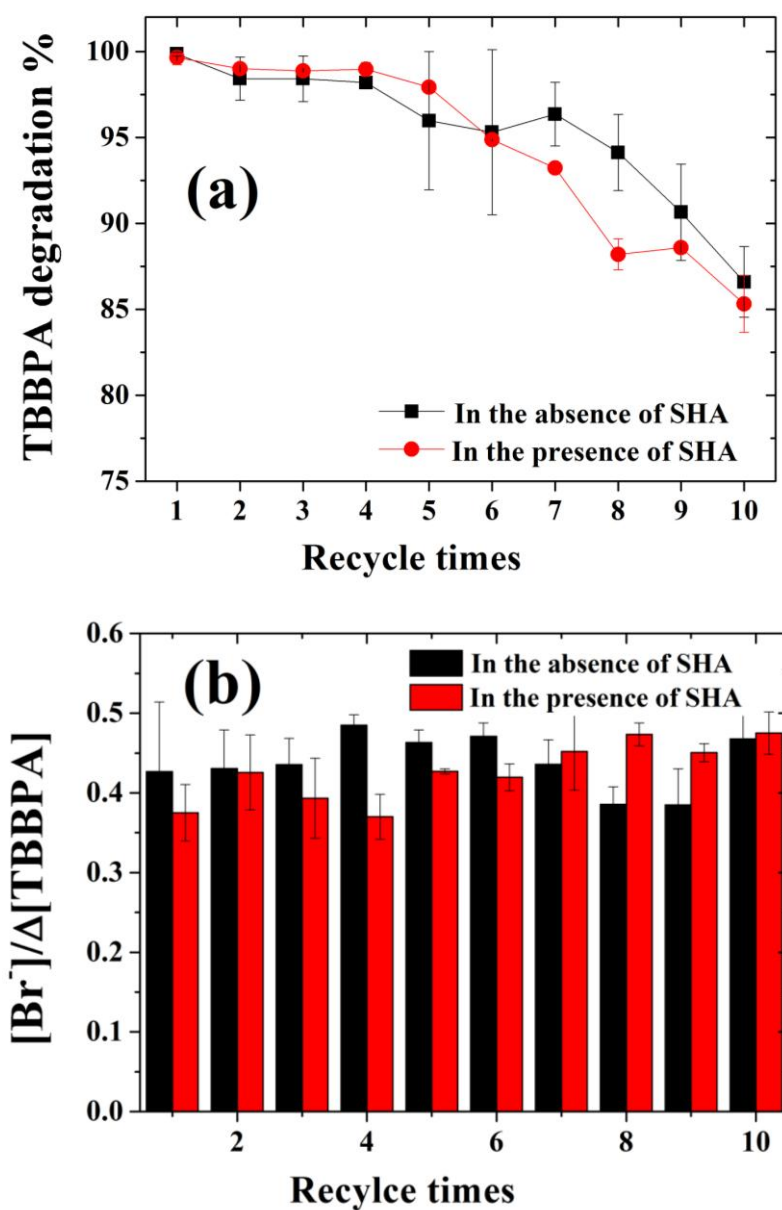
**Fig. 3.4.** GC/MS chromatograms of *n*-hexane extract from the reaction mixture at pH 8 in the presence of SHA. Reaction period (a) 1.5 h, (b) 5 h. Reaction conditions: [TBBPA]<sub>0</sub>, 50  $\mu\text{M}$ ; [FeTPPS/IPS], 10  $\mu\text{M}$  (0.3 g L<sup>-1</sup>); [KHSO<sub>5</sub>], 1.0 mM; [SHA], 25 mg L<sup>-1</sup>, temperature 25 °C.



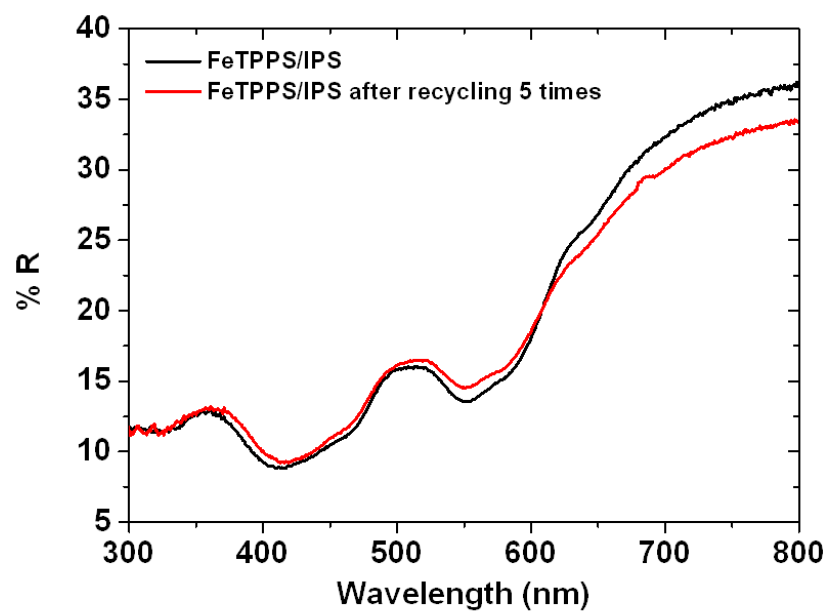
**Fig. 3.5.** Influence of FeTPPS/IPS concentration on the degradation and debromination of TBBPA.  $[\text{TBBPA}]_0$ , 50 μM; pH = 8;  $[\text{KHSO}_5]$ , 1 mM; temperature, 25 °C; reaction time, 35 min. The FeTPPS/IPS concentration at 0.3 g L<sup>-1</sup> corresponds to 10 μM.



**Fig. 3.6.** Influence of SHA concentration on the pseudo-first-order rate constant ( $k_{\text{obs}}$ ) for TBBPA degradation and variations in the percent TBBPA degradation (insertion). The reaction conditions were as follow: [TBBPA]<sub>0</sub>, 50  $\mu\text{M}$ ; [FeTPPS/IPS], 10  $\mu\text{M}$  (0.3 g L<sup>-1</sup>); [KHSO<sub>5</sub>], 1.0 mM; pH = 8; temperature, 25 °C.



**Fig. 3.7.** Reusability of the catalyst (a) TBBPA degradation, (b) number of bromide ions released. The reaction conditions were as follow:  $[TBBPA]_0$ , 50  $\mu\text{M}$ ;  $[\text{FeTPPS/IPS}]$ , 10  $\mu\text{M}$  (0.3  $\text{g L}^{-1}$ );  $[\text{KHSO}_5]$ , 1.0 mM;  $[\text{SHA}]$ , 25  $\text{mg L}^{-1}$ ; temperature, 25  $^\circ\text{C}$ ; pH = 8; reaction time, 4 h (in the absence of SHA), 20 h (in the presence of SHA).



**Fig. 3.8.** Diffuse reflectance UV-vis spectra for the FeTPPS/IPS catalyst before and after five recyclings.

### 3.5. References

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# Chapter 4

***Oxidative degradation of pentabromophenol in the  
presence of humic substances catalyzed by a  
SBA-15 supported iron-porphyrin catalyst***

#### 4.1. Introduction

As described in section 1.3, humic substances (HSs) are heterogeneous macromolecules that play important roles in both biogeochemical and pollutant redox reactions [1]. The presence of HSs affects the concentrations and lifetimes of reactive oxidants by quenching reactive species and donating electrons to radical intermediates that are formed during the degradation of pollutants [2]. Thus, the efficiency of the oxidative degradation of organic pollutants is decreased when HSs are present [3–5]. For heterogeneous catalytic systems, HSs not only serve as competitors for oxidants but also as an adsorbate, where the catalytic centers are covered [3]. In landfill leachates, HSs are major contaminants and the water solubility of bromophenols is enhanced in the presence of HSs [6,7]. Therefore, the influence of HSs on the oxidative degradation of bromophenol and strategies for reducing the adverse effects of HSs are important issues for the practical use of the catalyst. As described in chapter 2 and chapter 3, the iron(III)-porphyrin was immobilized on the surface of silica to avoid the self-degradation and good reusability was observed. However, the inhibitions of HS on the bromophenols degradation were not effectively suppressed by anion-exclusion from the catalyst with negative surface charge. The inhibitory effects of HSs on the oxidation of bromophenols continue to pose a significant problem in this area of research [8–11].

Mesoporous molecular sieves have attracted much attention in the field of catalysis because of their huge surface areas, well-ordered channels, uniform pore size, rapid mass transport, good thermal/oxidative stability, and molecular sieving capability [12]. In particular, Santa Barbara Amorphous-15 (SBA-15) has a large pore size (4.6 – 10 nm) compared to that of the MS41 family and zeolites (0.3 – 1.2 nm) [13].

Metalloporphyrins, which cannot be fixed within the porous structure of the zeolites because of their large molecule size (1.0 – 1.4 nm), can be easily encapsulated in the porous structure of SBA-15 [14], and bromophenols can also easily access the catalytic center in the channel of the SBA-15. In contrast, a large molecule, such as HSs (20 – 300 nm), is not incorporated into the catalytic center in the channel of SBA-15 [15]. Thus, the uniform pore size of SBA-15 serves as a size-selective molecular switch, which would permit bromophenols to be selectively degraded. In addition, the inhibitory effects of HSs on the degradation reaction could be efficiently suppressed. In this chapter, iron(III)-5,10,15,20-tetrakis(4-pyridyl)-porphyrin (FeTPyP) was synthesized and immobilized on mesoporous silica, SBA-15, and the activity of the catalyst for degrading PBP as a model bromophenol was examined in the presence of natural organic matter (NOM), fulvic (FA) and humic (HA) acids. In addition, the catalytic activities of FeTPyP supported on SBA-15 (FeTPyP-SBA-15) were compared with the corresponding values for FeTPyP supported on amorphous SiO<sub>2</sub> (FeTPyP-SiO<sub>2</sub>) as a control.

## 4.2. Materials and Methods

### 4.2.1. Materials

The soil HA sample (SHA) used in this study was extracted from Shinshinotsu peat soil, as described in a previous report [16]. Nordic Lake HA (NHA), Nordic Lake fulvic acid (NFA), Elliott soil fulvic acid (SFA) and NOM from Nordic Lake (NOM) were obtained from the International Humic Substances Society (St. Paul, MN, USA). The elemental compositions and contents of acidic functional groups for these HSs are

summarized in the Table 4.1, and are based on data from a previous report [17]. PBP, 5,10,15,20-tetrakis(4-pyridyl)-21*H*,23*H*-porphyrin ( $\text{H}_2\text{TPyP}$ ),  $\text{FeCl}_2$ , 3-chloropropyltrimethoxysilane (3-CPTMS), and tetraethyl orthosilicate (TEOS) were purchased from Tokyo Chemical Industry. Pluronic P123 (poly(ethylene glycol)–poly(propylene glycol)–poly(ethylene glycol); average molecular mass 5800 Da) was purchased from Sigma-Aldrich. Potassium monopersulfate ( $\text{KHSO}_5$ ) was obtained as the triple salt,  $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$  (Merck).

#### **4.2.2. Synthesis of SBA-15 supported FeTPyP catalyst**

All processes for the synthesis of the FeTPyP-SBA-15 catalyst are summarized in Scheme 4.1.

##### *Synthesis of FeTPyP*

In a 3-neck flask,  $\text{H}_2\text{TPyP}$  100 mg and  $\text{CH}_3\text{COONa}$  0.5 g were added in 50 mL DMF, after which, 102.7 mg of  $\text{FeCl}_2$  was added. The mixture was refluxed under a nitrogen atmosphere for 2 h. The reaction was monitored by UV-vis absorption spectra using a V-630 type spectrophotometer (Japan Spectroscopic Co. Ltd.). After cooling the resulting solution to room temperature, the purple precipitate were collected by centrifugation and washed with DMF and water. The resulting solid was purified by column chromatography over silica gel using a mixture of chloroform, methanol and triethylamine (100:10:0.5, v/v/v) as the eluent. The UV-vis absorption spectrum of FeTPyP shows 3 peaks at 411 (Soret band), 568 and 605 nm (Q-bands). The ESI-MS results were as follows:  $m/z$  627.1, fragment ion  $[\text{M}-\text{Cl}]^+$ .

##### *Synthesis of CP-SBA-15*

The SBA-15 was synthesized according to the procedures reported by Zhao et al.

[13]. In a 3-neck flask, 1.0 g of SBA-15 and 1.63 g 3-chloropropyltrimethoxysilane (3-CPTMS) were suspended in 30 mL of dry toluene. The mixture was refluxed for 24 h under a nitrogen atmosphere. After cooling the resulting solution to room temperature, the resulting solid was isolated, washed with dichloromethane overnight in a Soxhlet extractor, and then dried *in vacuo* to give chloropropyl functionalized SBA-15. Results of the elemental analysis of CP-SBA-15 were as follows: C 6.08%, H 1.36%, Cl 4.06%.

#### *Synthesis of FeTPyP-SBA-15*

Into a round bottom flask, 1.0 g of CP-SBA-15 and 0.18 g FeTPyP were suspended in 50 mL of tetrahydrofuran (THF) and the suspension was then refluxed for 24 h. After cooling the resulting solution to room temperature, the product was isolated on a filter and dried. The resulting solid was washed with chloroform, ethanol, and the supernatant was checked by UV-vis absorption spectra. The FeTPyP-SBA-15 was then dried at 40 °C *in vacuo* for 10 h. Results of the elemental analysis of FeTPyP-SBA-15 were as follows: C 6.56%, H 1.39%, Cl 3.68%.

The FeTPyP-SiO<sub>2</sub>, used as a control catalyst, was synthesized based on similar procedures as described for the synthesis of FeTPyP-SBA-15.

#### **4.2.3. Characterization of the synthesized catalyst**

Elemental analysis was performed on a Yanaco MT-6 type CHN instrument. The amount of Fe loaded in the FeTPyP-SBA-15 catalyst was determined by ICP-AES (ICPE9000, Shimadzu) after wet-digestion of the solid catalysts. Diffuse Reflectance UV-vis spectra of the FeTPyP-SBA-15 were obtained using a V-650 iRM type spectrophotometer with an ISV-722 integrating sphere (Japan Spectroscopic Co. Ltd.). FT-IR spectra of the SBA-15, CP-SBA-15 and FeTPyP-SBA-15 preparations were

collected using a FT/IR 600-type spectrophotometer (Japan Spectroscopic Co Ltd.). Spectra were recorded between 4000 and 400  $\text{cm}^{-1}$  at a resolution of 2  $\text{cm}^{-1}$ , using a KBr disk. The ESI-MS spectrum of FeTPyP was recorded using a JEOL JMS-T100LP mass spectrometer. Small angle X-ray diffraction (SAXRD) patterns were collected on a Rigaku Nano-scale X-ray analyzer with Cu  $K\alpha$  radiation. Transmission electron microscopy (TEM) measurements were carried out on a JEM-2100F instrument (JEOL). The pore diameter, pore volume, and surface area of the samples were determined from a  $\text{N}_2$  sorption isotherm at 77 K using a BECKMAN COULTER SA3100 instrument. The Zeta potential and particle size of the samples were recorded on an ELSZ-1000 type Zeta-potential & Particle size Analyzer (Otsuka electronics Co. Ltd).

#### **4.2.4. Assay for PBP degradation**

##### *Homogenous system*

A 2 mL aliquot of 0.02 M citrate/phosphate buffer at pH 3 – 8 was placed in a test tube. A 10  $\mu\text{L}$  aliquot of 0.01 M PBP in acetonitrile and 50  $\mu\text{L}$  of 200  $\mu\text{M}$  FeTPyP in THF were then added to the buffer. Subsequently, 100  $\mu\text{L}$  of 1000  $\text{mg L}^{-1}$  HS in 0.05 M NaOH solution and 2.5  $\mu\text{L}$  of 0.1 M aqueous  $\text{KHSO}_5$  were added, and the test tube was then shaken at 25°C for 30 min in an incubator. After the reaction, 1 mL of 2-propanol was added to the reaction mixture and a 20  $\mu\text{L}$  aliquot of the resulting solution was injected into a PU-980 type HPLC system (Japan Spectroscopic. Co.). The mobile phase consisted of a mixture of 0.08% phosphate acid aqueous and methanol (20:80, v / v) and the flow rate was set at 1  $\text{mL min}^{-1}$ . A 5C18-MS Cosmosil packed column (4.6 mm i.d.  $\times$  250 mm, Nacalai Tesque) was used as the solid phase, and the column temperature was maintained at 50 °C. The UV absorption of PBP was measured at 220 nm. Bromide

ions in the reaction mixture were analyzed by ion chromatography (ICS-90 type, Dionex).

#### *Heterogeneous system*

A 20 mL aliquot of a 0.02 M citrate/phosphate (pH 3 – 8), sodium bicarbonate/sodium carbonate (pH 9 – 10) buffer was placed in a 100-mL Erlenmeyer flask. A 100  $\mu$ L aliquot of 0.01 M PBP in acetonitrile and 2 mg of FeTPyP-SBA-15 or FeTPyP-SiO<sub>2</sub> was then added to the buffer. A 1 mL aliquot of 1000 mg L<sup>-1</sup> HS in 0.05 M NaOH aqueous and 25  $\mu$ L of 0.1 M aqueous KHSO<sub>5</sub> were added, and the flask was then subjected to shaking at 25 °C in an incubator. After the reaction, the concentrations of the remaining PBP and the released Br<sup>-</sup> were determined by HPLC and ion chromatography, respectively.

### **4.3. Results and Discussion**

#### **4.3.1. Characterization of Catalyst**

The total chloropropyl group content in CP-SBA-15 and CP-SiO<sub>2</sub> was estimated to be 40.1 mg g<sup>-1</sup> and 37.3 mg g<sup>-1</sup>, respectively, based on the elemental analysis data. The amount of FeTPyP loaded in the FeTPyP-SBA-15 and FeTPyP-SiO<sub>2</sub> were determined to be 23  $\mu$ mol g<sup>-1</sup> and 6  $\mu$ mol g<sup>-1</sup>, respectively.

The N<sub>2</sub> adsorption isotherms and pore size distribution calculated from the desorption branch for SBA-15, CP-SBA-15 and FeTPyP-SBA-15 are illustrated in Figs. 4.1a and b, respectively. The structural characteristics of the samples are further summarized in Table 4.2. The specific surface area (*S*) was determined by the BET method, and the total pore volume (*V<sub>p</sub>*) was derived from the amount adsorbed at a

relative pressure of  $p_s/p_o = 0.98$  under the assumption that  $N_2$  had completely filled the pores in its normal liquid state (density =  $0.807 \text{ g cm}^{-3}$ ). Finally, pore size distribution was deduced from the Barrett-Joyner-Halenda (BJH) relationship, as shown in Table 4.2. Cylindrical pore geometry was assumed and pore sizes were estimated at the maximum of the pore size distribution from the desorption branch data of adsorption isotherms (Fig. 4.1b). The Nitrogen adsorption-desorption isotherms of the SBA-15, CP-SBA-15, and FeTPyP-SBA-15 were type IV isotherms. When SBA-15 was functionalized with chloropropyl and FeTPyP, the position of the capillary condensation branch was shifted toward lower relative pressure, which indicates smaller pore sizes. The BJH pore diameters of the SBA-15, CP-SBA-15 and FeTPyP-SBA-15 were determined to be 6.35 nm, 5.30 nm and 5.02 nm, respectively. The decreases in BET surface area and pore diameter indicate that the modification of SBA-15 occurred in the channels. The surface area of the FeTPyP-SiO<sub>2</sub> ( $320 \text{ m}^2 \text{ g}^{-1}$ ), determined by the BET method, was smaller than that for the FeTPyP-SBA-15 ( $512 \text{ m}^2 \text{ g}^{-1}$ ).

Figure 4.2a shows low angle XRD powder patterns of the SBA-15, CP-SBA-15 and FeTPyP-SBA-15. All of the XRD patterns exhibited three well-resolved diffraction peaks at  $2\theta$  of  $0.91^\circ - 0.93^\circ$  and two peaks at a higher degree in the range of  $2\theta$  of  $1.5^\circ - 2.0^\circ$ . The intensity of the  $d_{100}$  reflection decreases as a function of the amount of functionalized SBA-15 materials, indicating that the crystallinity of the SBA-15 materials was decreased after immobilized with FeTPyP. Figure 4.2b shows a TEM image of the FeTPyP-SBA-15, showing the orderly pore structure of the catalysts.

The change in the surface chemistry of the silica was characterized from zeta potential data, which is related to the surface charge (Fig. 4.3). Unmodified SBA-15 had a large negative zeta potential over a wide pH range (pH from 2 to 12), reflecting a large

negative charge due to the presence of deprotonated silanol groups. The zeta potential of the chloropropyl functionalized SBA-15 was similar to that for the SBA-15. However, the FeTPyP-SBA-15 with pyridyl groups could have a net positive, neutral or negative charge, depending on the pH of the solution. The FeTPyP-SBA-15 had a positive charge at pH values below 3.8 due to the protonation of the pyridyl group and a negative surface charge when pH was above 3.8.

FT-IR spectra of SBA-15, CP-SBA-15, and FeTPyP-SBA-15 are shown in Fig. 4.4. Typical bands associated with the stretching, bending, and out of plane deformation vibrations of Si-O-Si bonds at 1227, 1082, 807, and 456  $\text{cm}^{-1}$  were present in all cases [18]. The broad bands at around 3437 and 1637  $\text{cm}^{-1}$  were assigned to the stretching and bending modes of the O-H groups, respectively. The FT-IR spectrum of CP-SBA-15 contained characteristic vibration bands at around 2861 and 2853  $\text{cm}^{-1}$ , which were due to the symmetrical and asymmetrical C-H stretching vibrations of the chloropropyl group. The absorption bands at 1594 and 1413  $\text{cm}^{-1}$  associated with C=C, C=N ring stretching (skeletal bands) were present in the spectra of FeTPyP-SBA-15 [19]. These bands indicate that FeTPyP was introduced in the FeTPyP-SBA-15 samples, confirming the success of the procedure.

#### ***4.3.2. Effect of pH on the degradation of PBP in homogeneous and heterogeneous systems***

The PBP degradation testing was performed in both homogeneous and heterogeneous systems (Fig. 4.5). Because the percent degradation of PBP in the homogeneous system rapidly reached a plateau within 1 min, interpreting the kinetics of the process was difficult. Thus, the influence of pH was evaluated based on the percent

degradation at a period when the reaction had stagnated (30 min). In the homogeneous system (Fig. 4.5a), the percent degradation of PBP was optimal at pH 4 – 6 and over 98% of the PBP was degraded in the absence of SHA. However, in neutral and alkaline conditions at pH 7 and 8, which are normally found for landfill leachates [20], PBP was poorly degraded both in the presence and absence of SHA. The catalytic activity of FeTPyP for PBP degradation was also examined in the presence of SHA. However, the percent degradation of PBP was lower than 33% in the range from pH 3 to 8 in the presence of SHA, indicating inhibition by the SHA.

In the heterogeneous system using the FeTPyP-SBA-15 catalyst, the 4-h period where the reaction stagnated was selected for evaluating the percent degradation. For the case of FeTPyP-SBA-15, the effective pH range for PBP degradation was expanded to pH 5 – 9 and over 90% of the PBP was degraded in the absence of SHA (Fig. 4.5b). In the presence of 25 mg L<sup>-1</sup> SHA, the percent degradation of PBP increased and over 99% was degraded at pH 7 and 8, which is the typical pH range of leachates, while the percent degradation of PBP decreased significantly at pH 9 and 10. These results suggest that the FeTPyP-SBA-15 catalyst is effective in the degradation of PBP at pH 8, which is average pH value for landfill leachates [20] .

Catalyst reusability is an important factor in the evaluation of catalyst stability. The reusability of FeTPyP-SBA-15 was investigated at pH 8, and this catalyst showed a high reusability. After 5 recyclings, the percent PBP degradation was maintained (Fig. 4.6). Based on small angle XRD patterns (Fig. 4.7), the structure of the FeTPyP-SBA-15 remained unchanged after 5 recyclings but the intensity of the FeTPyP-SBA-15 was decreased, indicating that the crystallinity of the FeTPyP-SBA-15 was decreased as the result of recycling. Diffuse Reflectance-UV-vis spectra (Fig. 4.8)

showed that the catalytic center, FeTPyP, remained stable and intact after recycling.

#### **4.3.3. Effect of FeTPyP-SBA-15 concentration on the kinetics of degradation of PBP**

The effect of the dosage of FeTPyP-SBA-15 on catalyst performance was studied for a low molar ratio of  $\text{KHSO}_5/\text{PBP}$  (2.5) at pH 8. Fig. 4.9a shows the PBP degradation as a function of catalyst dosage. A higher FeTPyP-SBA-15 dosage resulted in a higher PBP degradation efficiency and rate (Figs. 4.9a and 4.9b). Increasing the catalyst dosage would provide more catalytic active sites available for the activation of  $\text{KHSO}_5$ , and thus would lead to a significant enhancement in the reaction rate. As shown in Fig. 4.9b, the pseudo-first-order rate constant ( $k$ ) increased with increasing catalyst dosage, and the second-order rate constant for PBP degradation by the FeTPyP-SBA-15 was estimated to be  $2.17 \times 10^{-6} \text{ M}^{-1} \text{ h}^{-1}$ .

#### **4.3.4. Effect of catalyst type on the degradation kinetics of PBP.**

The FeTPyP-SBA-15 showed a higher catalytic activity at pH 8, even in the presence of SHA. The ordered channel structures of SBA-15 that shield the active center in the catalyst may play a key role on the retarded the inhibition of the HS during the degradation reaction. FeTPyP immobilized on amorphous silica (FeTPyP-SiO<sub>2</sub>) was also investigated for PBP degradation in the absence and presence of SHA.

Figure 4.10a provides information on the degradation of PBP in the case of FeTPyP loaded heterogeneous catalysts with 0.1 g L<sup>-1</sup> of catalyst. PBP was efficiently degraded by the catalytic system with FeTPyP-SiO<sub>2</sub> and FeTPyP-SBA-15 in the absence of SHA. The  $k$  value for the degradation of PBP using the FeTPyP-SBA-15 catalyst (5.06 h<sup>-1</sup>) was significantly higher than that with the FeTPyP-SiO<sub>2</sub> (1.20 h<sup>-1</sup>).

However, in the presence of 25 mg L<sup>-1</sup> SHA, the performance of both catalysts was dramatically altered. For the FeTPyP-SBA-15 catalyst, the  $k$  value for the PBP degradation in the presence of SHA (2.59 h<sup>-1</sup>) was slightly lower than that in the absence of SHA. However, the degradation of PBP catalyzed by FeTPyP-SiO<sub>2</sub> was largely inhibited by the presence of SHA, in which the  $k$  value (0.04 h<sup>-1</sup>) was remarkably decreased, indicating that the inhibition of SHA in the PBP degradation reaction was more significant for the FeTPyP-SiO<sub>2</sub> catalyst.

Considering the differences in the loading amount of FeTPyP and the surface area of the two catalysts, the FeTPyP-SiO<sub>2</sub> dosage was increased to 0.4 g L<sup>-1</sup> (2.4 μM). As shown in Fig. 4.10b, the  $k$  value for the degradation of PBP for 0.4 g L<sup>-1</sup> FeTPyP-SiO<sub>2</sub> (4.49 h<sup>-1</sup>) increased compared to that for 0.1 g L<sup>-1</sup> of the catalyst (1.20 h<sup>-1</sup>) in the absence of SHA. Although the  $k$  value in the presence of SHA for 0.4 g L<sup>-1</sup> FeTPyP-SiO<sub>2</sub> catalyst increased up to 0.70 h<sup>-1</sup> as compared to that in the absence of SHA, the oxidation of PBP was largely inhibited by SHA. In addition, turnover frequencies (TOFs) for FeTPyP-SiO<sub>2</sub> and FeTPyP-SBA-15 were calculated by dividing the degradation rate (μM h<sup>-1</sup>) by the concentration of catalyst (2.4 μM) in the presence of 25 mg L<sup>-1</sup> SHA. The TOF for the FeTPyP-SBA-15 (58.3 h<sup>-1</sup>) was larger than that for FeTPyP-SiO<sub>2</sub> (16.7 h<sup>-1</sup>). Because the loading amount of FeTPyP-SBA-15 and FeTPyP-SiO<sub>2</sub> were different, the dosage of the catalyst and total surface area of the FeTPyP-SiO<sub>2</sub> system (0.4 g L<sup>-1</sup>) was higher than that for the FeTPyP-SBA-15 system. The higher surface area could cause higher levels of SHA to be adsorbed to the catalyst surface. The SBA-15 immobilized FeTPyP with lower amounts of FeTPyP loaded (4.7 μmol g<sup>-1</sup>) was synthesized and applied to the degradation of PBP in the presence of SHA. As shown in Fig. 4.10b, with same molar amount of FeTPyP, the  $k$  value for the

degradation of PBP with  $0.5 \text{ g L}^{-1}$  lower dosage of FeTPyP-SBA-15 ( $5.15 \text{ h}^{-1}$ ) was similar to that for  $0.1 \text{ g L}^{-1}$  FeTPyP-SBA-15 and  $0.4 \text{ g L}^{-1}$  FeTPyP-SiO<sub>2</sub>. Although the total surface area of the  $0.5 \text{ g L}^{-1}$  FeTPyP-SBA-15 system was higher than FeTPyP-SiO<sub>2</sub>, the  $k$  value in the presence of SHA for the FeTPyP-SBA-15 catalyst ( $1.30 \text{ h}^{-1}$ ) was much higher than that for the  $0.4 \text{ g L}^{-1}$  FeTPyP-SiO<sub>2</sub> catalyst ( $0.70 \text{ h}^{-1}$ ) in the presence of SHA, indicating that the inhibition of SHA was suppressed in the presence of the SBA supported catalyst.

In the case of the FeTPyP-SiO<sub>2</sub> system, the inhibition of PBP oxidative degradation by the SHA can be attributed to the adsorption of HSs. In the case of the FeTPyP-SiO<sub>2</sub> catalyst, the FeTPyP is loaded on the surface of the SiO<sub>2</sub>. Because of this, the SHA adsorbed on the catalyst may inhibit the reaction between PBP and the catalyst. To demonstrate the adsorption of SHA on the catalyst surface, the FeTPyP-SiO<sub>2</sub> catalyst was soaked in a SHA solution for 24 h and the zeta potential was measured after a 20 min centrifugation. Figure 4.11 shows the zeta potential for the fresh FeTPyP-SiO<sub>2</sub> catalyst and that for the catalyst after soaking in the SHA solution. The zeta potentials for FeTPyP-SiO<sub>2</sub> were largely shifted to negative values after soaking in SHA, thus confirming its adsorption.

The trend for the zeta potential data for FeTPyP-SBA-15 was similar to the case of FeTPyP-SiO<sub>2</sub> in the absence and presence of SHA. Thus, some SHA adsorption occurred for the FeTPyP-SBA-15 catalyst. However, compared with the FeTPyP-SiO<sub>2</sub> catalyst, the FeTPyP-SBA-15 catalyst was tolerant to the presence of SHA, and the inhibition of SHA was effectively suppressed in the FeTPyP-SBA-15 catalytic system. The FeTPyP-SBA-15 has well-ordered channels, a uniform pore size with a pore diameter of 5.02 nm. The distribution of SHA (the supernatant of the SHA solution after

a 20 min centrifugation) showed that the average diameter is 31.3 nm (Table 4.3). These results suggest that the well-ordered channels of FeTPyP-SBA-15 allow PBP molecules to access the catalytic center more easily, while the SHA accesses the catalytic center in the channel of the FeTPyP-SBA-15 catalyst with difficulty, due to its higher molecular size. Thus, the ordered structure of FeTPyP-SBA-15 serves as a size selective molecular-switch for the degradation of PBP.

Although the inhibition of SHA was negligible when the SHA concentration was lower than 25 mg L<sup>-1</sup>, the degree of inhibition became obvious with increasing concentrations of SHA (Fig. 4.12). When the SHA dosage was higher than 50 mg L<sup>-1</sup>, the degradation of PBP reached only 90% for a 4 h reaction period. Even in the presence of 100 mg L<sup>-1</sup> SHA, 50% of the PBP was degraded in the 4 h reaction period, indicating that the FeTPyP-SBA-15 maintains a high catalytic activity in concentrations of SHA under 50 mg L<sup>-1</sup>.

#### ***4.3.5. Influence of HS type on the degradation kinetics of PBP***

The structural features of the HSs are significantly different based on their origins and the conditions used for their preparation [21]. Thus, the influence of HS type on the kinetic of degradation of PBP was investigated (Table 4.3 and Fig. 4.13). Natural organic matter from Nordic lake (NOM), fulvic (NFA), and humic acids (NHA) from Nordic lake (NHA), Elliott Soil fulvic acid (SFA), and Shinshinotsu peat humic acid (SHA) were investigated. The SHA and SFA were obtained from peat soils that were formed under anaerobic conditions, similar to the process that occurs in landfills. To investigate the influence of HSs from aquatic origins similar to leachates, NLHA, NLFA and NOM were examined. PBP was effectively degraded by FeTPyP-SBA-15 in the

presence of 50 mg L<sup>-1</sup>, with more than 80% of the PBP being degraded (Fig. 4.13).

However, the degradation rate was dependent on the HS type. Because the molecular size of the HS was larger than the pore size of the catalyst, even after centrifugation (Table 4.3), the differences in the inhibition are dependent on the properties of the HSs. The highest PBP degradation rate was obtained in the presence of NOM. NOM has the lowest C and N content, which is related to lower organic fragments and functional group content. That may contribute to its low electron donating capacities [2], lower adsorption ability and lower competitive nature. The inhibition for the humic acid, SHA and NHA was higher than that for fulvic acid (SFA and NFA). The significant differences in the structural features for those HAs and FAs are the content of carboxyl group and phenolic hydroxyl group, which contribute to their surface charge and electron donating capacities [2]. In those HSs, the HAs contained a higher phenolic hydroxyl group and lower carboxyl group content. The HSs, which have higher levels of phenolic hydroxyl groups, would be expected to consume oxidative species, reduce the lifetime of oxidative species and finally decrease catalytic activity. On the other hand, FAs with higher levels of carboxyl groups would have a larger negative surface charge. Thus, the FA with a large negative electrostatic field might be easily excluded from the negatively charged surface of the FeTPyP-SBA-15 catalyst due to electrostatic repulsion.

#### 4.4. Conclusion

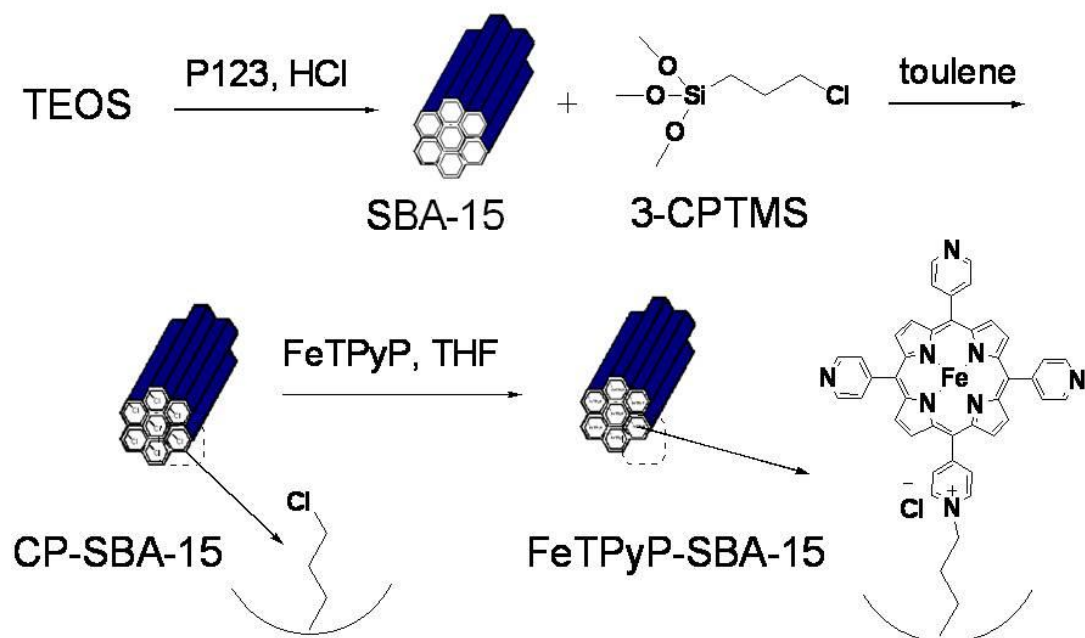
A FeTPyP catalyst supported on SBA-15 (FeTPyP-SBA-15), a mesoporous silica material, was synthesized and applied to the catalytic oxidation of PBP, a type of widely used BFR. Although the degradation of PBP was inhibited in the presence of HSs, the

catalytic activity of the FeTPyP-SBA-15 catalyst was much higher than that for the FeTPyP-SBA-SiO<sub>2</sub> as a control catalyst. As shown in Fig. 4. 14, such suppression of HS inhibition in the FeTPyP-SBA-15 catalyst can be attributed to the exclusion of larger molecular weight HSs from the channels of SBA-15 that contained the FeTPyP.

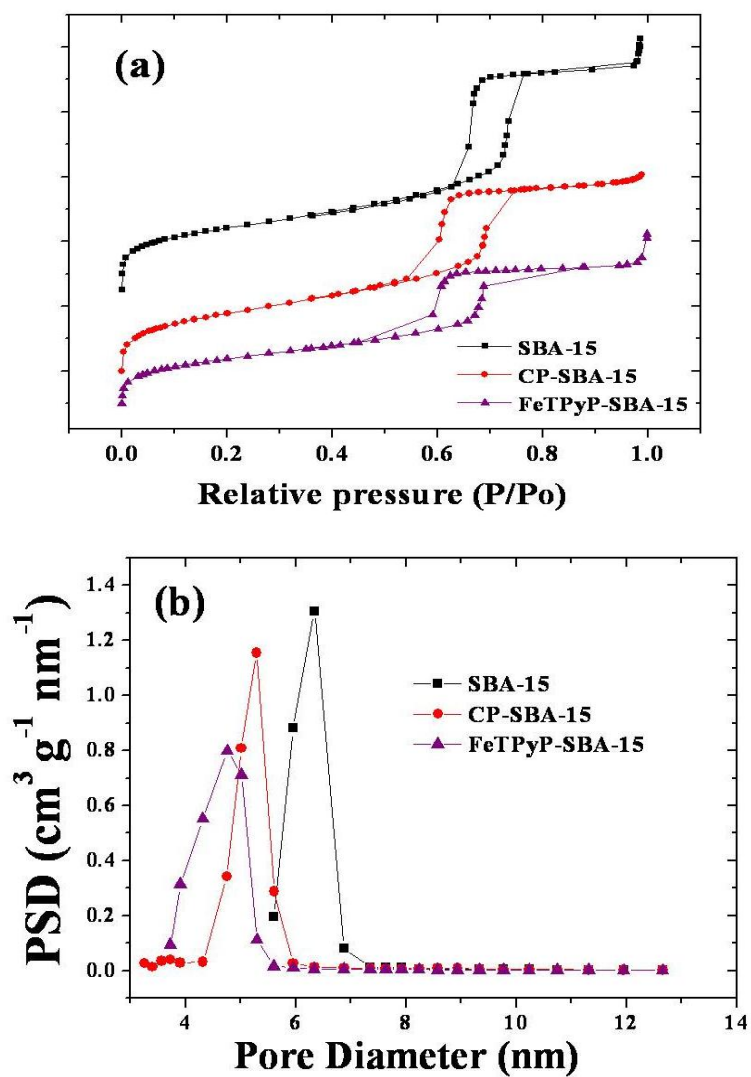
**Table 4.1.** Elemental composition and acidic functional group content of the HSs.

| HS samples | Elemental composition (wt. %) |     |     |      |     | Acidic functional groups (meq g <sup>-1</sup> ) |                                                         |
|------------|-------------------------------|-----|-----|------|-----|-------------------------------------------------|---------------------------------------------------------|
|            | C                             | H   | N   | O    | S   | Ash                                             |                                                         |
| SHA        | 57.9                          | 5.5 | 1.8 | 33.9 | 0.9 | ND <sup>a</sup>                                 | Carboxyl group<br>2.1<br>Phenolic hydroxyl group<br>3.8 |
| NHA        | 53.3                          | 4.0 | 1.2 | 43.1 | 0.6 | 0.3                                             | 4.9<br>1.7                                              |
| NFA        | 52.3                          | 4.0 | 0.7 | 45.1 | 0.5 | 0.5                                             | 5.9<br>1.7                                              |
| SFA        | 50.1                          | 4.3 | 3.8 | 42.6 | 0.9 | 1.0                                             | 6.6<br>1.2                                              |
| NOM        | 31.2                          | 2.9 | 0.7 | 31.5 | 4.2 | 29.5                                            | 1.2<br>1.6                                              |

<sup>a</sup>Not detected.



**Scheme 4.1.** Synthesis of the FeTPyP-SBA-15

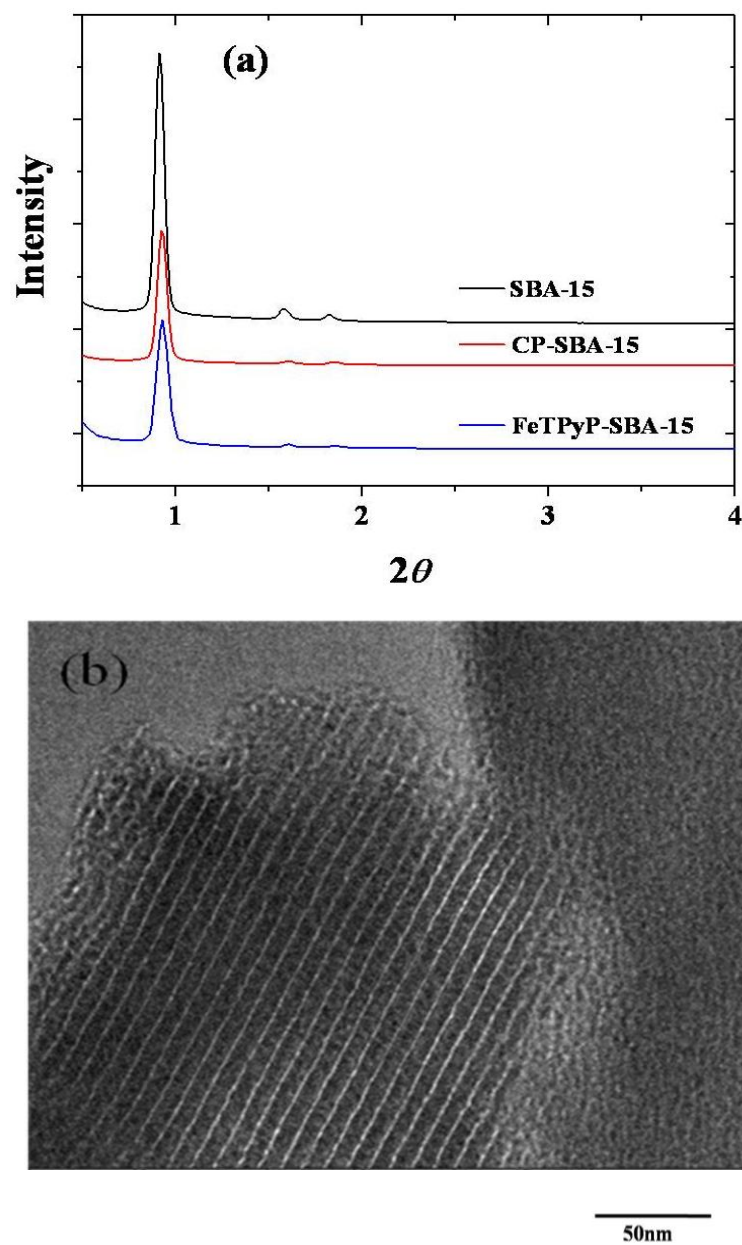


**Fig. 4.1.**  $N_2$  adsorption-desorption isotherms (a) and pore size distribution calculated from the desorption branch (b) for SBA-15, CP-SBA-15 and FeTPyP-SBA-15.

**Table 4.2.**Physicochemical properties from N<sub>2</sub>-BET and XRD analyses for FeTPyP-SBA-15.

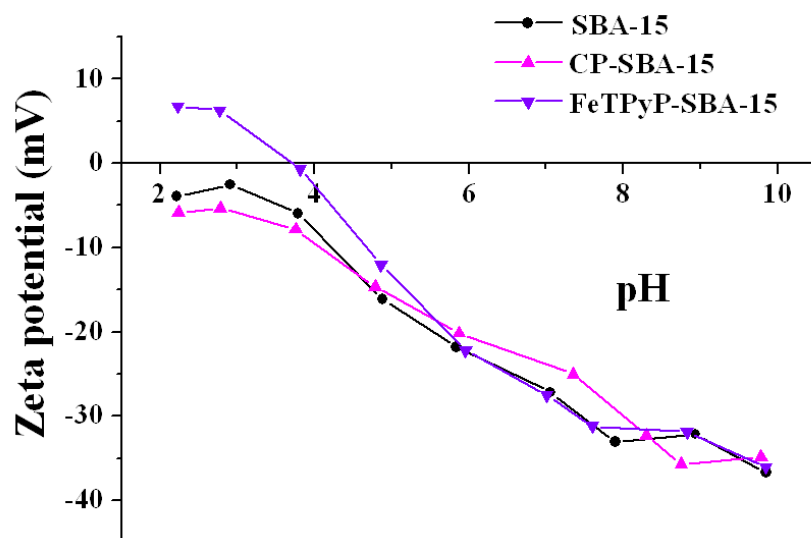
| Sample        | N <sub>2</sub> adsorption-desorption analysis                  |                                    |                                                                         | XRD                                   |                                     |                                        |
|---------------|----------------------------------------------------------------|------------------------------------|-------------------------------------------------------------------------|---------------------------------------|-------------------------------------|----------------------------------------|
|               | Surface area<br>(m <sup>2</sup> g <sup>-1</sup> ) <sup>a</sup> | Pore diameter<br>(nm) <sup>b</sup> | Total pore<br>volume<br>(cm <sup>3</sup> g <sup>-1</sup> ) <sup>c</sup> | d <sub>100</sub><br>(nm) <sup>d</sup> | a <sub>0</sub><br>(nm) <sup>e</sup> | Wall<br>thickness<br>(nm) <sup>f</sup> |
| SBA-15        | 696                                                            | 6.34                               | 1.11                                                                    | 9.67                                  | 11.16                               | 4.82                                   |
| CP-SBA-15     | 663                                                            | 5.3                                | 0.92                                                                    | 9.55                                  | 11.03                               | 5.73                                   |
| FeTPyP-SBA-15 | 512                                                            | 5.02                               | 0.77                                                                    | 9.49                                  | 10.96                               | 5.94                                   |

<sup>a</sup> Surface area calculated by the BET method. <sup>b</sup> Pore size diameter calculated by BJH method.<sup>c</sup> Total pore volume recorded at  $P/P_0 = 0.98$ . <sup>d</sup> Inter planar spacing. <sup>e</sup>  $a_0$  (nm) =  $2d_{100}/\sqrt{3}$ .<sup>f</sup> Wall thickness =  $a_0$  - pore size.

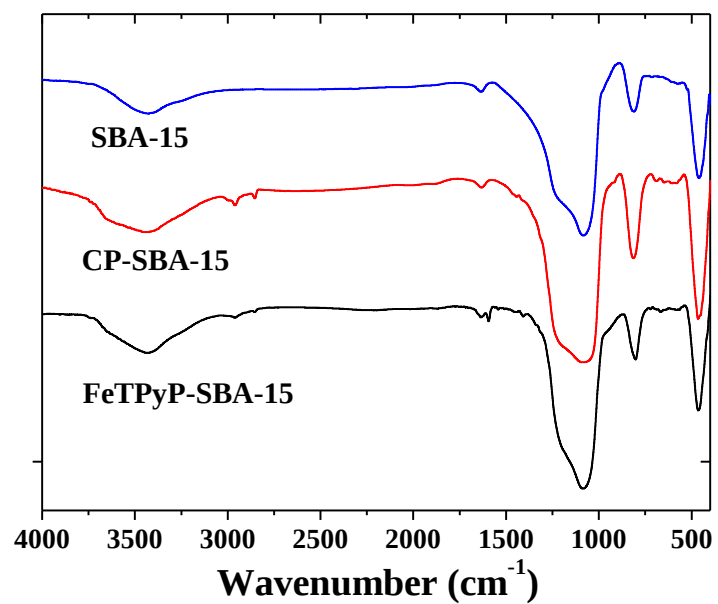


**Fig. 4.2.** (a) Small angle XRD patterns of SBA-15, CP-SBA-15 and FeTPyP-SBA-15.

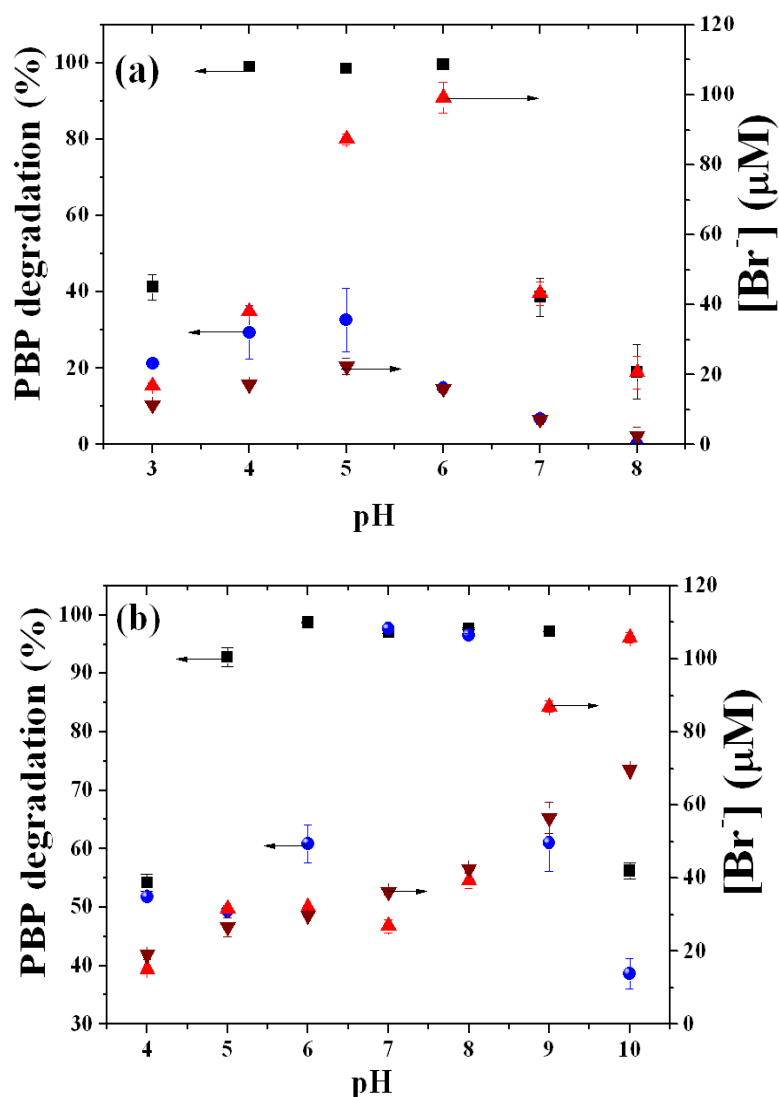
(b) TEM image of the FeTPyP-SBA-15.



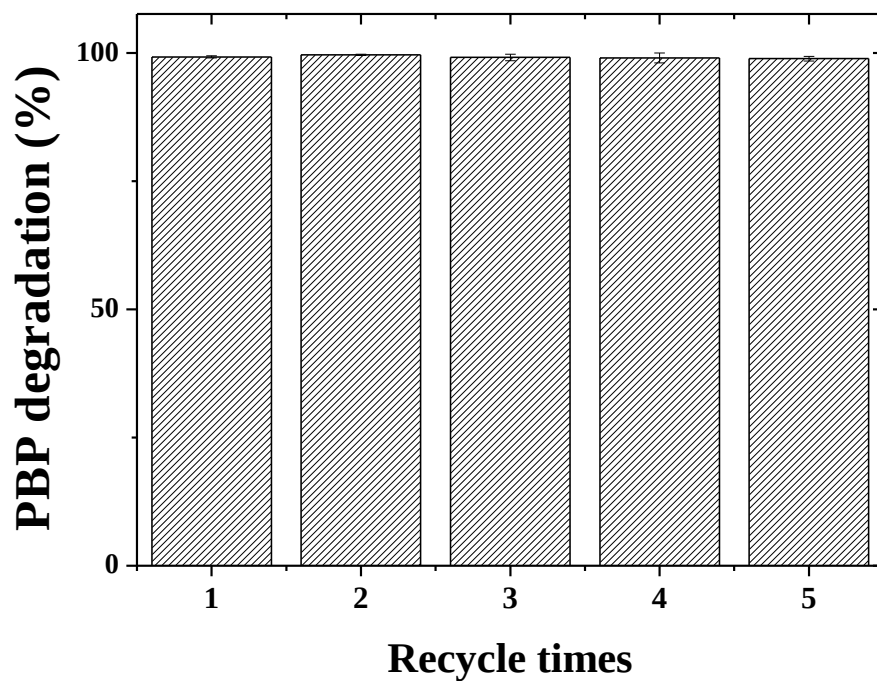
**Fig. 4.3.** The pH dependence on the Zeta potential for SBA-15, CP-SBA-15, and FeTPyP-SBA-15.



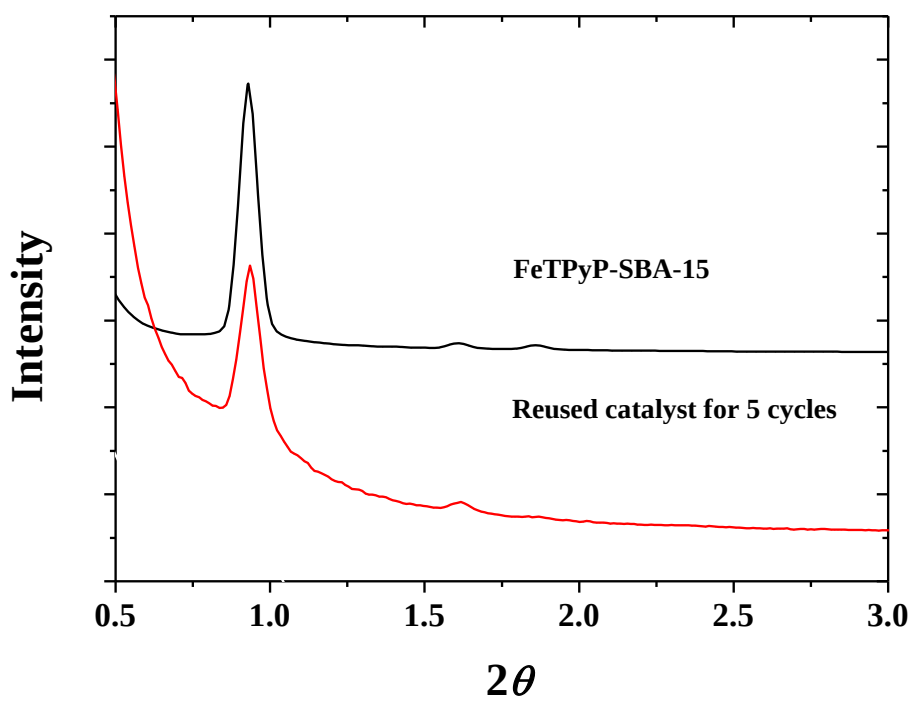
**Fig. 4.4.** FT-IR spectra of SBA-15, CP-SBA-15 and FeTPyP-SBA-15.



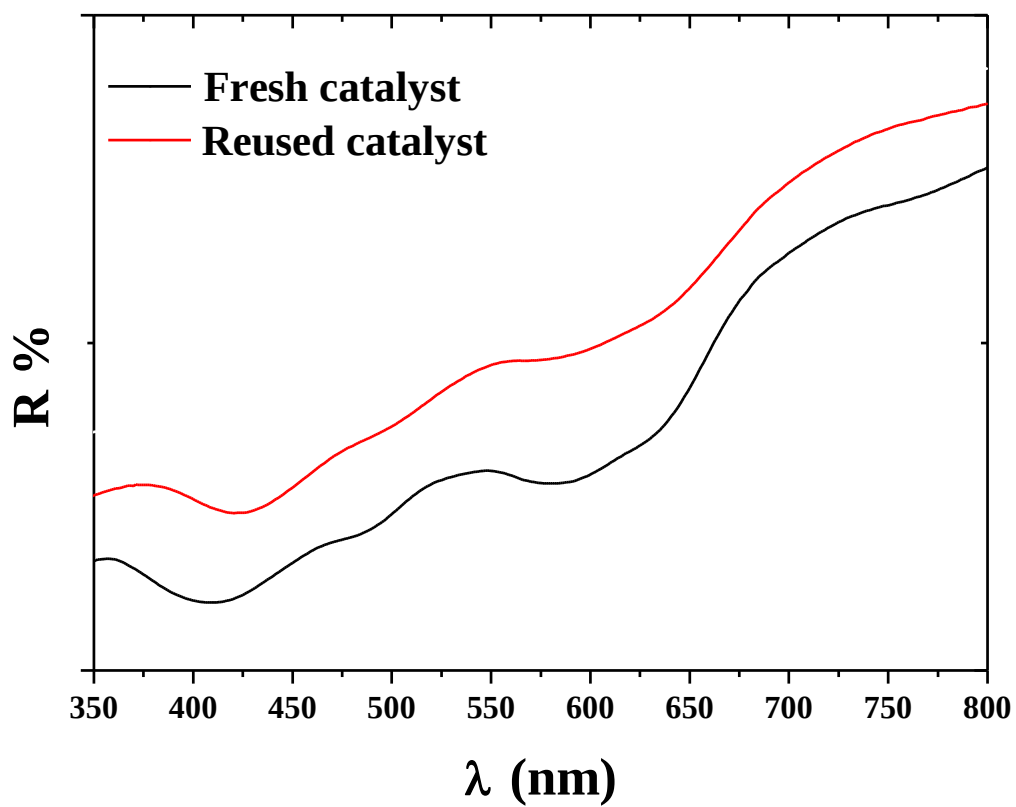
**Fig. 4.5.** The influence of pH on the degradation of PBP. The reaction conditions were as follows: (a)  $[FeTPyP]$  5  $\mu M$ ,  $[KHSO_5]$  125  $\mu M$ ,  $[PBP]$  50  $\mu M$ ,  $[SHA]$  50  $mg\ L^{-1}$ , reaction time 0.5 h; (b)  $[FeTPyP-SBA-15]$  0.1  $g\ L^{-1}$  (2.3  $\mu M$ ),  $[KHSO_5]$  125  $\mu M$ ,  $[PBP]$  50  $\mu M$ ,  $[SHA]$  25  $mg\ L^{-1}$ , reaction time 4 h. ■ PBP degradation, in the absence of SHA, ● PBP degradation, in the presence of SHA, ▲ Debromination, in the absence of SHA, ▼ Debromination, in the presence of SHA



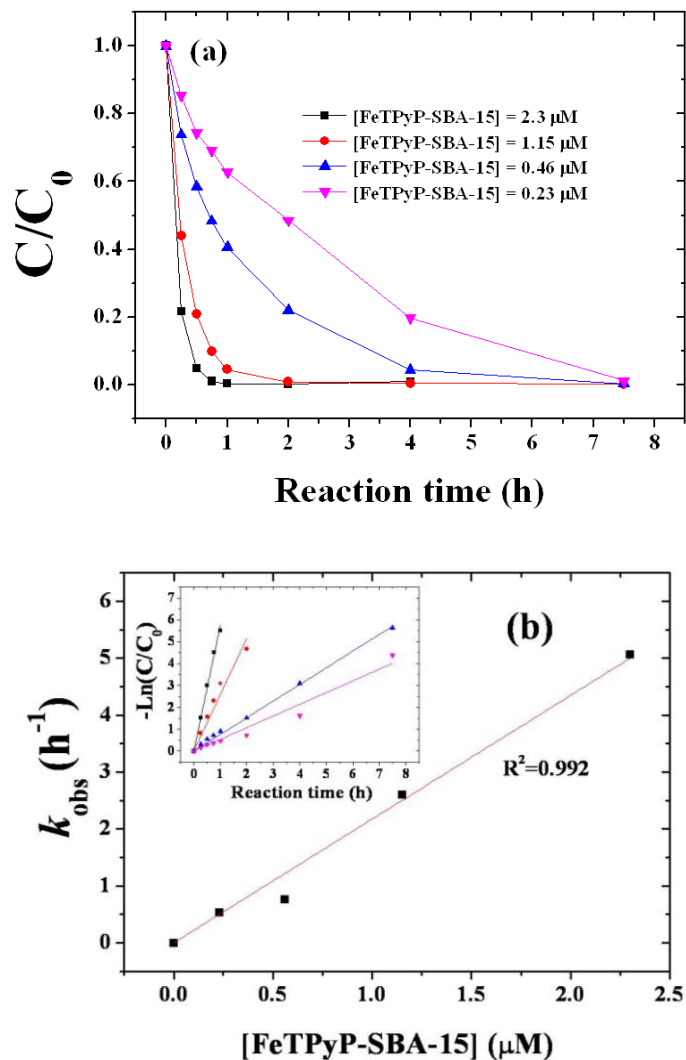
**Fig. 4.6.** The reusability of FeTPyP-SBA-15. Reaction conditions were as follows: [FeTPyP-SBA-15]  $0.1 \text{ g L}^{-1}$  ( $2.3 \text{ }\mu\text{M}$ ), [PBP]  $50 \text{ }\mu\text{M}$ , [ $\text{KHSO}_5$ ]  $125 \text{ }\mu\text{M}$ , reaction time 4 h.



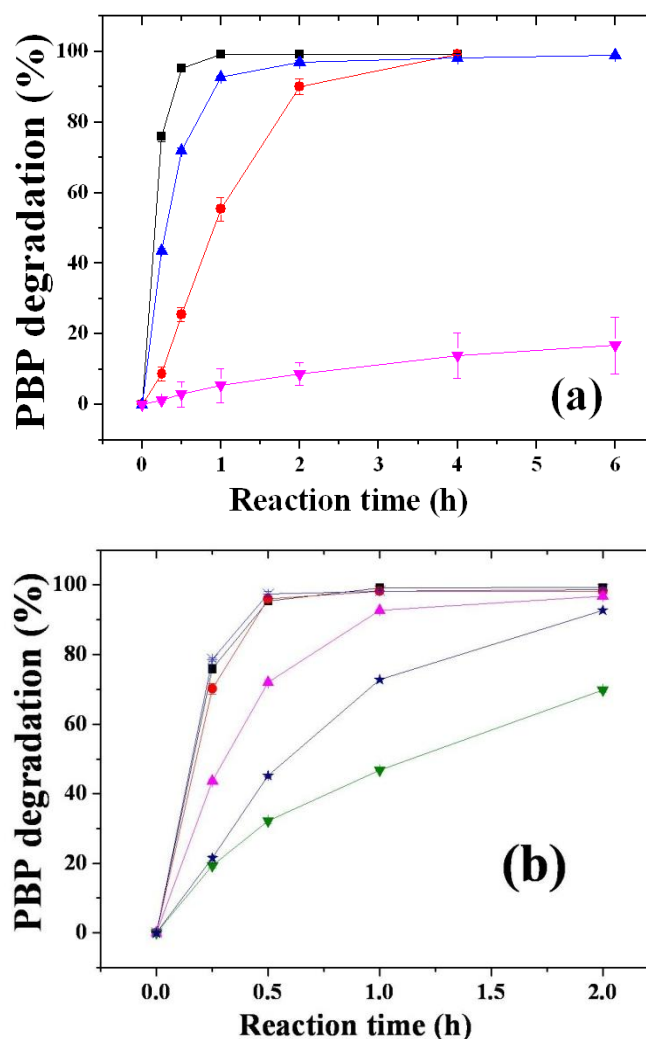
**Fig. 4.7.** Small angle XRD patterns of FeTPyP-SBA-15 and recycled FeTPyP-SBA-15



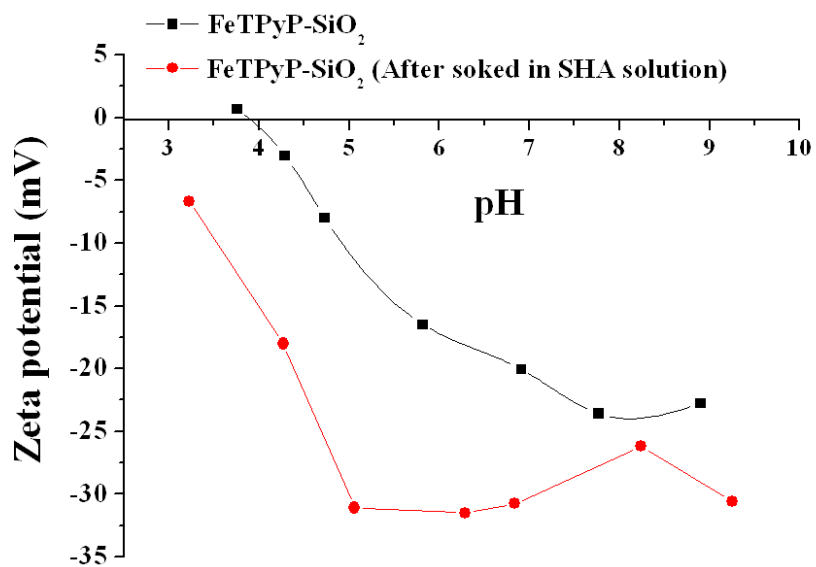
**Fig. 4.8.** Diffuse reflectance UV-vis spectra of FeTPyP-SBA-15 and recycled FeTPyP-SBA-15



**Fig. 4.9.** The influence of FeTPyP-SBA-15 dosage on the kinetics of degradation of PBP (a) and the relationship between pseudo-first-order rate constant ( $k$ ) and catalyst concentration (b). Insertion of (b) shows the kinetic interpretations for pseudo-first-order reaction. The reaction conditions were as follows:  $[\text{FeTPyP-SBA-15}]$  0.01 g L<sup>-1</sup> (0.23 μM), 0.02 g L<sup>-1</sup> (0.46 μM), 0.05 g L<sup>-1</sup> (1.15 μM), 0.1 g L<sup>-1</sup> (2.3 μM),  $[\text{PBP}]$  50 μM,  $[\text{KHSO}_5]$  125 μM.



**Fig. 4.10.** Kinetics of degradation of PBP with the FeTPyP-SBA-15 or FeTPyP-SiO<sub>2</sub> catalyst in the presence or absence of SHA. (a) ■ [FeTPyP-SBA-15] 0.1 g L<sup>-1</sup> (2.3 μM), ● [FeTPyP-SBA-15] 0.1 g L<sup>-1</sup> (2.3 μM), [SHA] 25 mg L<sup>-1</sup>, ▲ [FeTPyP-SiO<sub>2</sub>] 0.1 g L<sup>-1</sup> (0.6 μM), ▼ [FeTPyP-SiO<sub>2</sub>] 0.1 g L<sup>-1</sup> (0.6 μM), [SHA] 25 mg L<sup>-1</sup>, (b) ■ [FeTPyP-SBA-15] 0.1 g L<sup>-1</sup> (2.3 μM), ● [FeTPyP-SBA-15] 0.1 g L<sup>-1</sup> (2.3 μM), [SHA] 25 mg L<sup>-1</sup>, ▲ [FeTPyP-SiO<sub>2</sub>] 0.4 g L<sup>-1</sup> (2.4 μM), ▼ [FeTPyP-SiO<sub>2</sub>] 0.4 g L<sup>-1</sup> (2.4 μM), [SHA] 25 mg L<sup>-1</sup>, \* [FeTPyP-SBA-15] 0.5 g L<sup>-1</sup> (2.4 μM) ★ [FeTPyP-SBA-15] 0.5 g L<sup>-1</sup> (2.4 μM), [SHA] 25 mg L<sup>-1</sup>. The other reaction conditions were as follows: [KHSO<sub>5</sub>] 125 μM, [PBP] 50 μM.



**Fig. 4.11.** The pH dependence on the Zeta potential of FeTPyP-SiO<sub>2</sub> and the FeTPyP-SiO<sub>2</sub> after soaking in a SHA solution.

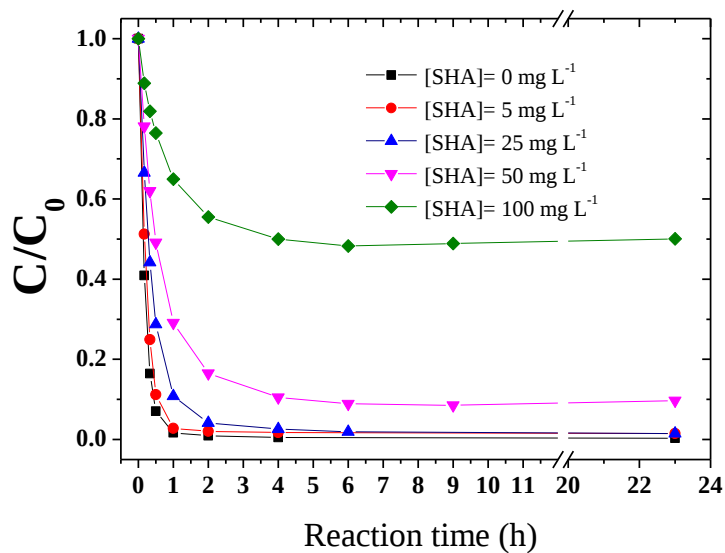
**Table 4.3.**

Summary of average particle sizes for each HS, pseudo-first-order rate constants ( $k$ ) and turnover frequency (TOF) in the presence of 50 mg L<sup>-1</sup> HSs.

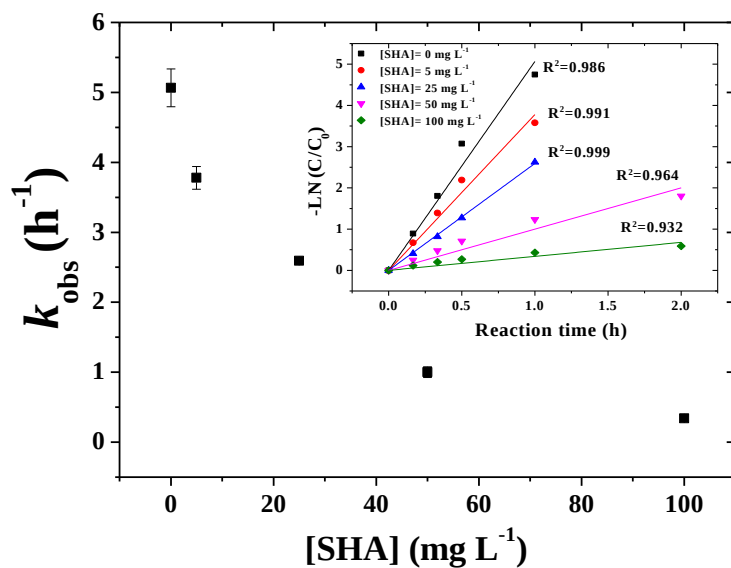
| HS Samples | Average particle size (nm) <sup>a</sup> | $k$ (h <sup>-1</sup> ) | TOF (h <sup>-1</sup> ) |
|------------|-----------------------------------------|------------------------|------------------------|
| SHA        | 31.3 <sup>b</sup> , 67.9                | 0.93                   | 22.2                   |
| NHA        | 137                                     | 0.88                   | 19.0                   |
| NFA        | ND <sup>c</sup>                         | 1.19                   | 22.3                   |
| SFA        | ND <sup>c</sup>                         | 1.35                   | 23.2                   |
| NOM        | ND <sup>c</sup>                         | 1.95                   | 33.8                   |

<sup>a</sup> Number distribution. <sup>b</sup> The sample was analyzed after 20 min centrifugation (10000 rpm). <sup>c</sup> The particle size distributions for these samples could not be determined.

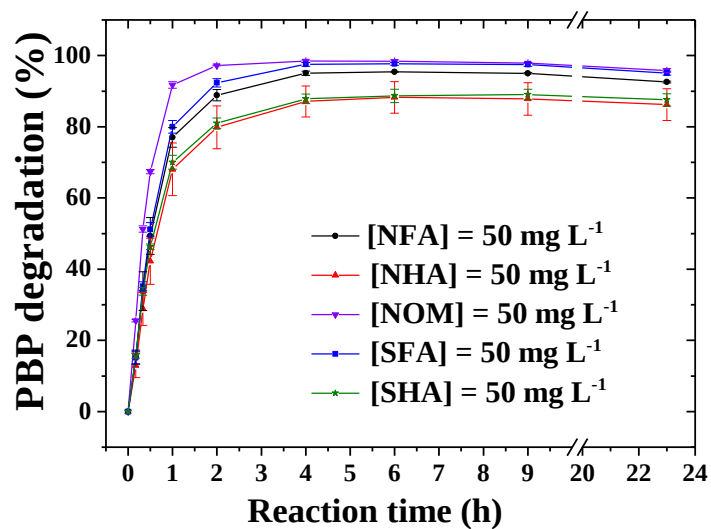
(a)



(b)



**Fig. 4.12.** Influence of SHA concentration on the degradation of PBP ((a) PBP degradation, (b) PBP degradation kinetics.). Reaction conditions were as follows: [FeTPyP-SBA-15], 0.1 g L<sup>-1</sup> (2.3 μM), [PBP], 50 μM, [KHSO<sub>5</sub>], 125 μM.



**Fig. 4.13.** Influence of HSs type on the kinetics of degradation of PBP. Reaction conditions were as follows:  $[\text{FeTPyP-SBA-15}]$   $0.1 \text{ g L}^{-1}$  ( $2.3 \text{ }\mu\text{M}$ ),  $[\text{PBP}]$   $50 \text{ }\mu\text{M}$ ,  $[\text{KHSO}_5]$   $125 \text{ }\mu\text{M}$ ,  $[\text{HSs}]$   $50 \text{ mg L}^{-1}$ .

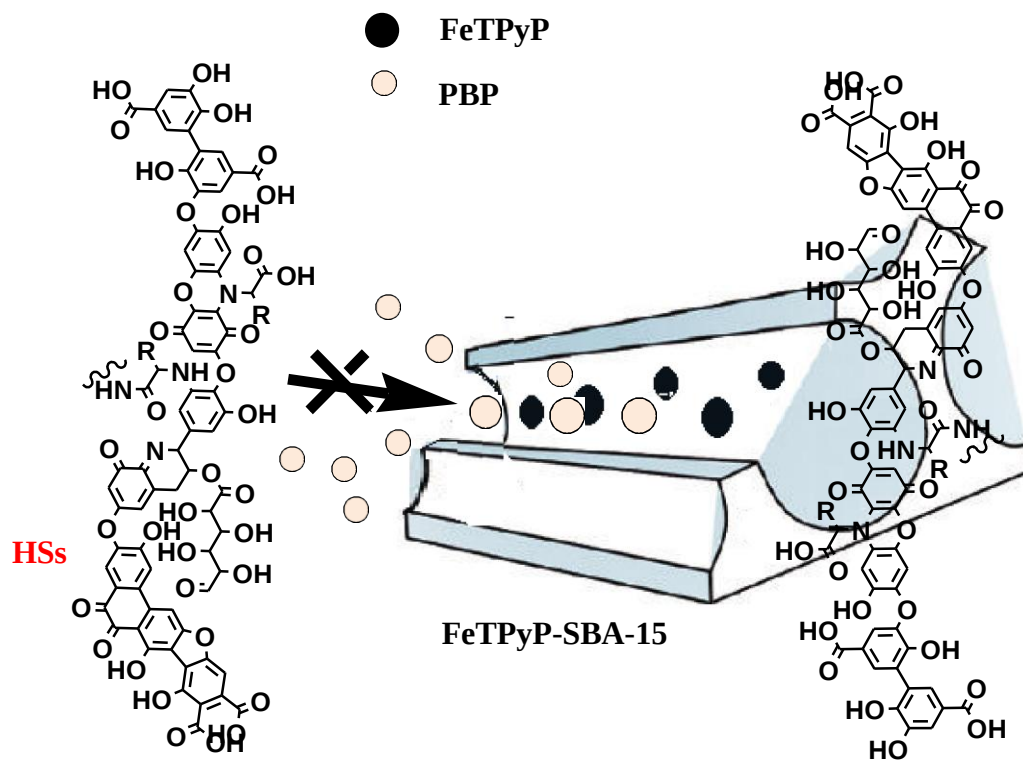


Fig. 4.14. The proposed reaction processes for FeTPyP-SBA-15.

## 4.5. References

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# Chapter 5

*Monopersulfate oxidation of 2,4,6-tribromophenol using  
an iron(III)-tetrakis(p-sulfonatephenyl) porphyrin  
catalyst supported on an ionic liquid functionalized  
 $Fe_3O_4$  coated with silica*

## 5.1. Introduction

Iron(III)-porphyrins have high catalytic activity for the oxidation of halogenated phenols in homogeneous and heterogeneous systems [1–14]. However, the practical use of iron(III)-porphyrins in homogenous systems was restricted due to the deactivation and unrecyclable. To circumvent those problems, iron(III)-porphyrin catalysts are supported on solids, such as  $SiO_2$  [6,7,12,13,15], mesoporous silica [5], polymers [13] and ion-exchange resins [4,16] to suppress self-degradation and enhance their recyclability. However, the catalytic activities (e.g., TOF and mineralization) of such complexes have not been correspondingly increased because of mass transfer limitations, the leaching of catalysts from the solid support, coverage of substrates and/or byproducts and competitive inhibition by other contaminants, such as HAs, in leachates [5–7]. In terms of catalytic activities, homogeneous catalytic systems are more advantageous than heterogeneous systems. For example, homogeneous iron(III)-porphyrin catalysts that are incorporated into polyelectrolytes can be used to mineralize chlorophenols [1,14].

To overcome the disadvantages associated with heterogeneous catalysts, “liquid phase” methodologies have been introduced into solid catalysts in attempts to “restore” homogeneous catalytic conditions. For this purpose, ionic liquids (ILs) can be used as mobile and versatile “carriers” [17–21]. Supported-IL-phase (SILP) catalysts have recently been reported to be an alternative approach for the development of novel heterogeneous catalysts with advantages in facilitating separation workup and “restoring” homogeneous catalytic efficiency [22–24]. Among the numerous solid supports that have been applied to SILP catalysts, magnetite ( $Fe_3O_4$ ) has attached considerable

attention due to the capability of magnetic separation [25], and this is advantageous in practical use of such catalysts. In the present study, the IL was covalently anchored on the surface of  $Fe_3O_4$  coated with silica and an iron(III)-tetrakis(*p*-sulfonatephenyl)porphyrin (FeTPPS) was introduced via the formation of an ion-pair by electrostatic interactions. The synthesized  $Fe_3O_4$ -IL-FeTPPS catalyst was characterized, and its catalytic activities were evaluated with respect to the oxidation of TrBP (degradation kinetics, inhibition by HA and mineralization).

## 5.2. Materials and Methods

### 5.2.1. Materials

The soil HA (SHA) sample used in this study was extracted from a Shinshinotsu peat soil, as described in a previous report [26]. The FeTPPS was synthesized as described in a previous report [27].  $FeCl_3$ , TrBP, ethylene glycol,  $CH_3COONa$ , 3-chloropropyltrimethoxysilane (CPTMS), 1-methylimidazole and tetraethyl orthosilicate (TEOS) were purchased from Tokyo Chemical Industry. 2,6-Dibromo-*p*-benzoquinone (DBQ) was synthesized as described in a previous report [4]. Potassium monopersulfate ( $KHSO_5$ ) was obtained as a triple salt,  $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$  (Merck). 5,5-Dimethyl-1-pyrrolidine-*N*-oxide (DMPO, 99%) was purchased from Labotec.

### 5.2.2. Synthesis of $Fe_3O_4$ -IL-FeTPPS

The synthesis of the  $Fe_3O_4$ -IL-FeTPPS catalyst is summarized in Scheme 5.1.

*Synthesis of  $Fe_3O_4$*

The  $\text{Fe}_3\text{O}_4$  was synthesized through a hydrothermal reaction according to the procedures reported by Zhang et al. [25] with minor modifications. Briefly,  $\text{FeCl}_3$  (0.8 g) was dissolved in ethylene glycol (40 mL) to form a clear solution under magnetic stirring.  $\text{CH}_3\text{COONa}$  (2.7 g) and polyethylene glycol (1.0 g) were then added to the solution and the resulting solution was stirred vigorously for 30 min and then sealed in a Teflon-lined stainless-steel autoclave (50-mL capacity). The autoclave was heated to 200 °C and maintained at that temperature for 8 h. After cooling to room temperature, the black-colored products were washed several times with water, ethanol and then dried *in vacuo* at room temperature.

#### *Synthesis of IL functionalized $\text{Fe}_3\text{O}_4$*

A 0.10 g portion of  $\text{Fe}_3\text{O}_4$  particles (~ 300 nm in diameter) was treated with a 0.01 M HCl aqueous solution (50 mL) by ultrasonic irradiation. After treating for 10 min, the  $\text{Fe}_3\text{O}_4$  particles were separated using a magnet and washed with ultrapure water, and then homogeneously dispersed in a mixture of ethanol (80 mL), ultrapure water (20 mL) and a concentrated aqueous ammonia solution (1.0 mL, 28 wt.%), followed by the addition of TEOS (0.03 g, 0.144 mmol). After stirring for 6 h at room temperature, the silica coated ( $\text{Fe}_3\text{O}_4\text{-SiO}_2$ ) microspheres were separated, washed with ethanol, water, and then dried *in vacuo*. The prepared  $\text{Fe}_3\text{O}_4\text{-SiO}_2$  (0.1g) was redispersed in 80 mL ethanol containing concentrated ammonia aqueous (1.00 mL, 28 wt %) by ultrasonication. The mixed solution was homogenized by mechanical stirring for 0.5 h to form a uniform dispersion. The IL (1-methyl-3-(triethoxysilylpropyl)-imidazolium chloride) was then synthesized according to a previous report [28], and 0.1 g of the prepared IL was then added dropwise to the dispersion with continuous stirring. After stirring for 24 h, the product was collected with a magnet, washed several times with

ethanol and water. Finally, the IL coated Fe<sub>3</sub>O<sub>4</sub> (Fe<sub>3</sub>O<sub>4</sub>-IL) was dried at room temperature *in vacuo*.

#### *Incorporation of FeTPPS into the IL functionalized Fe<sub>3</sub>O<sub>4</sub>*

The Fe<sub>3</sub>O<sub>4</sub>-IL (0.6 g) was dispersed in 30 mL of a FeTPPS aqueous solution (3 mM) followed by shaking in an incubator at 25 °C for 42 h. After the reaction, the product was collected with a magnet and washed repeatedly with ultra-pure water until no Q-band for FeTPPS at 529 nm was detected in UV-vis absorption spectra. The final product, Fe<sub>3</sub>O<sub>4</sub>-IL-FeTPPS, was dried at room temperature *in vacuo* for 24 h.

#### **5.2.3. Characterization of the synthesized catalyst**

The loading amount of FeTPPS into the Fe<sub>3</sub>O<sub>4</sub>-IL-FeTPPS catalyst was estimated using UV-visible absorption spectroscopy on a V-650 iRM type spectrophotometer (Japan Spectroscopic Co. Ltd.). X-ray diffraction (XRD) patterns were collected using a RINT 2200 X-ray analyzer (Rigaku) with Cu K $\alpha$  radiation. Transmission electron microscopy-Energy dispersive X-Ray (TEM-EDX) measurements were carried out on a JEM-2100F instrument (JEOL) at an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) images were obtained with a JEOL JSM-6501L instrument (JEOL). The Zeta potential and particle size of the samples were recorded on an ELSZ-1000 type Zeta-potential & Particle size Analyzer (Otsuka Electronics Co. Ltd).

#### **5.2.4. Assay for TrBP degradation**

A 20 mL aliquot of a 0.02 M phosphate buffer (pH 4 – 8) was placed in a 100-mL Erlenmeyer flask. A 400  $\mu$ L aliquot of 0.01 M TrBP in acetonitrile and 20 mg of catalyst were then added to the buffer. A 100  $\mu$ L aliquot of 0.1 M aqueous KHSO<sub>5</sub> was added,

and the flask was then allowed to shake at 25 °C in an incubator. After the reaction, the concentrations of the remaining TrBP and a major degradation intermediate, DBQ, were measured by a standard method using HPLC with a UV detector. Separation was accomplished with a COSMOSIL 5C<sub>18</sub>-AR-II column (4.6 × 250 mm). The mobile phase was a mixture of methanol and water (68:32 in volume), acidified with aqueous 0.08% H<sub>3</sub>PO<sub>4</sub>. The flow rate was set at 1.0 mL min<sup>-1</sup>, and the detection wavelength was at 290 nm. The released Br<sup>-</sup> was analyzed by ion chromatography (ICS-90 type, Dionex). The mobile phase was a solution of 2.7 mM Na<sub>2</sub>CO<sub>3</sub> and 0.3 mM NaHCO<sub>3</sub>, and the flow rate was set at 1.5 mL min<sup>-1</sup>. Electron Spin Resonance (ESR) spectra were recorded at room temperature using a quartz flat cell on a JEOL JES-TE300 ESR Spectrometer under the following conditions: microwave power 10 mW; microwave frequency 9.42 GHz; magnetic field 335 mT; field amplitude ± 5 mT; modulation amplitude 0.079 mT; modulation width 20 μT; sweep time 2 min; and the time constant was 0.03 s. The Fe in the aqueous phase of the reaction mixture was determined by ICP-AES (ICPE9000, Shimadzu).

### 5.3. Results and Discussion

#### 5.3.1. Characterization of $Fe_3O_4$ and $Fe_3O_4$ -IL-FeTPPS

Analysis of the loading amount of FeTPPS in the  $Fe_3O_4$ -IL by UV-vis absorption spectra showed that content of FeTPPS in the  $Fe_3O_4$ -IL-FeTPPS catalyst was estimated to be 4.2 μmol g<sup>-1</sup>.

The morphology of  $Fe_3O_4$ ,  $Fe_3O_4$ -IL and  $Fe_3O_4$ -IL-FeTPPS microspheres was examined from SEM images. The SEM image shown in Fig. 5.1, suggested that the

particles formed sphere-like shapes. These microspheres appeared to be well-distributed with an average diameter about 300 nm. The XRD patterns in Fig. 5.2 showed that the diffraction peaks for the  $\text{Fe}_3\text{O}_4$ -IL-FeTPPS and  $\text{Fe}_3\text{O}_4$  microspheres had similar locations, in good agreement with a previous report [25], in which the synthesized  $\text{Fe}_3\text{O}_4$ -IL-FeTPPS microspheres were reported to have the same crystal structure as naked  $\text{Fe}_3\text{O}_4$  particles. The EDX spectra of  $\text{Fe}_3\text{O}_4$ - $\text{SiO}_2$  and  $\text{Fe}_3\text{O}_4$ -IL microspheres confirm the successful functionalization of the coating of the silica layer and the IL on the magnetic core. The strong silica peak appeared in the TEM-EDX spectrum of  $\text{Fe}_3\text{O}_4$ - $\text{SiO}_2$  (Fig. 5.3a.) and the chlorine peak (Fig. 5.3b), which was likely derived from a counter anion of IL, was clearly visible in the TEM-EDX spectrum of the  $\text{Fe}_3\text{O}_4$ -IL. In addition, the Fe signal in the XPS spectrum of  $\text{Fe}_3\text{O}_4$ -IL had disappeared, compared with naked  $\text{Fe}_3\text{O}_4$  (Fig. 5.4). These results suggest that the  $\text{Fe}_3\text{O}_4$  surfaces were successfully coated with silica and IL.

Changes in the surface chemistry of the magnetite were characterized from zeta potential data, which is related to the surface charge (Fig. 5.5). Unmodified  $\text{Fe}_3\text{O}_4$  had a positive surface charge at pH values below 4.6 and a negative charge at pH values higher than 4.6 due to the dissociation of acidic surface hydroxyl groups. The point of zero charge (PZC) of  $\text{Fe}_3\text{O}_4$ -IL shifted to lower a pH value at 3.7, consistent with IL being modified on the  $\text{Fe}_3\text{O}_4$ - $\text{SiO}_2$  surface. However, the PZC for  $\text{Fe}_3\text{O}_4$ -IL-FeTPPS was similar to that for  $\text{Fe}_3\text{O}_4$ . This may be due to the introduction of FeTPPS as an anionic porphyrin. The higher negative zeta potential values above pH 4.7 indicate that the  $\text{Fe}_3\text{O}_4$ -IL-FeTPPS had a larger amount of negative charge, compared to  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4$ -IL.

### 5.3.2. Comparison of catalytic activities for $Fe_3O_4$ , $Fe_3O_4$ -IL and $Fe_3O_4$ -IL-FeTPPS

The catalytic activities of  $Fe_3O_4$ ,  $Fe_3O_4$ -SiO<sub>2</sub>,  $Fe_3O_4$ -IL, and  $Fe_3O_4$ -IL-FeTPPS were investigated for a  $[KHSO_5]_0/[TrBP]_0 = 2.5$ . The initial concentrations of TrBP and  $KHSO_5$  were set at 200  $\mu$ M and 500  $\mu$ M, respectively. Although the naked  $Fe_3O_4$  showed catalytic activity for the degradation of TrBP, around 40% of the TrBP was degraded within 4 h. As shown in the ESR spectra (Fig. 5.7), in the presence of  $KHSO_5$  and  $Fe_3O_4$ , a nine-line peak in the ESR spectrum with hyperfine splitting constants of  $A_N = 7.2$  G and  $A_H (2H) = 4.2$  G were observed, which was identified as DMPOX (5,5-dimethyl-2-oxo-pyrroline-1-oxyl), as assigned previously [29]. The DMPOX signal disappeared after 18 min and peaks corresponding to  $^{\bullet}DMPO-HO$  then appeared in the presence of  $Fe_3O_4$  (Fig. 5.7.). The activation of  $KHSO_5$  may produce sulfate, peroxy-sulfate and hydroxyl radicals [30]. Hydroxyl radicals may be generated by the reaction of sulfate radical with H<sub>2</sub>O [30]. To identify the major reactive species generated in the  $Fe_3O_4/KHSO_5$  system, alcohols were added to reaction solution as quenching agents. Ethanol (EtOH) reacts with  $HO^{\bullet}$  and  $SO_4^{\bullet-}$  at high and comparable rates [31]. However, *tert*-butyl alcohol (TBA) reacts with  $HO^{\bullet}$  faster than with  $SO_4^{\bullet-}$  [31]. As shown in Fig. 5.8, when no quenching agents were added, about 40% of the TrBP was degraded in 4 h. However, the addition of 0.1 M TBA and 0.1 M EtOH resulted in a decreased TrBP removal (in 4 h) to 36% and 17%, respectively. The much larger decrease in the removal of TrBP in the presence of EtOH than by TBA suggests that the main radical species generated during the activation of  $KHSO_5$  by  $Fe_3O_4$  were sulfate radicals. However, due to the lower sensitivity and short lifetime of  $^{\bullet}DMPO-SO_4^-$ , a signal for  $^{\bullet}DMPO-SO_4^-$  was not detected [32]. Those results suggest that  $SO_4^{\bullet-}$  is a critical factor in the degradation of TrBP using the  $Fe_3O_4/KHSO_5$  system.

After coating the Fe<sub>3</sub>O<sub>4</sub> surface with silica and IL, the catalytic activities for Fe<sub>3</sub>O<sub>4</sub>-SiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>-IL decreased significantly. The intensity of the <sup>•</sup>DMPO-HO peaks remarkably decreased in the Fe<sub>3</sub>O<sub>4</sub>-IL/KHSO<sub>5</sub> system (Fig. 5.9a). This suggests that the surface ferrous ions of Fe<sub>3</sub>O<sub>4</sub> play a key role in the generation of SO<sub>4</sub><sup>•-</sup>.

As shown in Fig. 5.6, Fe<sub>3</sub>O<sub>4</sub>-IL-FeTPPS significantly enhanced the catalytic oxidation of TrBP (TOF, 54.1 h<sup>-1</sup> at 0.67 h of period). However, except for the DMPOX peak at 5 min, no other radical species were observed (Fig. 5.9b). The enhanced catalytic activities for the Fe<sub>3</sub>O<sub>4</sub>-IL-FeTPPS may be due to oxo-ferryl porphyrin species derived from the conventional peroxidase shunt pathway [1,9] but this does not account for the production of SO<sub>4</sub><sup>•-</sup>. It has been reported that the platinum nanocatalysts are stabilized in IL, and the catalytic activities for the hydrogenation of chloro-nitrobenzene to chloroaniline are enhanced [33]. The FeTPPS, homogeneous systems show a higher catalytic activity, although the immediate deactivation is caused via the self-degradation [8]. Thus, the higher catalytic activity in the Fe<sub>3</sub>O<sub>4</sub>-IL-FeTPPS/KHSO<sub>5</sub> system may be due to the stabilization of the FeTPPS catalyst in the IL phase and the restoration of homogeneous conditions on the surface of the Fe<sub>3</sub>O<sub>4</sub>.

### 5.3.3. Influence of catalyst dosage on the TrBP degradation

Fig. 5.10 shows the influence of catalyst concentration on the TrBP degradation and DBQ concentration. The pseudo-first-order rate constant for the degradation of TrBP increased with increasing catalyst concentration (Fig. 5.10a). However, the TOF decreased with increasing catalyst concentration. In the presence of 1 and 2 g L<sup>-1</sup> Fe<sub>3</sub>O<sub>4</sub>-IL-FeTPPS, approximately 100% of the TrBP was degraded within 30 min. Fig. 5.10b shows the kinetics of DBQ formation as a result of the oxidation of TrBP. The

DBQ initially increased and then gradually decreased. However, the maximum value and the initial rate for the formation of DBQ increased with increasing  $Fe_3O_4$ -IL-FeTPPS concentration. The reaction time for the highest DBQ level was retarded and the highest DBQ concentration decreased with decreasing catalyst dosage. After the reaching the maximum value, the DBQ concentration decreased gradually, accompanied by the further degradation of DBQ via the oxidation with the  $Fe_3O_4$ -IL-FeTPPS/ $KHSO_5$  catalytic system. Catalyst reusability is an important factor in the evaluation of catalyst stability. The reusability of  $Fe_3O_4$ -IL-FeTPPS was investigated at pH 6. The percent of TrBP degradation remained constant after 3 recyclings (Fig. 5.11). To evaluate the stability of  $Fe_3O_4$  and  $Fe_3O_4$ -IL-FeTPPS, the leaching of iron was measured after 4 h period of TrBP degradation with  $1\text{ g L}^{-1}$  of catalyst. An ICP-AES analysis indicated that the leaching of iron was about  $40\text{ }\mu\text{g L}^{-1}$  in the  $Fe_3O_4$ / $KHSO_5$  system, while less than  $10\text{ }\mu\text{g L}^{-1}$  was found in the case of the  $Fe_3O_4$ -IL-FeTPPS/ $KHSO_5$ .

#### **5.3.4. Influence of pH on the TrBP degradation**

Because the redox potentials of  $KHSO_5$ , TrBP and other dissolved species are pH dependent, the influence of pH on the oxidative degradation of TrBP was investigated after a 2 h incubation period. Fig. 5.12 illustrates the effect of pH on TrBP degradation, the formation of a major oxidation product, DBQ, and the released  $Br^-$ . Concentrations of the degraded TrBP ( $\Delta[\text{TrBP}]$ ) and DBQ ( $[\text{DBQ}]$ ) increased with an increase in pH, reaching a maximum at pH 6, and then decreased at pH values above 6. At pH 4 and 5, the  $[\text{DBQ}]$  was slightly lower than the  $\Delta[\text{TrBP}]$  and the released  $[\text{Br}^-]$  was almost the same as the level of the  $\Delta[\text{TrBP}]$ . These results show that the degraded TrBP is nearly

completely transformed into DBQ and one Br atom is released into the solution. From pH 6 to 8, the  $\Delta[\text{TrBP}]$  and the level of released  $[\text{Br}^-]$  increased, compared to a lower pH range, and 100% of the TrBP was degraded at pH 6.

### 5.3.5. Influence of HA dosage on the TrBP degradation

HAs are a major component of landfill leachates, and play a key role in the leaching, transition and degradation of organic pollutants [34]. It has been reported that HAs function as inhibitors of the degradation of bromophenols [7,8,35]. The inhibition of HA is mainly caused by competition for oxidative species, because HAs contain large amounts of quinones and phenolic moieties and the inhibition occurs via interactions of substrates and/or catalysts due to the colloidal heterogeneous properties of HAs [5,36]. Thus, the influence of HAs on TrBP degradation was investigated in the pH range from 4 to 8 in the presence of  $25 \text{ mg L}^{-1}$  SHA, as summarized in Table 5.1. The  $\Delta[\text{TrBP}]_{\text{HA}}$  and  $\Delta[\text{TrBP}]$  in Table 5.1 represent the concentrations of degraded TrBP in the presence and absence of SHA ( $25 \text{ mg L}^{-1}$ ), respectively. Values lower than 1 indicate the inhibition of TrBP degradation by SHA. The degradation of TrBP was not inhibited at pH 4 – 6, while inhibition was observed at pH 7 and 8. As shown in Fig. 5.12, the formation of the major byproduct, DBQ, indicated a maximum value at pH 6, in which DBQ formation was slightly inhibited. Debromination was slightly inhibited in the presence of SHA at pH 4, 6 and 7, while substantial inhibition by SHA was observed at pH 8.

Because of the highest  $\Delta[\text{TrBP}]$ , the influences of SHA concentration on the kinetics of degradation and debromination were investigated at pH 6 (Fig. 5.13). Table 5.2 summarizes the TOF values and pseudo-first-order rate constants ( $k_{\text{obs}}$ ). The TOF

values and  $k_{obs}$  were relatively constant in the presence of 0 – 50 mg L<sup>-1</sup> SHA. However, the presence of 173 mg L<sup>-1</sup> SHA resulted in the significant inhibition of the degradation and debromination of TrBP. For the case of iron(III)-porphyrins supported on the silica surface and mesoporous silica [5–7], only 25 mg L<sup>-1</sup> of SHA led to a significant inhibition of bromophenol oxidation. Thus,  $Fe_3O_4$ -IL-FeTPPS is effective in eliminating the inhibition of TrBP degradation in the presence of HAs.

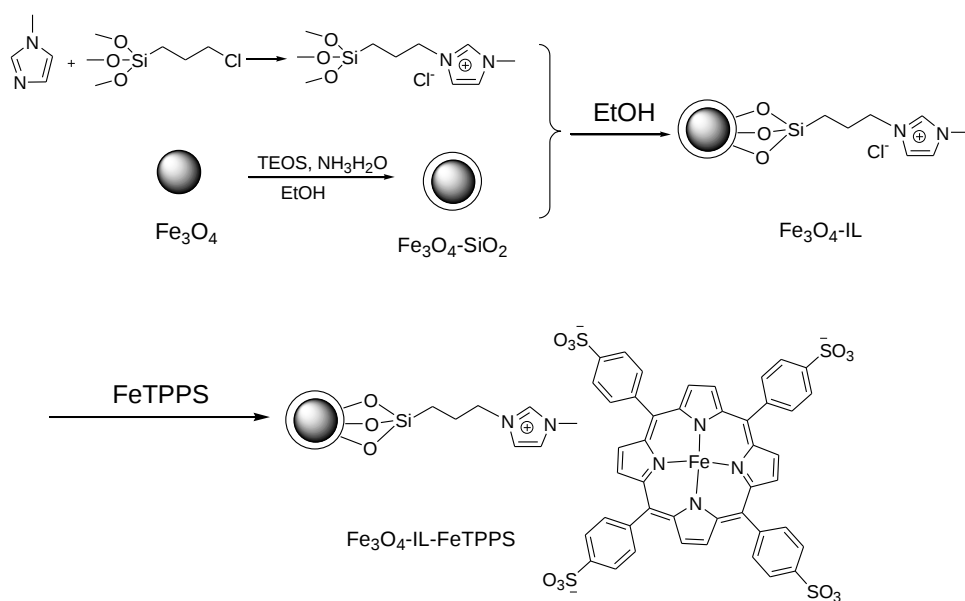
### 5.3.6. The mineralization of TrBP

As shown in Fig. 5.10, DBQ degraded after its formation at the initial stage of the oxidation reaction. The oxidative degradation of a quinone leads to the formation of organic acids via ring-cleavage and then mineralization to CO<sub>2</sub> [37]. There are a few reports on the mineralization of chlorophenols by iron(III)-porphyrins/KHSO<sub>5</sub> catalytic systems [1,14]. However, in the iron(III)-porphyrin/KHSO<sub>5</sub> system, the oxidation of bromophenol is more difficult than those of fluoro- and chlorophenols [38]. Thus, mineralization was examined by the analysis of TOC in a reaction mixture at pH 6. To achieve the mineralization of TrBP, the reaction was examined when KHSO<sub>5</sub> was sequentially added at 24 h intervals (↓ in Fig. 5.14a and 5.14b). In the first 24 h of the reaction, 15% of the TrBP was mineralized when the  $Fe_3O_4$ -IL-FeTPPS catalyst was used. Even though the debromination was observed with  $Fe_3O_4$ , no mineralization was detected. After two additions of KHSO<sub>5</sub>, the mineralization of TrBP significantly increased to 48% in the presence of  $Fe_3O_4$ -IL-FeTPPS catalyst. In the same time, the percent mineralization with  $Fe_3O_4$  was increased to 17%. The highest mineralization (55%) was achieved after adding 3 portions of KHSO<sub>5</sub> with the  $Fe_3O_4$ -IL-FeTPPS catalyst. The mineralization of TrBP in the  $Fe_3O_4$ -IL-FeTPPS/KHSO<sub>5</sub> system was

monitored by UV-vis absorption spectra (Fig. 5.15). The absorption peaks for TrBP at 210 nm, 250 nm and 318 nm disappeared, indicative of the degradation of TrBP. Moreover, as the reaction proceeded, the intensity of an absorption corresponding to a  $\pi$ - $\pi^*$  transition of an aromatic ring in DBQ at 200 – 220 nm and 290 nm in the UV region also decreased, suggesting that DBQ was decomposed and that TrBP had been mineralized. The debromination reaction is shown in Fig 5.14b. Debromination decreased slightly with the addition of  $KHSO_5$  in the  $Fe_3O_4/KHSO_5$  system. In the  $Fe_3O_4$ -IL-FeTPPS/ $KHSO_5$  system, the debromination decreased slightly after the second addition, and 43% of the debromination was achieved after the third addition. The decrease in debromination by sequentially adding  $KHSO_5$  can be attributed to the oxidation of  $Br^-$  [14].

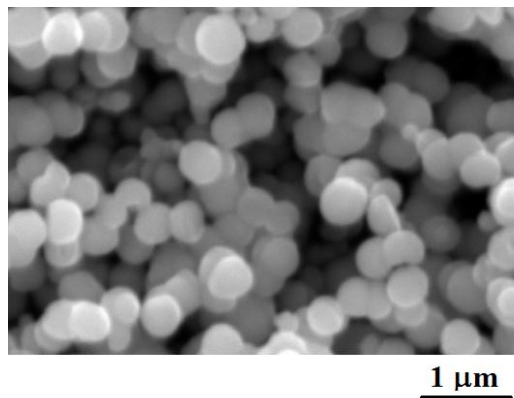
#### 5.4. Conclusion

The  $Fe_3O_4$ -IL-FeTPPS catalyst was found to be effective for TrBP degradation at pH 6. Although the major oxidation product was DBQ, it also disappeared further, suggesting the occurrence of mineralization. 55% of the TrBP was mineralized with the  $Fe_3O_4$ -IL-FeTPPS catalyst. The presence of HA, a major component in leachates, has usually an adverse effect on the oxidation of TrBP. However, significant decrease in catalytic activity for TrBP degradation was not observed in the presence of  $86\text{ mg L}^{-1}$  SHA for the  $Fe_3O_4$ -IL-FeTPPS/ $KHSO_5$  catalytic system. The higher catalytic activity of the  $Fe_3O_4$ -IL-FeTPPS catalyst can be attributed to the fact that the IL modified surface plays an important role in restoring homogeneous catalytic efficiency to the supported FeTPPS.

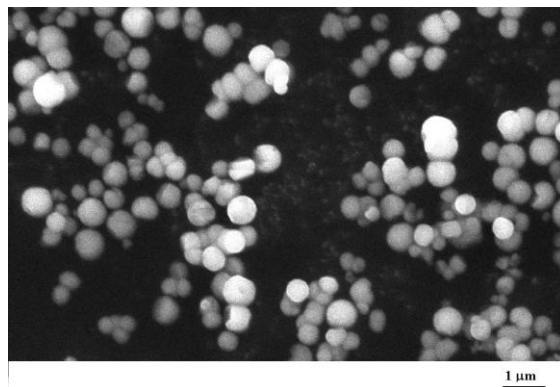


**Scheme 5.1.** Synthesis of the  $Fe_3O_4$ -IL-FeTPPS catalyst.

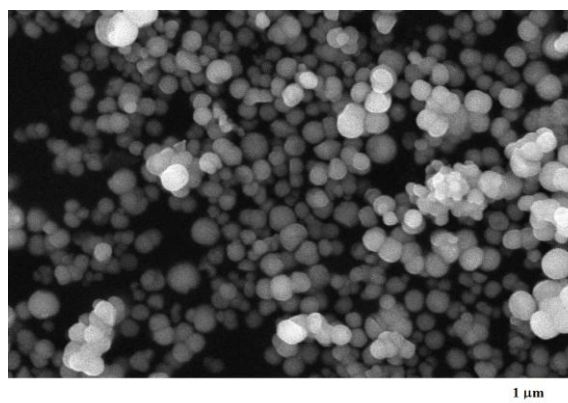
(a)



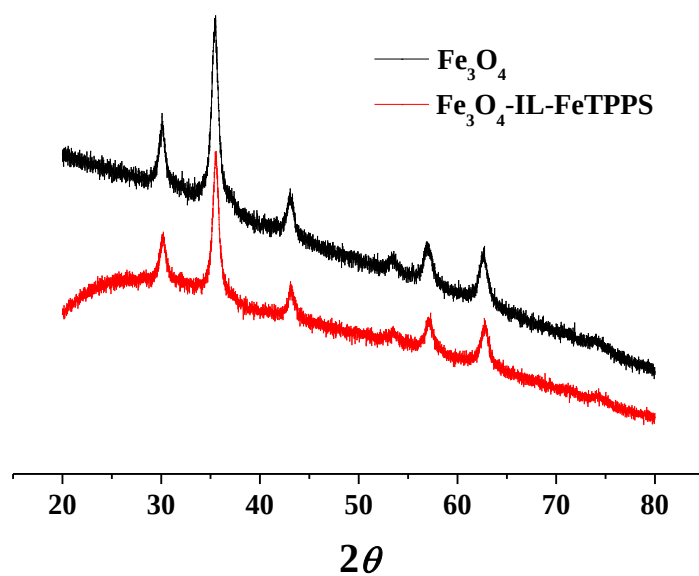
(b)



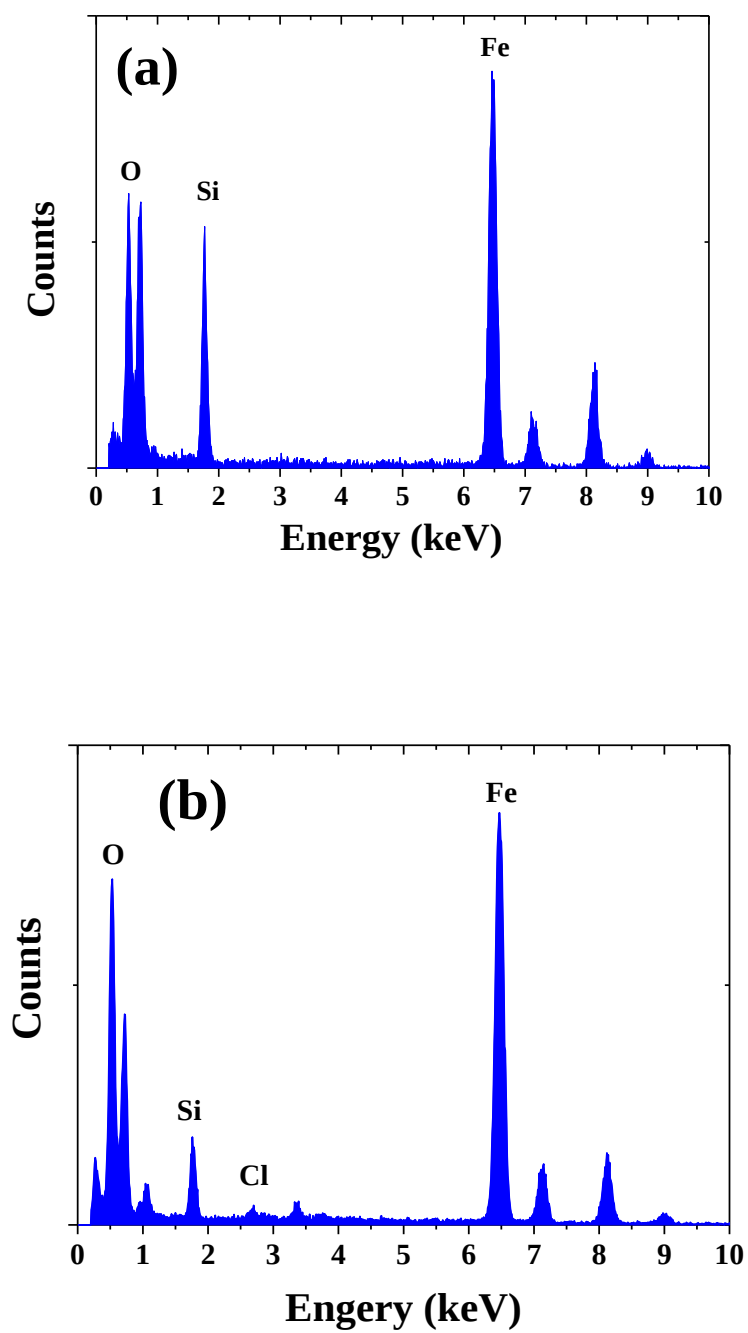
(c)



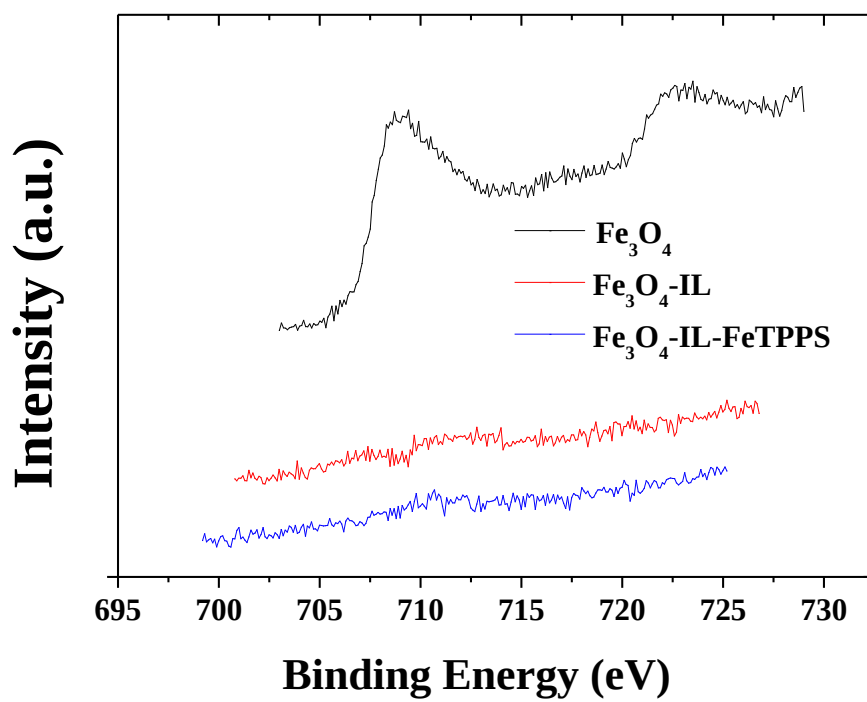
**Fig. 5.1.** SEM image of  $Fe_3O_4$  (a),  $Fe_3O_4$ -IL (b) and  $Fe_3O_4$ -IL-FeTPPS (c).



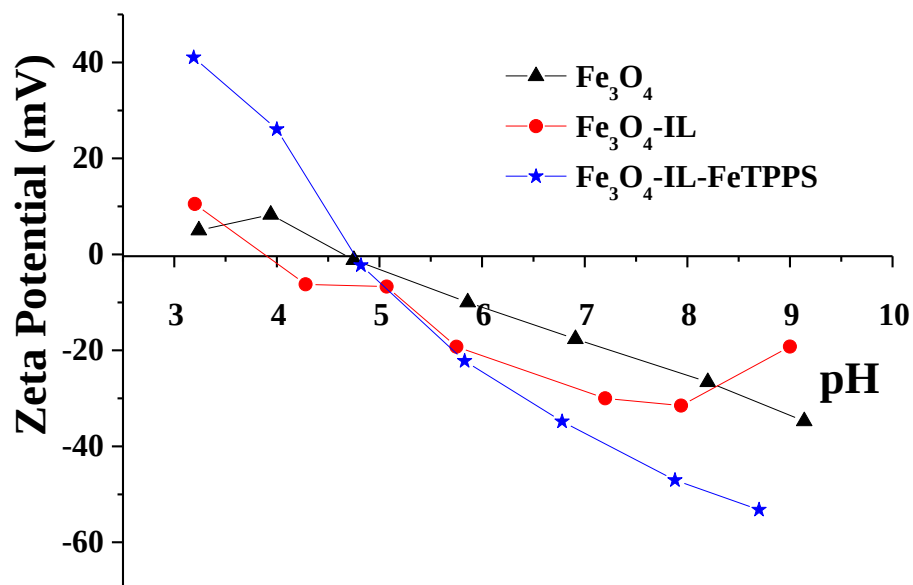
**Fig. 5.2.** XRD patterns of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4$ -IL-FeTPPS.



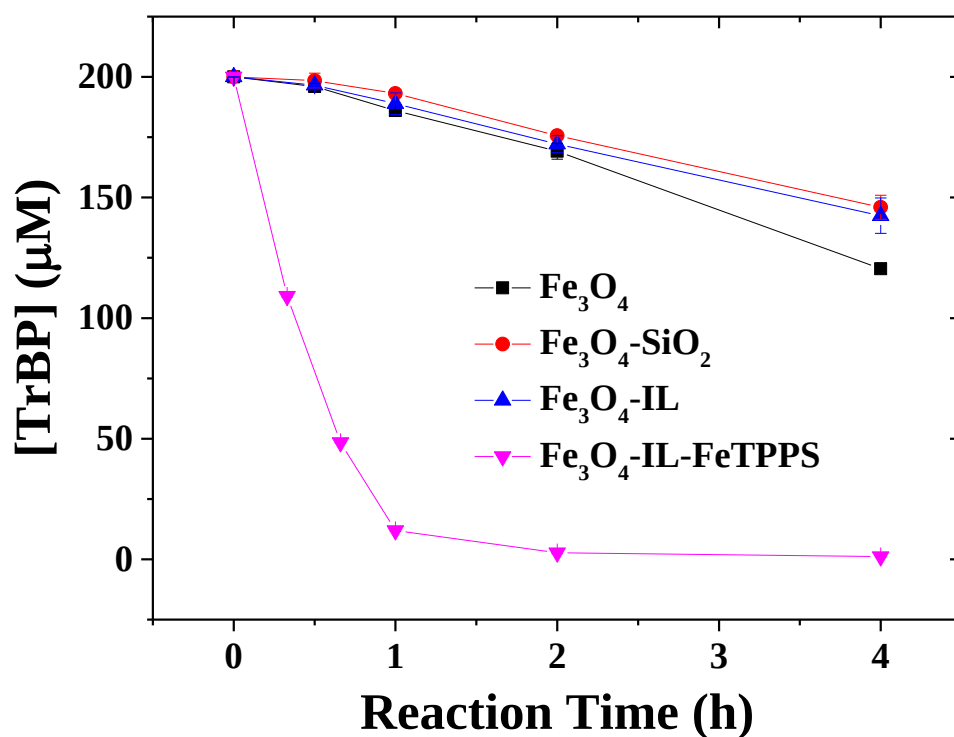
**Fig. 5.3.** TEM-EDX spectra of  $Fe_3O_4$ - $SiO_2$  (a) and  $Fe_3O_4$ -IL (b).



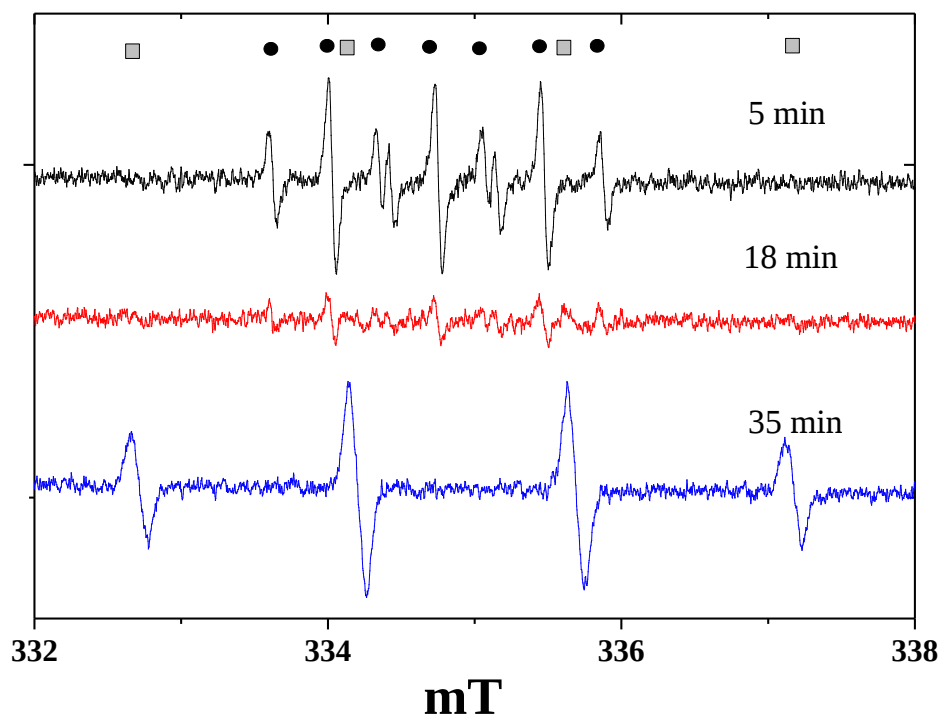
**Fig. 5.4.** XPS spectrum of  $Fe_3O_4$ ,  $Fe_3O_4$ -IL and  $Fe_3O_4$ -IL-FeTPPS.



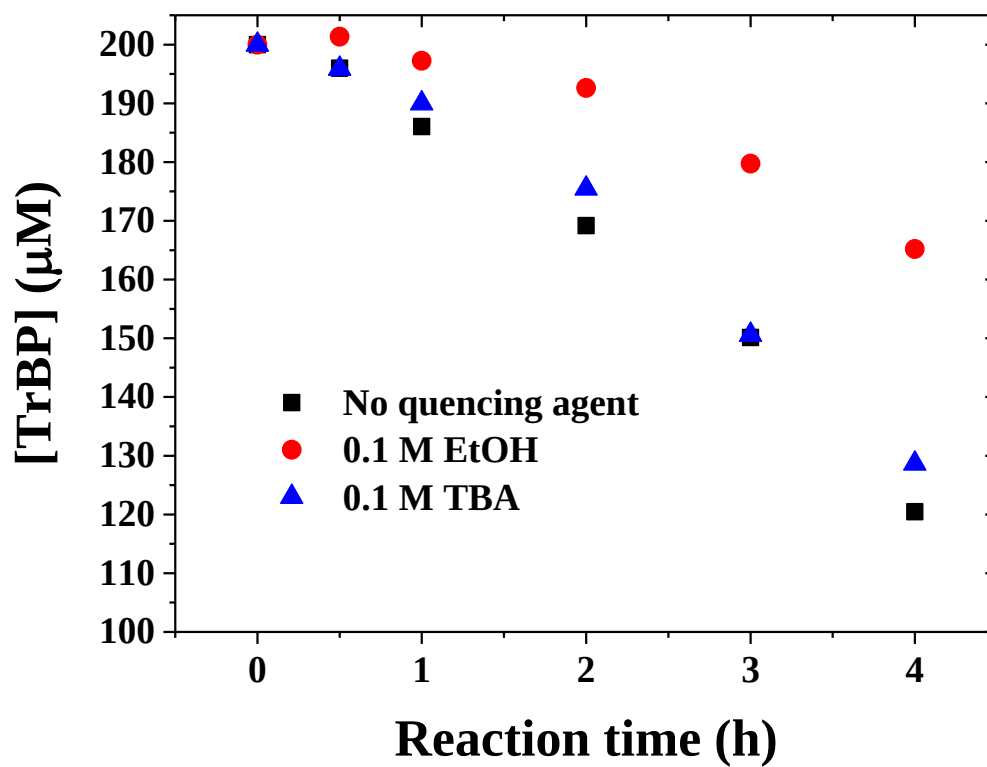
**Fig. 5.5.** The pH dependence on the Zeta potential for  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4\text{-IL}$ , and  $\text{Fe}_3\text{O}_4\text{-IL-FeTPPS}$ .



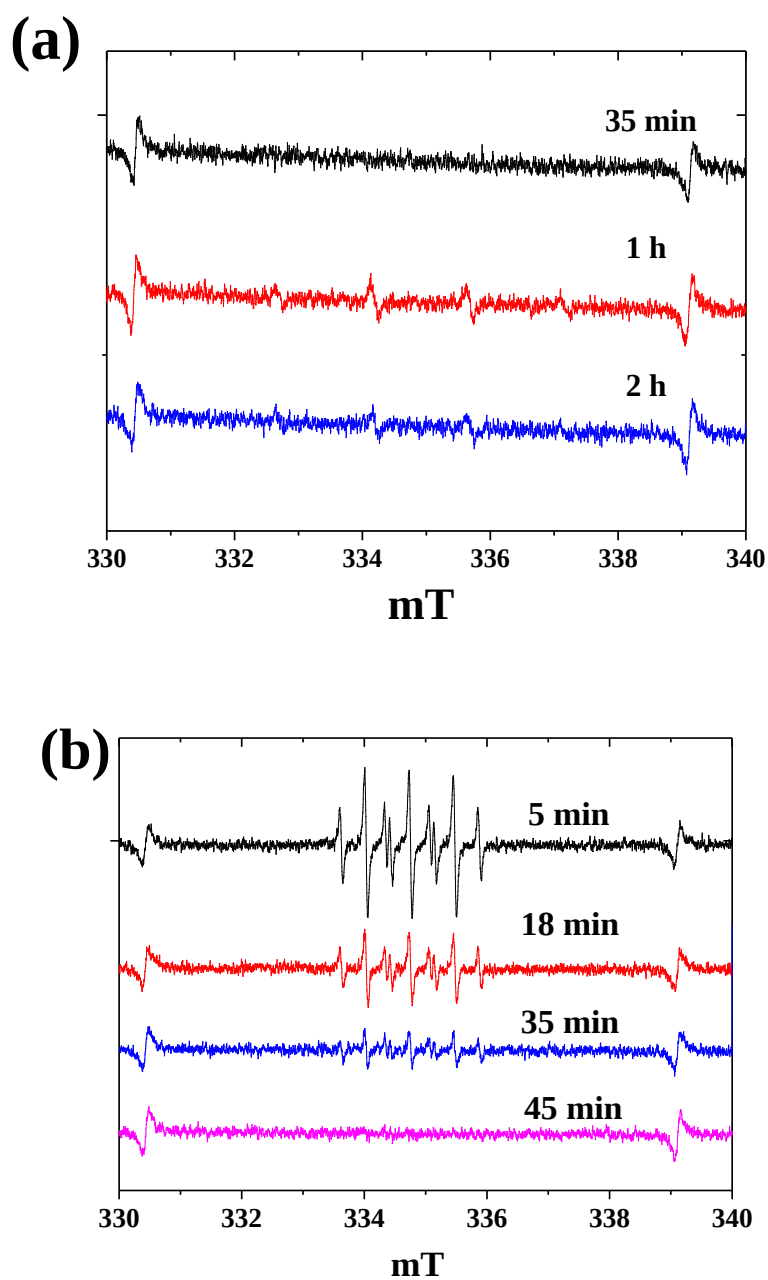
**Fig. 5.6.** Influence of catalyst type on the TrBP degradation. The reaction conditions were as follows: [catalysts]  $1 \text{ g L}^{-1}$ ,  $[\text{KHSO}_5]_0$   $500 \mu\text{M}$ ,  $[\text{TrBP}]_0$   $200 \mu\text{M}$ , and pH 6.



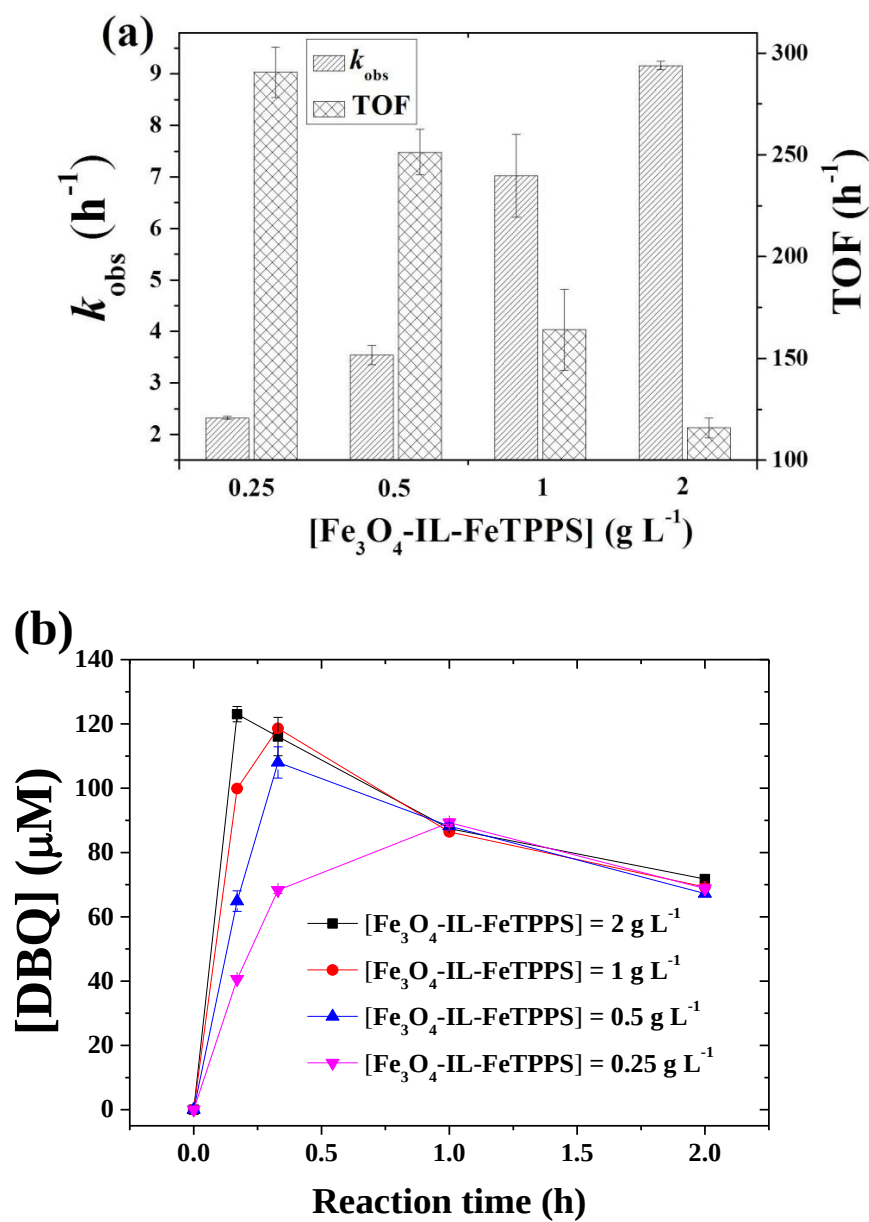
**Fig. 5.7.** ESR spectra of aqueous mixture for  $Fe_3O_4$ ,  $KHSO_5$  and DMPO at different reaction period after adding  $KHSO_5$ . Reaction conditions:  $[Fe_3O_4]$   $1\text{ g L}^{-1}$ ,  $[KHSO_5]$   $500\text{ }\mu\text{M}$ , pH 6, and  $[DMPO]$   $0.1\text{ M}$ .



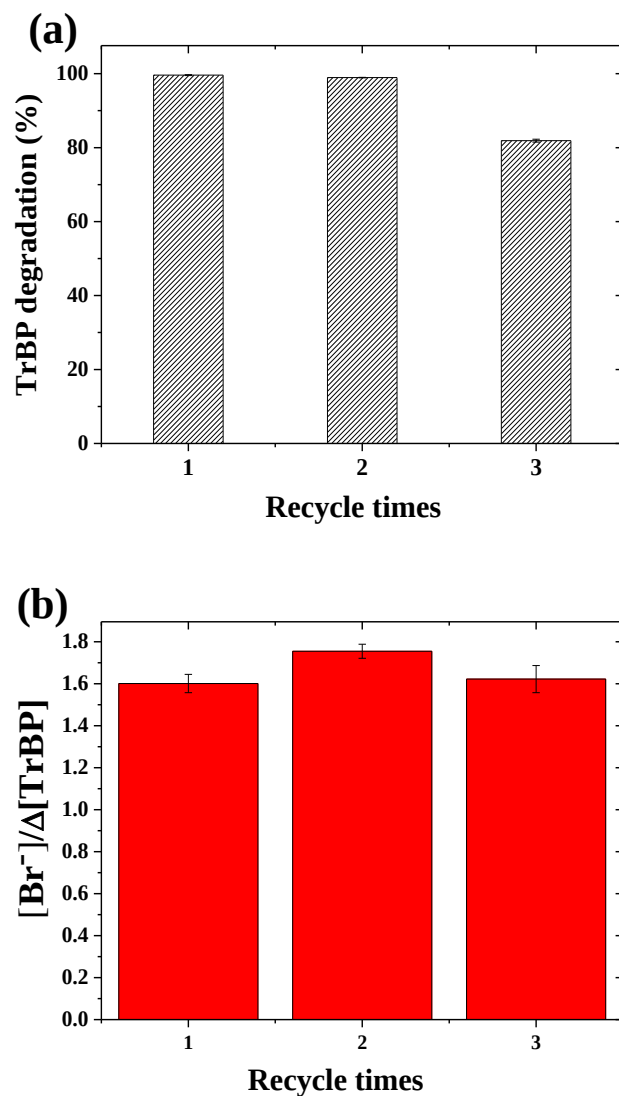
**Fig. 5.8.** Kinetics of degradation of TrBP in the  $Fe_3O_4/KHSO_5$  system without and with the quenching agent TBA ( $0.1 \text{ mol L}^{-1}$ ) and EtOH ( $0.1 \text{ mol L}^{-1}$ ). Reaction conditions:  $[Fe_3O_4]$   $1 \text{ g L}^{-1}$ ,  $[TrBP]_0$   $200 \text{ } \mu M$ ,  $[KHSO_5]_0$   $500 \text{ } \mu M$ , and  $pH = 6$ .



**Fig. 5.9.** ESR spectrum of  $Fe_3O_4$ -IL (a) and  $Fe_3O_4$ -IL-FeTPPS at different reaction periods after adding  $KHSO_5$  (b). Reaction conditions: [Catalyst]  $1\text{ g L}^{-1}$ ,  $[KHSO_5]_0$   $500\text{ }\mu\text{M}$ , pH = 6, and [DMPO]  $0.1\text{ M}$ .



**Fig. 5.10.** Influence of catalyst dosage on the TrBP degradation (a) and DBQ concentration (b). Reaction conditions:  $[\text{Fe}_3\text{O}_4\text{-IL-FeTPPS}]$  1 g L<sup>-1</sup>,  $[\text{KHSO}_5]_0$  1 mM,  $[\text{TrBP}]_0$  200 μM, pH 6.



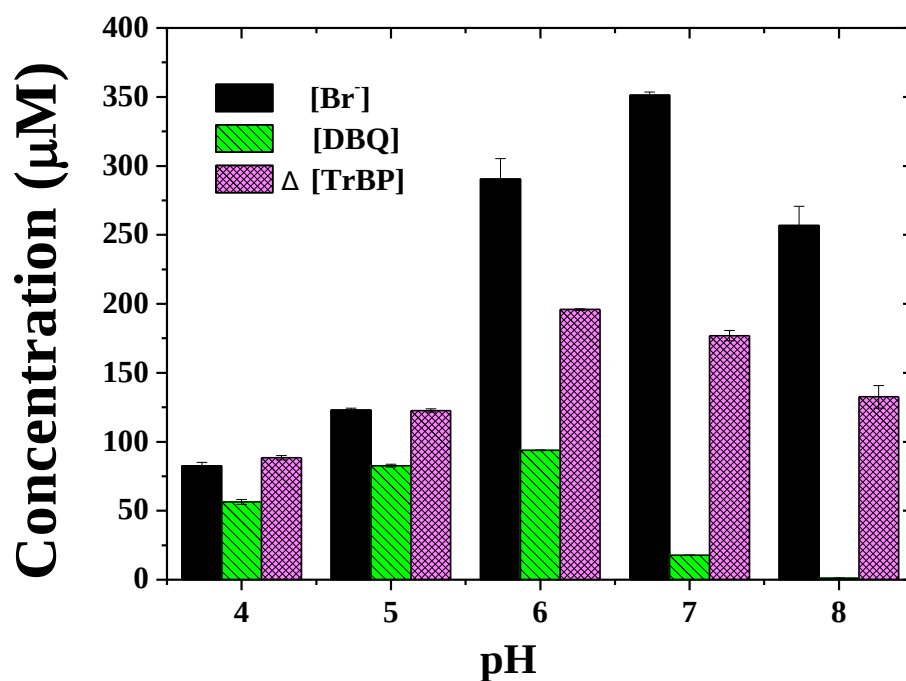
**Fig. 5.11.** Reusability of  $Fe_3O_4$ -IL-FeTPPS on (a) TrBP degradation and (b) debromination. The reaction conditions were as follows: [catalysts]  $1\text{ g L}^{-1}$ ,  $[KHSO_5]_0$   $500\text{ }\mu\text{M}$ ,  $[TrBP]_0$   $200\text{ }\mu\text{M}$ ,  $\text{pH} = 6$ , and reaction period 4 h.

**Table 5.1.** Influence of SHA on the concentration of degraded TrBP, DBQ and released  $Br^-$ .<sup>a</sup>

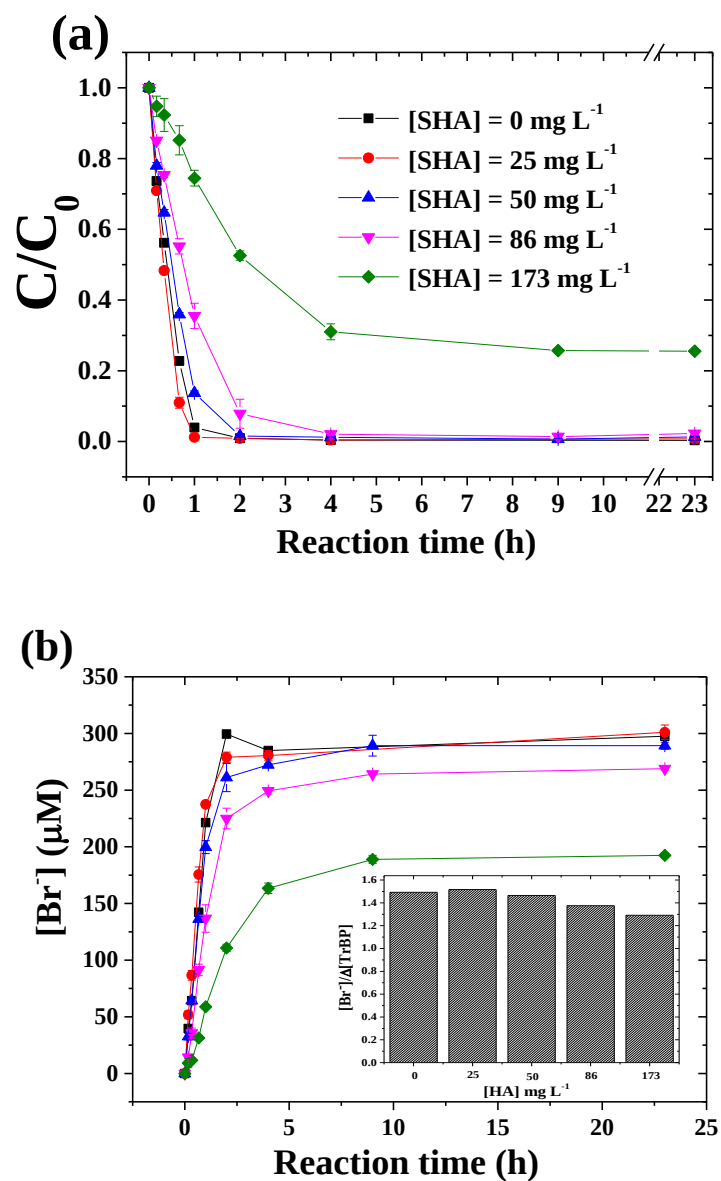
| pH | $\Delta[TrBP]$<br>( $\mu M$ ) <sup>b</sup> | $\frac{\Delta[TrBP]_{HA}}{\Delta[TrBP]}$ | [DBQ]<br>( $\mu M$ ) | $\frac{[DBQ]_{HA}}{[DBQ]}$ | $[Br^-]/\Delta[TrBP]$ | $\frac{[Br^-]_{HA}/\Delta[TrBP]_{HA}}{[Br^-]/\Delta[TrBP]}$ |
|----|--------------------------------------------|------------------------------------------|----------------------|----------------------------|-----------------------|-------------------------------------------------------------|
| 4  | 88.5                                       | 1.00                                     | 76.9                 | 1.36                       | 0.87                  | 0.93                                                        |
| 5  | 156.2                                      | 1.27                                     | 118.9                | 1.44                       | 0.84                  | 0.84                                                        |
| 6  | 196.3                                      | 1.00                                     | 91.3                 | 0.97                       | 1.40                  | 0.94                                                        |
| 7  | 159.8                                      | 0.90                                     | 13.9                 | 0.78                       | 1.89                  | 0.95                                                        |
| 8  | 97.7                                       | 0.74                                     | 0.0                  | 0.00                       | 1.44                  | 0.74                                                        |

<sup>a</sup> Reaction conditions:  $[Fe_3O_4-IL-FeTPPS]$  1 g L<sup>-1</sup>,  $[KHSO_5]_0$  0.5 mM,  $[TrBP]_0$  200  $\mu M$ ,  $[SHA]$  25 mg L<sup>-1</sup>, reaction time 2 h.

<sup>b</sup> The concentration of degraded TrBP



**Fig. 5.12.** Influence of pH on the TrBP degradation, DBQ formation and released  $Br^-$ . Reaction conditions:  $[Fe_3O_4\text{-IL-FeTPPS}]$   $1\text{ g L}^{-1}$ ,  $[KHSO_5]_0$   $500\text{ }\mu\text{M}$ ,  $[TrBP]_0$   $200\text{ }\mu\text{M}$ , and reaction period 2 h.



**Fig. 5.13.** Influence of SHA concentration on the TrBP degradation (a) and debromination (b). Reaction conditions:  $[Fe_3O_4\text{-IL-FeTPPS}]$   $1 \text{ g L}^{-1}$ ,  $[KHSO_5]_0$   $0.5 \text{ mM}$ ,  $[TrBP]_0$   $200 \text{ μM}$ , and pH 6.

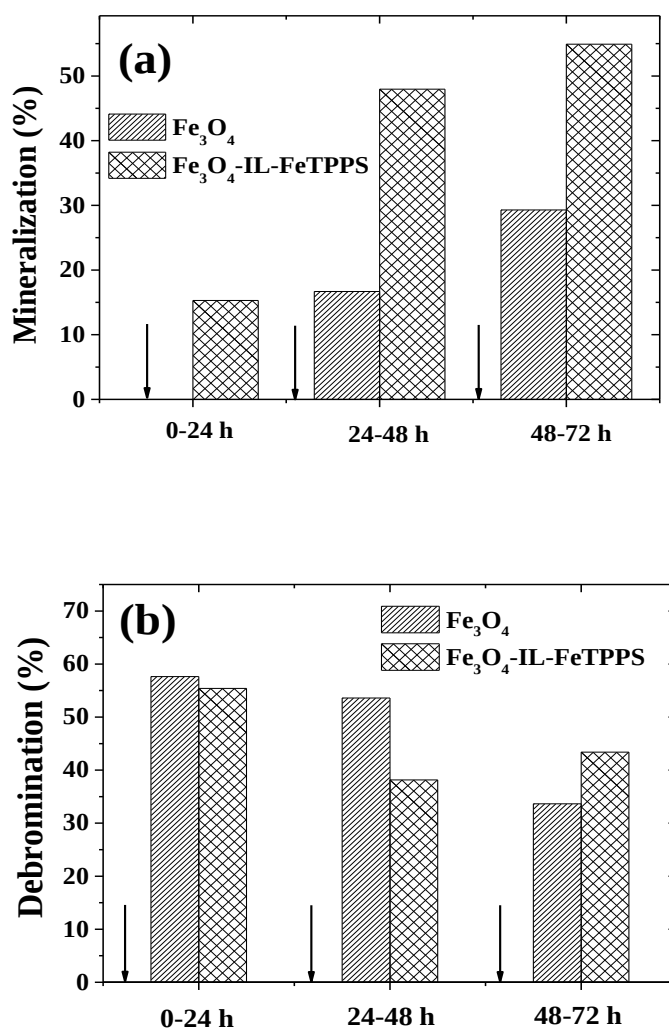
**Table 5.2.** Influence of SHA concentration on the TOF and  $k_{obs}$  for TrBP degradation.<sup>a</sup>

| [SHA] (mg L <sup>-1</sup> ) | $k_{obs}$ (h <sup>-1</sup> ) <sup>b</sup> | TOF (h <sup>-1</sup> ) <sup>c</sup> |                 |
|-----------------------------|-------------------------------------------|-------------------------------------|-----------------|
|                             |                                           | TrBP                                | Br <sup>-</sup> |
| 0                           | 2.5                                       | 62.6                                | 45.8            |
| 25                          | 2.8                                       | 73.8                                | 61.9            |
| 50                          | 2.0                                       | 50.4                                | 46.0            |
| 86                          | 1.2                                       | 35.2                                | 25.5            |
| 173                         | 0.3                                       | 11.0                                | 8.3             |

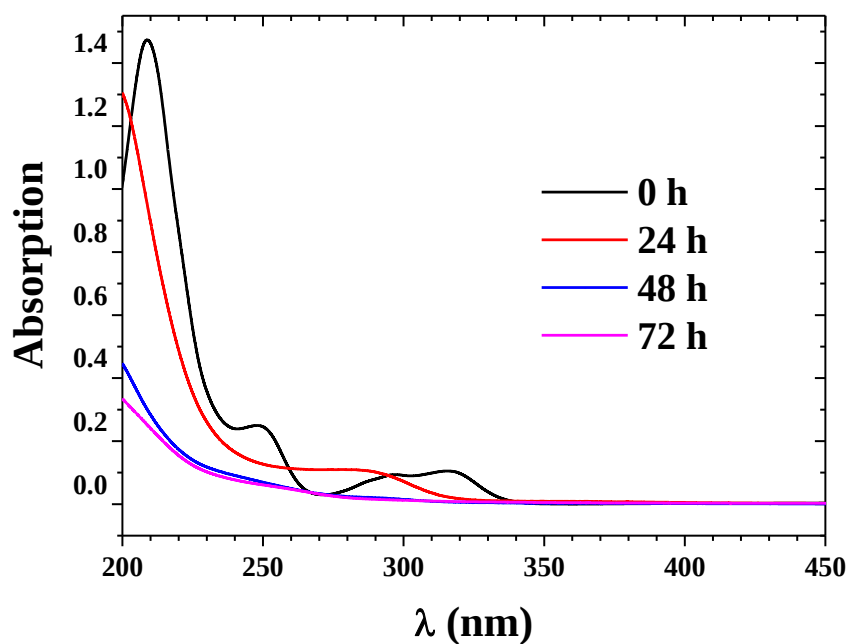
<sup>a</sup> Reaction conditions: [Fe<sub>3</sub>O<sub>4</sub>-IL-FeTPPS] 1 g L<sup>-1</sup>, [KHSO<sub>5</sub>]<sub>0</sub> 0.5 mM, [TrBP]<sub>0</sub> 200 μM, pH 6.

<sup>b</sup> Pseudo first-order rate constant

<sup>c</sup> Turnover frequencies (TOFs) were calculated by dividing the TrBP degradation rate (μM h<sup>-1</sup>) or debromination rate at 0.33 h of reaction period by the concentration of catalyst (4.2 μM).



**Fig. 5.14.** The variations in the percent mineralization (a) and debromination (b) at pH 6 by the sequential addition of  $KHSO_5$  after 24 h period,  $[TrBP]_0$  200  $\mu M$ ,  $[KHSO_5]$  1 mM, and  $[Fe_3O_4$ -IL-FeTPPS] 1 g L<sup>-1</sup>



**Fig. 5.15.** UV-vis absorption spectra of the TrBP degradation by the sequential addition of  $KHSO_5$  after a 24 h period,  $[TrBP]_0$  200  $\mu M$ ,  $[KHSO_5]$  1 mM, and  $[Fe_3O_4\text{-IL-FeTPPS}]$  1 g L<sup>-1</sup>.

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# **Chapter 6**

## ***Conclusion***

Iron-porphyrins as green catalysts have potential application to the degradation and detoxification of bromophenols in landfill leachates, because of their high catalytic activity and environmental friendly properties. The formation of oxo-ferryl porphyrin species plays the key roles on the catalytic activity of iron-porphyrin. However, the deactivation of iron-porphyrin which was caused by self-degradation in the presence of an oxygen donor, such as  $\text{KHSO}_5$  and  $\text{H}_2\text{O}_2$ , and dimerization was observed in homogeneous conditions. To suppress the deactivation and enhance the reusability of iron-porphyrin catalyst, the immobilized iron-porphyrins were focused in the present study. Throughout my research works, iron-porphyrin catalysts were immobilized on silica (Chapter 2 and Chapter 3), mesoporous silica (Chapter 4) and magnetite (Chapter 5). The reusability was significantly enhanced and the deactivation of iron-porphyrin was suppressed by the immobilization.

However, the oxidation of bromophenols was inhibited in the presence of HSs, which are contained in landfill leachates as major concomitant. To eliminate the inhibition by HSs, the anionic support like  $\text{SiO}_2$  was first employed to support iron(III)-porphyrin catalysts, because the HSs with large negative electrostatic field might be excluded from the catalyst surfaces via electrostatic repulsion. However, the inhibition was not sufficiently removed. To exclude HSs from the vicinity of iron(III)-porphyrin site, the iron(III)-porphyrin was secondly supported on the channel of mesoporous silica, SBA-15. The SBA-15 supported iron(III)-porphyrin catalyst indicated the higher activity than these for the  $\text{SiO}_2$  supported catalysts, as shown in Table 6-1. The disadvantage of supported iron-porphyrin was that the catalytic activity decreased compared with homogeneous catalysts due to the mass transfer, and therefore the dosage of oxidant should be increased for efficient degradation. Thus, the use of

ionic liquid to “restore” the homogeneous catalytic efficiency of the supported catalysts may enhance the catalytic activity of heterogeneous catalyst. The prepared iron(III)-porphyrin catalyst that was supported on the ionic liquid functionalized magnetite coated with silica indicated the highest catalytic activity of all prepared catalysts, even in the presence of HS (Table 6-1). Followings are conclusions in each chapter.

Chapter 1 is general introduction. First, the production volume, utilization and potential environmental risks of bromophenols, distribution of bromophenol contamination in landfill leachates, and the importance in their degradation and detoxification were described as a background of the present study. Secondly, features of the oxidation of halogenated phenols by iron(III)-porphyrin catalysts were explained, and their advantages and disadvantages were extracted, based on the previous reports. Subsequently, the problems to overcome were focused on the suppression of iron-porphyrin self-degradation and the elimination of HS inhibition. Finally, my strategies of the catalyst synthesis to overcome those problems were discussed, and aims and purposes of the present study were described.

In Chapter 2, the silica immobilized FeTCPP ( $\text{SiO}_2\text{-FeTCPP}$ ) was synthesized and applied to the oxidative degradation of TrBP, one of the widely used bromophenol. The TrBP was efficiently degraded in the pH range from 3 to 8 in the absence of HS, while the optimal pH for the reaction was in the range of pH 5-7 in the presence of HS. Although the  $\text{SiO}_2\text{-FeTCPP}$  showed the negative surface charge, the inhibition of HS in the catalytic oxidation by  $\text{SiO}_2\text{-FeTCPP}$  at pH 7 that was the optimal value for TrBP degradation was not sufficiently removed. However, more than 90% of TrBP was finally degraded at HS concentrations below  $50 \text{ mg L}^{-1}$ . The prepared  $\text{SiO}_2\text{-FeTCPP}$  could be

reused up to 10 times even in the presence of HS.

In Chapter 3, an iron(III)-tetrakis(*p*-sulfonatophenyl)porphyrin (FeTPPS) was immobilized on imidazole modified silica (FeTPPS/IPS) via coordinating the Fe(III) with the nitrogen atom in imidazole to suppress self-degradation and to enhance the reusability of the catalyst. The catalytic activity of FeTPPS/IPS was examined for catalytic degradation of TBBPA, a commonly used brominated flame retardant, and an endocrine disruptor. This catalytic system was pH independent in the absence of HA, and more than 95% of the TBBPA was degraded in the pH range from 3 to 8, while the optimal pH for the reaction was at pH 8 in the presence of HA. The intermediate degradation was assigned as 4-(2-hydroxyisopropyl)-2,6-dibromophenol (2HIP-2,6DBP). Although the TOF was decreased in the presence of HA, over 95% of the TBBPA was degraded within 12 h in the presence of 28 mg-C L<sup>-1</sup> of HA. At pH 8, the FeTPPS/IPS catalyst could be reused up to 10 times without any detectable loss of activity for TBBPA degradation and debromination, even in the presence of HA.

In Chapter 4, the mesoporous molecular sieve, SBA-15, supported FeTPyP (FeTPyP-SBA-15), was synthesized to suppress the negative influence of HS on the TrBP degradation. The synthesized FeTPyP-SBA-15 has orderly pore structure with pore diameters 5.02 nm. The FeTPyP-SBA-15 was used to catalytic degradation the relatively hydrophobic bromophenol, PBP. The prepared FeTPyP-SBA-15 showed a high catalytic activity, and 50 μM of PBP was efficiently degraded at pH 7 and 8 using 125 μM KHSO<sub>5</sub> even in the presence of 25 mg L<sup>-1</sup> HS. The amorphous silica immobilized FeTPyP (FeTPyP-SiO<sub>2</sub>) was synthesized as a control catalyst. The TOF for the FeTPyP-SBA-15 in the presence of 25 mg L<sup>-1</sup> HS (58.3 h<sup>-1</sup>) was larger than that for a control catalyst, FeTPyP-SiO<sub>2</sub> (16.7 h<sup>-1</sup>). Thus, FeTPyP-SBA-15 selectively degraded

PBP in the presence of HS. The well ordered channels of FeTPyP-SBA-15 play the key role on the suppressing the adverse effect of HS on the TrBP degradation.

In Chapter 5, FeTPPS was immobilized on the ionic liquid functionalized magnetite ( $\text{Fe}_3\text{O}_4\text{-IL-FeTPPS}$ ) to create the homogenous-like condition for overcoming the disadvantages of heterogeneous catalyst with relatively lower catalytic activity.  $\text{Fe}_3\text{O}_4$  has been shown some catalytic activity on TrBP degradation, while the catalytic activity was significantly enhanced with the FeTPPS immobilization. The influences of pH and catalyst dosage of  $\text{Fe}_3\text{O}_4\text{-IL-FeTPPS}$  were investigated. The highest TrBP degradation percent was observed at pH 6. Although no mineralization of bromophenols was observed in other prepared catalysts ( $\text{SiO}_2\text{-FeTCPP}$ , FeTPPS/ISP and FeTPyP-SBA-15), 55% of mineralization was achieved for the  $\text{Fe}_3\text{O}_4\text{-IL-FeTPPS}$  catalyst. The influence of HS was investigated at pH 6. The significant decrease in catalytic activity for TrBP degradations was not observed up to  $86 \text{ mg L}^{-1}$  HS for the  $\text{Fe}_3\text{O}_4\text{-IL-FeTPPS/KHSO}_5$  catalytic system. Such the higher catalytic activity of  $\text{Fe}_3\text{O}_4\text{-IL-FeTPPS}$  catalyst can be attributed to the fact that the IL modified surface plays an important role in restoring homogeneous catalytic efficiency of the supported FeTPPS.

In conclusion, while bromophenols was catalytically degraded by the prepared immobilized iron(III)-porphyrin catalysts, some of those indicated the adverse effects in the presence of HSs. However, iron(III)-porphyrin catalysts immobilized in mesoporous silica not only significantly suppressed the self-degradation but also enhanced the selectivity for the degradation of bromophenol in the presence of HS. In addition, the use of ionic liquid functionalized support was found to be effective in enhancing catalytic activity in the presence of HS. The finding in the present study will contribute

to further understanding the function of HS on the bromophenol degradation and provide useful immobilization strategies for the practical use of iron(III)-porphyrin in the waste water treatment.

Table 6.1. Summary of catalytic activities in the presence of 25 mg L<sup>-1</sup> HS for the synthesized catalysts

| Prepared Catalyst                         | Catalytic center | Support                            | Substrates | TOF (h <sup>-1</sup> ) | Reaction conditions                                                                                                                                  |
|-------------------------------------------|------------------|------------------------------------|------------|------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------|
| SiO <sub>2</sub> -FeTCPP                  | FeTCPP           | SiO <sub>2</sub> -NH <sub>2</sub>  | TrBP       | 38.8                   | [TrBP] <sub>0</sub> 200 μM, [KHSO <sub>5</sub> ] <sub>0</sub> 1.25 mM, [SiO <sub>2</sub> -FeTCPP] 2.7 μM, [HS] 25 mg L <sup>-1</sup>                 |
| FeTPPS/IPS                                | FeTPPS           | SiO <sub>2</sub> -IPS              | TBBPA      | 1.22                   | [TBBPA] <sub>0</sub> 50 μM, [KHSO <sub>5</sub> ] <sub>0</sub> 1 mM, [FeTPPS/IPS] 10 μM, [HS] 25 mg L <sup>-1</sup>                                   |
| FeTPyP-SBA-15                             | FeTPyP           | SBA-CP                             | PBP        | 58.3                   | [PBP] <sub>0</sub> 50 μM, [KHSO <sub>5</sub> ] <sub>0</sub> 0.125 mM, [FeTPyP-SBA-15] 2.3 μM, [HS] 25 mg L <sup>-1</sup>                             |
| FeTPyP-SiO <sub>2</sub>                   | FeTPyP           | SiO <sub>2</sub> -CP               | PBP        | 16.7                   | [PBP] <sub>0</sub> 50 μM, [KHSO <sub>5</sub> ] <sub>0</sub> 0.125 mM, [FeTPyP-SiO <sub>2</sub> ] 2.4 μM, [HS] 25 mg L <sup>-1</sup>                  |
| Fe <sub>3</sub> O <sub>4</sub> -IL-FeTPPS | FeTPPS           | Fe <sub>3</sub> O <sub>4</sub> -IL | TrBP       | 73.8                   | [TrBP] <sub>0</sub> 200 μM, [KHSO <sub>5</sub> ] <sub>0</sub> 0.5 mM, [Fe <sub>3</sub> O <sub>4</sub> -IL-FeTPPS] 4.2 μM, [HS] 25 mg L <sup>-1</sup> |

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