Removal of nonylphenolic compounds from water and sewage sludge using ferrate

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Removal of nonylphenolic compounds from water and sewage sludge using ferrate

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Abstract

Nonylphenol (NP) and nonylphenol monoethoxylate (NP1EO) have toxic and persistent characteristics and are incompletely degraded in conventional wastewater treatment processes. These compounds are present in sewage sludge that can be reused as fertilizers or soil conditioners. Accordingly, NP and NP1EO should be properly removed before being discharged in the environment. In this study, potassium ferrate (K_2FeO_4) containing hexavalent iron (Fe(VI)) was used as an environment-friendly oxidizing agent to mediate NP and NP1EO degradation. The purpose of this study was to investigate the removal of NP and NP1EO by Fe(VI). The effects of pH and Fe(VI) dosage on the degradation of NP and NP1EO were examined in water and anaerobically digested sewage sludge samples. In water samples, under conditions examined in this study, maximum removal efficiencies for NP and NP1EO were 98% and 92%, respectively. For digested sewage sludge samples, the maximum removal efficiencies of NP and NP1EO were 58% and 96%, respectively. The results demonstrated that Fe(VI) can potentially degrade NP and NP1EO in water and digested sewage sludge samples. However, organic matter as a matrix in the sludge sample would inhibit the degradation of NP and NP1EO by Fe(VI). The pH values before and after adding Fe(VI) to the samples had an obvious influence on the removal of NP and NP1EO.

Additionally, this study has evaluated the biodegradability of NP and its degradation products with Fe(VI) using NP labeled with ^{14}C as a tracer and activated sludge microorganisms as an inoculum. The addition of Fe(VI) to the NP solution spiked with the tracer resulted in a slight decrease in the concentration of ^{14}C, which indicates incomplete mineralization of NP and formation of degradation products. The biodegradability of NP degradation products with Fe(VI) was slightly higher than that of NP. This result suggested that NP was transformed into more biodegradable products through the treatment with Fe(VI). The degradation products from NP with Fe(VI) were estimated base on mass spectra, which detected a unique peak at *m/z* 223 at a low intensity. There might be a possibility that four hydrogen atoms were added to NP through the degradation with Fe(VI). Additionally, the effect of Fe(VI) dosage on the estrogenic activity of NP in water samples was studied using a yeast estrogen screen (YES). Fe(VI) was effective in lowering the estrogen activity of NP with an increase in Fe(VI) dosage. The effect of Fe(VI) dosage on the estrogenic activity of NP in water sample was investigated, suggesting that a mass ratio of Fe(VI) to NP more than 2.5 significantly decreased the estrogenic activity of NP.

Furthermore, this study has assessed the phosphorus bioavailability in sludge treated with Fe(VI) using different extraction reagents. The extraction efficiencies of phosphorus with 2% citric acid and neutral ammonium citrate were about 40% and about 70%, respectively. These results suggested that P in the sludge treated with Fe(VI) is bioavailable for plant uptake. Therefore, sludge treated with Fe(VI) could be utilized as a raw material for organic fertilizer, although this sludge requires to adjust the pH to around neutral value before the utilization as fertilizers.

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Chapter 1

Introduction

The volume of wastewater continues to increase as a result of population growth, economic development, and urban area spread. Sewerage systems generally allow human and industrial effluents to be discharged into water environments through wastewater treatment plants (WWTPs) to treat the effluent and sludge. The operation and performance of WWTPs have a significant influence on the qualities of treated effluent and sludge. As a result, the management of wastewater and sludge treatment processes is a critical issue.

1.1. Sewage sludge

Sewage sludge is a by-product of wastewater treatment processes as shown in Figure 1.1. Many countries have concerns about its increasing volume and impacts associated with their disposal. Sewage sludge contains useful substances such as nitrogen, phosphorus, and organic matter, which should be recycled. However, it also contains micropollutants such as organic chemicals, heavy metals, and pathogenic microorganisms that have adverse effects on the environment, animal, and human health.

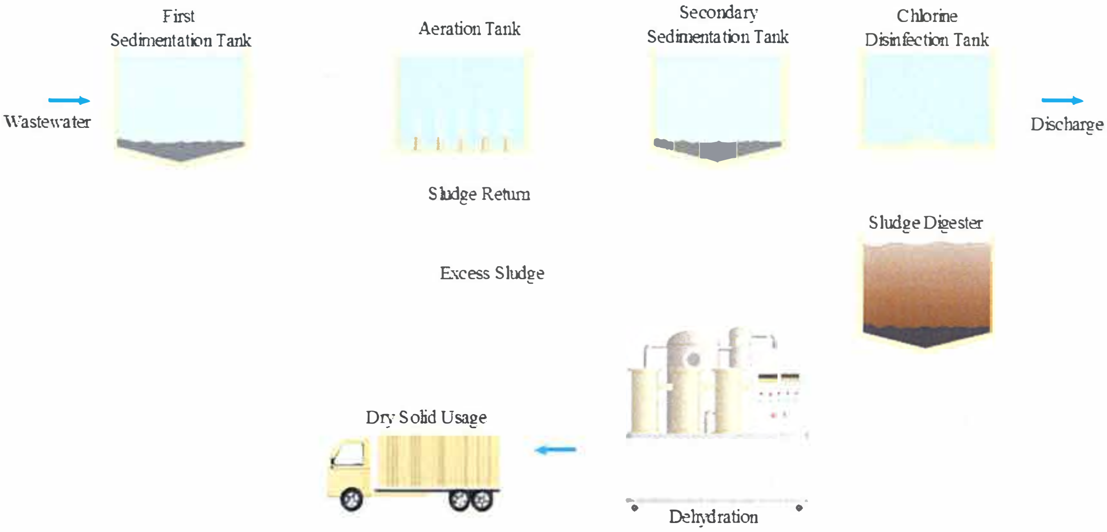


Figure 1.1 Schematic diagram of wastewater treatment processes.

The analysis of the official statistical data (Eurostat, 2017) shows discrepancies with regards to the amount of sludge generated by municipal sewage treatment plants in Europe. Figure 1.2 shows sewage sludge production in some EU countries from 2010 to 2016. Germany is the biggest sewage sludge producer, followed by France. The total quantities of sludge produced by countries are approximately 13 million tons of dry solids (DS) in 27 EU member countries (Milieu Ltd, 2010). The EU has managed the diversity of approaches to sludge issues. Figure 1.3 shows sewage sludge management methods of selected EU countries in 2016. However, the proportion of sludge recycled in agriculture varies widely between different regions. Agricultural use and incineration are the most used management methods in the EU since sludge contains organic matter and nutrients for proper plant growth.

The amount of sewage sludge produced in Japan is approximately 2 million tons of DS every year (MLIT, 2017). The annual sewage sludge production and the proportion recycled in Japan from 2000 to 2017 are shown in Figure 1.4. The recycling percent decreased in 2011 due to the accident in Fukushima and then has been recovering. The recycled percentage has increased from 2011 to 2017. Also, Japan has concerned about the increasing issues of sewage sludge disposal as the landfill site capacity is limited.

In Thailand, a small portion of the total urban wastewater generated is treated. The Bangkok metropolitan area generates an average sewage sludge production of 0.2 million tons of DS per year (Office of Natural Resources and Environmental Policy and Planning, 2013). Landfilling, incineration, and composting seems to be the most common disposal method for Thailand. Moreover, Thailand has concerned about the content of heavy metal and dissemination of contaminants in sludge, which were higher than the EU regulations for sewage sludge use in agriculture (Pasda et al., 2006).

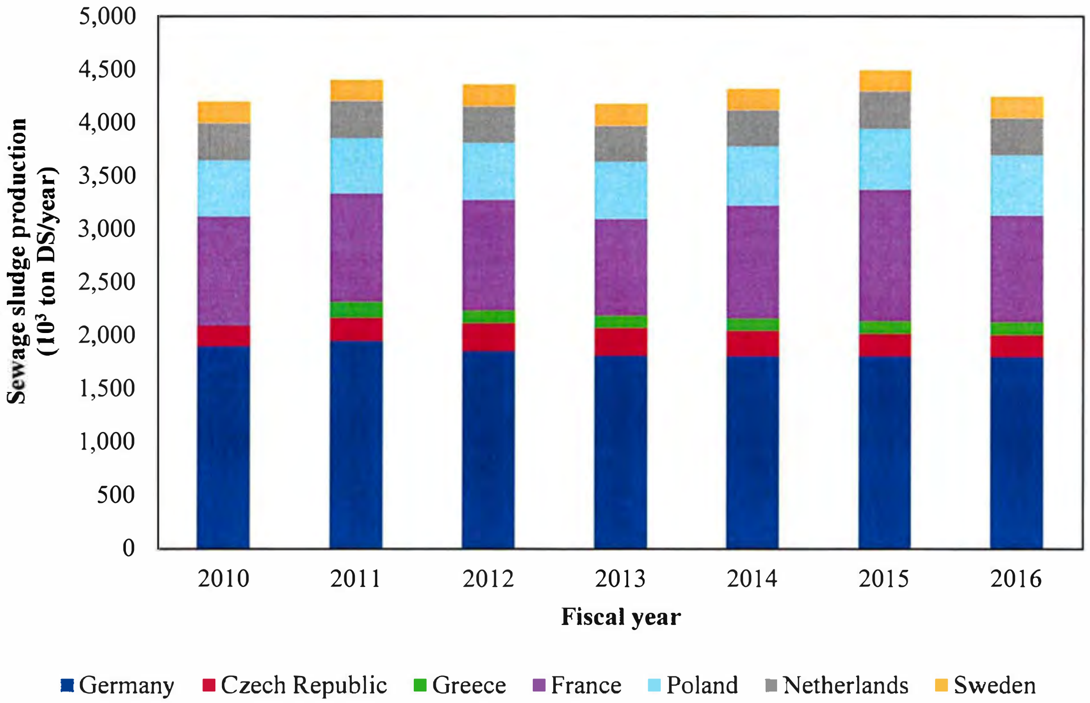


Figure 1.2 Amounts of sewage sludge production by selected countries in the EU.

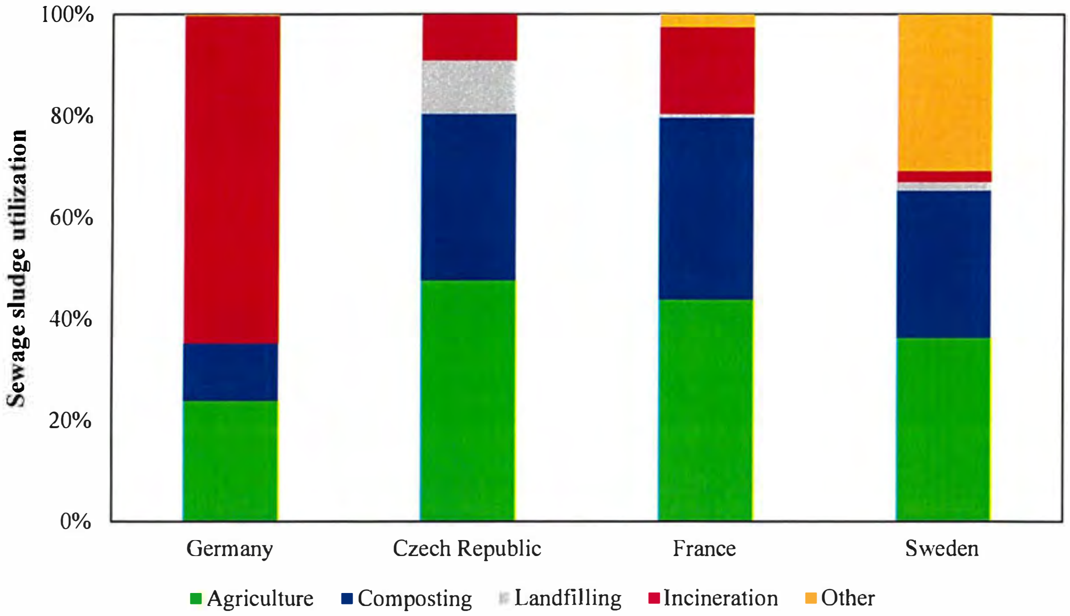


Figure 1.3 Sewage sludge utilization in selected countries.

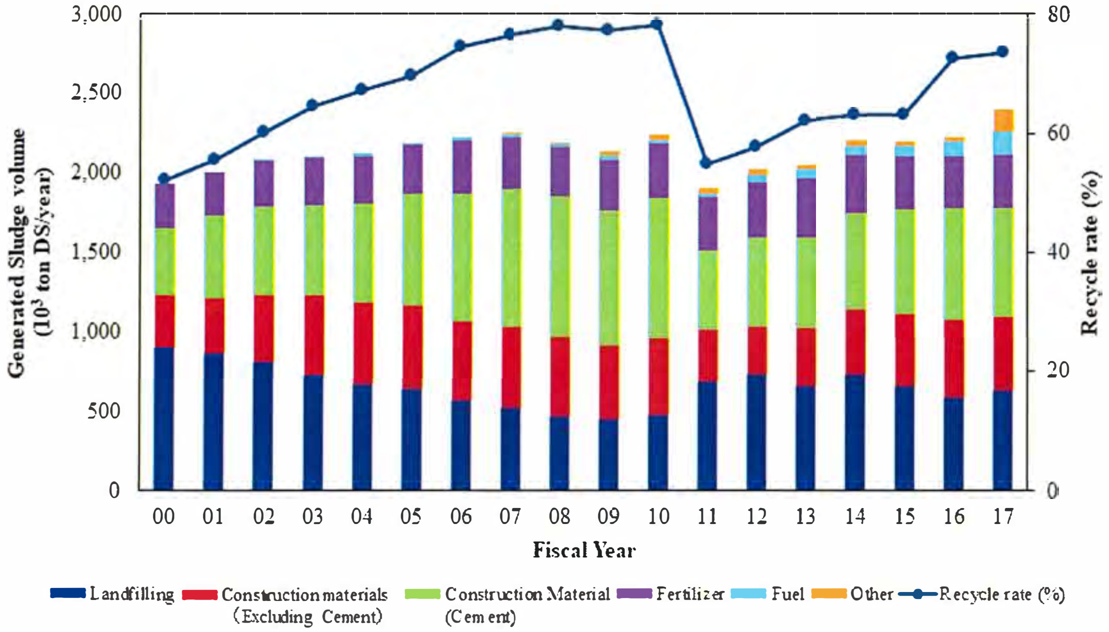


Figure 1.4 Annual sewage sludge production and its management in Japan.

The sludge treatment processes improve the suitability for use, storage, or transport of sewage sludge. Treatment of sewage sludge includes thickening, followed by anaerobic or aerobic digestion, dewatering, sludge pasteurization, and lime stabilization (Kelessidis and Stasinakis, 2012). Thickening is usually the first step in sludge treatment because it is impractical to handle thin sludge, a slurry of solids suspended in water. A thickener can reduce the total volume of sludge to less than half of the original amount. Sludge digestion is a biological process in which organic solids are decomposed into stable substances. Digestion reduces volatile solids, destroys pathogens, and makes it easier to dewater or dry the sludge. Digested sewage sludge is usually dewatered before disposal. Dewatered sludge contains a significant amount of water and may result in environmental deterioration due to the presence of pathogens, heavy metals, and organic pollutants (Archis and Jerry, 2019).

The utilizations of sludge compost and incineration ash in agriculture and construction are widely mentioned in discussions for recycling. As shown in Figures 1.3 and 1.4, sludge incineration seems to be the main practice for sludge disposal. However, incineration procedures are expensive and lead to concentrations of heavy metals into ash (Kominko et al., 2019). Although the incineration ash contains phosphorus (P), the P recover process from the ash is required because the amount of bioavailable P is very low in the ash (Ottosen et al., 2013). Moreover, the impacts on air pollution are still significant concern (Kelessidis and Stasinakis, 2012). Owing to these disadvantages, some countries are reluctant to use sludge incineration. Therefore, handling sewage sludge without incinerating is becoming a focus of attention in terms of cost reduction and environmentally acceptable alternatives.

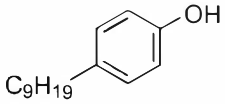
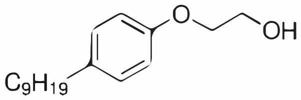
Many countries recommended the use of sludge to agriculture because the physical and chemical characteristics of sewage sludge may improve soil properties and its cost is lower compared to incineration or landfilling. Application of sewage sludge as a fertilizer in crop production provides essential nutrients for proper plant growth and improving soil structure that gives positive agricultural benefits and increases crop production (Wang et al., 2008, Latare et al., 2014). The advantage of using sewage sludge for agricultural purposes is phosphorus recycling, which is known to be limited. Besides, phosphate rock was listed as a critical raw material by the EU (Communication, 2017). About 60% of P was found in sewage sludge from WWTPs. It was approximately 11% of P in primary sludge, and 50% in secondary sludge after enhanced biological phosphorus removal and precipitation (Kominko et al., 2019). However, the use of sewage sludge in agriculture leads to an accumulation of pathogenic microorganisms, toxic organic compounds, and heavy metals. Therefore, the treatment and usage of sewage sludge have attracted attention.

1.2. Nonylphenol and nonylphenol monoethoxylate

Nonylphenol (NP) is a xenobiotic compound consisting of the phenols ring and a nine-carbon chain on the para-position (Soares et al., 2008). NP has a variety of isomers, depending on attaching positions and branching degree of the nine-carbon chain. In this thesis, NP means 4-NP. NP is clearly pale-color liquid, which is water-insoluble under typical conditions. Several researchers have reported that NP may have different toxicity and estrogenicity (Soares et al., 2008; Esteban et al., 2016; Priac et al., 2017).

NP is used primarily to produce nonylphenol ethoxylates (NPnEOs, n: number of ethoxy chains) which are widely used as surfactants in domestic, industrial, agricultural, and commercial products such as paints and latex paints, adhesives, inks, washing agents, paper, petroleum recovery chemicals, and personal care products (Priac et al., 2017). Longer-chain NPnEOs are transformed to short-chain NPnEOs during the biological wastewater treatment process, resulting in more persistent and toxic metabolites including nonylphenol diethoxylate (NP2EO), nonylphenol monoethoxylate (NP1EO), nonylphenol (NP), and acetic acid groups including nonylphenoxy acetic acid (NP1EC) and nonylphenoxyethoxy acetic acid (NP2EC) (Figure 1.5) (Núñez et al., 2007). The physicochemical properties of 4-NP and NP1EO are presented in Table 1.1.

Table 1.1 Physicochemical properties of 4-NP and NP1EO.

Compounds	**CAS number**	**Properties**		
		Molecular formula	**Molecular weight**	**Structure**
4-Nonylphenol (NP)	84852-15-3	$C_9H_{19}C_6H_4OH$	220.35	
Nonylphenol monoethoxylate (NP1EO)	27986-36-3	$C_{17}H_{28}O_2$	264.40	

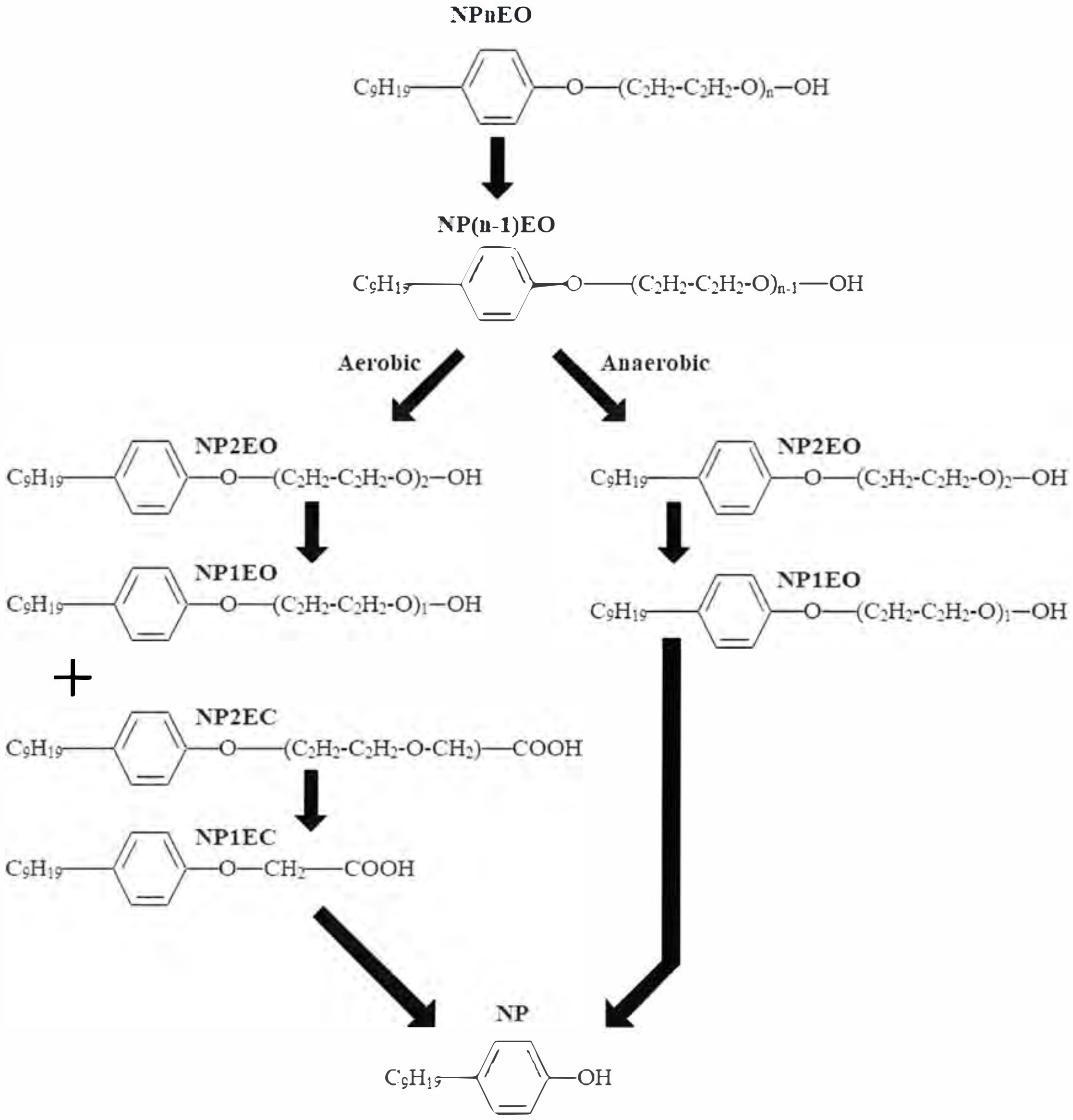


Figure 1.5 Biological degradation pathway of NPnEOs (Ömeroğlu and Sanin, 2014).

1.2.1. The occurrence of nonylphenol and nonylphenol monoethoxylate in the environment

NP and NP1EO are presently detected in all aquatic environments including freshwater, coastal, and marine ecosystems, which are mainly related to the discharge of effluents from WWTPs (Ying et al., 2002). Several researchers have been reporting a global occurrence of these compounds in surface water. Düring et al. (2002) reported that the partition of NP in the environment had been estimated to be higher than 60% in sediments, over 10% in soil, and nearly 25% in water. NP and NP1EO were detected in 51% and 46% of the samples from a survey in the US river, respectively. A study in European river waters revealed that NP was detected in 29% of collected samples, and the highest mean concentrations were 1,345 ng/L (Stasinakis et al., 2012). NP and NPEOs contained in the effluents and sludges from the wastewater treatment plant are discharged to the surface water, agricultural soil or authorized disposal sites. Many studies examining the presence of NPEOs compounds in WWTPs focused on concentrations in influents and effluents, sewage sludge, and then removal efficiencies (Samaras et al., 2013, Ömeroğlu et al., 2015, Mailler et al., 2016). Lian et al. (2009) investigated the behavior of NP and NP1EO in different Chinese WWTPs. The result indicated that NP and NP1EO tended to adsorb onto sludge flocs.

Additionally, Gao et al. (2017) reported that the removal efficiency of NP1EO was 50% in an activated sludge treatment process. Furthermore, NP1EO is the precursor of NP produced during aerobic and anaerobic conditions (Minamiyama et al., 2006, Ömeroğlu and Sanin, 2014). Since NP and NP1EO are highly persistent and highly hydrophobic (log K_{OW}: 5.74 and 4.74, respectively), they sorb onto activated sludge during biological wastewater treatment (Duan et al., 2016, Mailler et al., 2017). Therefore, these compounds can be found in higher levels in sludge than effluents. Table 1.2 shows the contents of NP and NP1EO in sludges in sewage treatment plants (STPs) in different countries. Sewage sludge can be recycled as a raw material for fertilizer because it contains nutrients such as nitrogen and phosphorous. However, the land application of sludge might cause an accumulation of micropollutants in soils and plants. According to EU Directive 2003/53/ of the European Parliament and of the council, the limit for the summation of the concentration of NP, NP1EO, and NP2EO in sludge for use on land is 450 mg/kg (Milinovic et al., 2015).

Table 1.2 Contents of NP and NP1EO in sludges in different countries.

Compounds	**Location**	**Type of sludge**	**Mean concentration (μg/kg)**	**References**
NP	UK	Raw	4,400	Jones et al. (2014)
	USA	Raw	49	Yu and Wu (2012)
	Spain	Digested and dewatered	102,100	González et al. (2010)
		Digested and dehydrated	131,000	Aparicio et al. (2009)
	Greece	Digested	170	Stasinakis et al. (2008)
		Thermally dried	10,590	Samaras et al. (2013)
	France	Thermally dried Limed	61,700	Ghanem et al. (2007)
NP1EO	UK	Raw	128,000	Jones et al. (2014)
	Spain	Digested and dewatered	5,000	González et al. (2010)
		Digested and dehydrated	53,200	Aparicio et al. (2009)

Compounds	**Location**	**Type of sludge**	**Mean concentration (μg/kg)**	**References**
	Greece	Digested	36,000	Stasinakis et al. (2008)
		Thermally dried	12,300	Samaras et al. (2013)
	France	Various	1,880	Mailler et al. (2014)
		Raw sludge	2,129	Mailler et al. (2017)
		Digested sludge	3,078	
		Centrifuged sludge	3,005	
		Thermally dried sludge	2,885	
		Sludge cake	5,980	

1.2.2. Environmental and sanitary impacts of nonylphenol and nonylphenol monoethoxylate

NP and NP1EO are well known as micropollutants having a potential risk to the environment, animal, and human health. These compounds were identified as priority hazardous substances by the European Union (Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008, European Union, 2008) that include the endocrine-disrupting chemicals (EDCs) group (Samaras et al., 2013). In Japan, NP is designated as one of the parameters in the environmental quality standards for water pollution (Environment, Government of Japan, 2012). Additionally, environmental quality standards (EQS) indicate the annual average concentration for NP in the water surface was proposed at 0.3 μg/L. Many Environmental Protection Agencies have also agreed with directives for this compounds listed as priority pollutants (Priac et al., 2017). Zhang et al.

(2017) reported that NP had been shown to mimic the effects of estrogen, inhibit the activity of antioxidant enzymes, and have mutagenic and carcinogenic properties. It also has tissue-specific effects that cause highly irritating and corrosion of skin and eyes. Also, OEHHA (2009) reported that NP is highly toxic to fish, aquatic invertebrates, and aquatic plants in a short time.

Moreover, NP has been linked to the feminization of male fish, the sex transposition in wildlife, the decline in sperm counts in men, and the increase in hormone-related cancers in humans (Kim et al., 2016). Besides, the exposure of humans to NP from background concentrations is of limited concern. Only a local high exposure could affect human health. As a result, many countries have limited the use of NPnEOs surfactants. However, some countries have continued to use them because of their high ability as surfactants (Gao et al., 2017).

Furthermore, the assessment of risk on NP by several researchers has demonstrated the estrogenic effects of NP on fish and mammals (CEPA, 1999). NP and NPEOs do exhibit estrogenic activity based on the results of both *in vitro* and *in vivo* tests involving terrestrial and aquatic organisms. The activity of NPEOs was found to increase with decreasing chain length and NP showed the highest activity. Most of the tests indicate that estrogenic effects may start to occur at around 10-20 μg/L (WHO, 2004). NP and NPEOs can interact with some proteins that may change the structure and activity of enzymes. CEPA (1999) reported the toxicity of NP and NPEOs to many species. The median lethal concentration (LC_{50}) values for NPnEOs increase with shortness of EO chain length. The 96-hour LC_{50} for NP has been determined for at least 18 different species of fish and it is reported that most of the values range from 100 to 300 μg/L. The LC_{50} for NP was similar after 10, 20 and 30 days from exposure.

1.2.3. Biodegradation of nonylphenol

The presence of NP in the environment is related to the biodegradation in STPs of NPnEOs. In WWTPs, NP was released into the environment as a mixture of NP and short chain NPnEOs and NPnECs (Figure 1.5) (Shao et al., 2003). The slow biodegradation of NP was found under aerobic conditions and the residual NP concentration was detected after 320 days (Ying et al., 2002). De Weert, J., et al. (2010) investigated aerobic biodegradation of NP from sediment and showed that NP biodegradation occurred within 8 days. Nitro-nonylphenol metabolites were formed, which were further degraded to unknown compounds during the biodegradation.

The earliest studies showed that biological process during anaerobic conditions was unable to remove NP (RazoFlores et al., 1996). Chang et al. (2005) observed that NP half-life time was 25 days under anaerobic degradation. Recently, Duan et al. (2019) reported that biodegradation of NP in waste activated sludge (WAS) was slowed under anaerobic conditions while the biodegradation efficiency of NP was found to be 55.5% within 8 days under acidogenic conditions. Additionally, Zheng et al. (2018) investigated the biodegradation of NP during aerobic composting and showed that 65% of NP was biodegraded with the microbial community. As a result, lower chain NPnEOs and NP tend to accumulate in sludge and sediments. Therefore, developing the method to remove these compounds during wastewater and sludge treatment processes is an important issue of environmental concern.

1.2.4. Removal of nonylphenol and nonylphenol monoethoxylate from water and wastewater

Several researchers have attempted to eliminate micropollutants from water and wastewater using various oxidation processes. Chemical oxidation is necessary when the water samples contain non-biodegradable pollutants in conventional treatment. The degradation of NP and NP1EO using O_3 and ultraviolet photocatalytic treatment (UV/TiO_2) was 75–80% and 25–50%, respectively (Ike et al., 2002). This suggests that the removal of NP is easier than NP1EO. Kim et al. (2005) compared ozonation and electrochemical degradation of NPs. Ozonation was efficient, but electrochemical oxidation was an alternative option for the treatment of NPEOs. Sun et al. (2008) studied the ozonation of NP and the estrogenic activity of ozonation by-products from NP. The results showed that the estrogenic activity of NP was ultimately eliminated after ozonation.

Additionally, ultraviolet-C radiation and hydrogen peroxide treatment ($UV\text{-}C/H_2O_2$) and photo-Fenton treatment of NPnEO in synthetic freshwater were investigated by Karci et al. (2014). NPnEO (n = 1–10) usually used in surfactants was selected for degradation. The short polyethoxy chain occurred during degradation of NPnEO, and the intensities of ethoxylates with longer chain decreased after 20–30 min; however, these researchers found that it was difficult to oxidize NP1EO. The removal of NP using the Fenton process has been reported (Toda et al., 2011). The removal efficiency of NP was 86% in anaerobically digested sewage sludge samples after 6 h in the presence of H_2O_2 and Fe ion. However, a much larger amount of H_2O_2 was required for sludge samples than for water samples.

Wenlong et al. (2012) studied that the removal of bisphenol-A, NP, estrone, 17 α-estradiol and estrogenic activity from secondary effluents of WWTP by TiO_2 photocatalysis. The removal efficiencies of bisphenol-A and NP in wastewater treatment were more sensitive to temperature than those of estrone and 17 α-estradiol. All the targeted EDCs were degraded by TiO_2 photocatalysis for 1 h. The estrogenic activity was also removed. TiO_2 photocatalysis is an effective method for the removal of EDCs and estrogenic activity from secondary effluents.

Lee et al. (2005) examined kinetics of the oxidation of β-estradiol, 17α-ethinylestradiol, and bisphenol A during water treatment with potassium ferrate (K_2FeO_4). The oxidation rate constant of this compounds was determined at pH 6 – 8. The oxidation followed second-order reaction kinetics, indicating that these compounds can be significantly removed during water treatment at a K_2FeO_4 concentration of a few milligrams per liter (1 – 2 mg/L) within 30 min. Sharma et al. (2009) also investigated the kinetics of NP oxidation by K_2FeO_4 in water samples. The effect of pH on the NP oxidation was investigated in a range of pH from 8 – 11. The observed second-order rate constants decreased with an increase in pH.

Additionally, Zhang et al. (2012) examined the effects of K_2FeO_4 on sludge dewatering in a range of pH values from 3 to 8. Sludge disintegration degree increased with an increase in K_2FeO_4 at pH 3. These suggested that K_2FeO_4 pretreatment at pH 3 is a useful method for enhancing dewaterability. Li et al. (2019) also confirmed that the products of K_2FeO_4 can flocculate small particles to reduce sludge viscosity. Several studies have pointed out the advantage of reducing sludge volume by the use of K_2FeO_4

for the oxidation of sludge. However, there is little information on the removal of micropollutants from sewage sludge with K_2FeO_4.

1.3. Objectives and outline of the research

1.3.1. To clarify the usability of K_2FeO_4 produced by a wet chemical method to degrade NP and NP1EO in water and anaerobically digested sewage sludge samples and to investigate the effects of reaction time, initial and final pH, and Fe(VI) dosage on the removal of NP and NP1EO from water and sludge samples.

1.3.2. To characterize degradation products from NP with Fe(VI) based on the information about biodegradability, mass spectrum and estrogenic activity.

1.3.3. To assess the potential bioavailability of phosphorus compounds precipitated in the sludge treated with Fe(VI) using different extraction reagents.

1.4. References

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Chapter 2

Preparation of potassium ferrate

2.1. Introduction

Potassium ferrate (K_2FeO_4) is a powerful oxidant in both acidic and alkaline conditions and is a black-purple compound. Ferrate(VI) is environment-friendly because the use of K_2FeO_4 forms no hazardous waste after decomposition. The reaction product (ferric ion, Fe(III)) generated from FeO_4^{2-} performs as a coagulant due to the formation of $Fe(OH)_3$ (Pepino Minetti et al., 2017). The oxidation and reduction potentials of FeO_4^{2-} are expressed in equations (1) and (2) in acidic ($pH < 6.5$) and alkaline (pH 8–12) solutions, respectively (Sharma et al., 2006).

$$FeO_4^{2-} + 8H^+ + 3e^- \rightarrow Fe^{3+} + 4H_2O \qquad E^0 = 2.20\ V \qquad (1)$$

$$FeO_4^{2-} + 4H_2O + 3e^- \rightarrow Fe(OH)_3 + 5OH^- \qquad E^0 = 0.70\ V \qquad (2)$$

Ferrate(VI) can be prepared in the wet chemical or electrochemical methods. K_2FeO_4 is not commercially available because of its instability. The wet chemical method relies on simple reaction equipment and is applicable for large-scale production, and the product can be stored for a long time. In the wet chemical method, ferric(III) oxides are oxidized by hypochlorite in a highly alkaline solution. Potassium ferrate(VI) was prepared according to the reaction:

$$Fe(NO_3)_3 \cdot 9H_2O + 5KOH + 3/2KClO \rightarrow 3/2KCl + 23/2H_2O + K_2FeO_4 + 3KNO_3 \qquad (3)$$

However, the electrochemical method is promising for ferrate(VI) preparation as it has a simpler and relatively cleaner process and does not require hypochlorite and generate byproducts such as KCl and KNO_3. The electrochemical method involves the use of iron anode in an alkaline solution with an electric current supplying to oxidize zero valent Fe to Fe(VI) (equation (4)). The hydrogen gas is generated at the cathode (equation (5)) (Alsheyab et al., 2010).

Anode Reaction:

$$Fe + 8OH^- \rightarrow FeO_4^{2-} + 4H_2O + 6e^- \tag{4}$$

Cathode Reaction:

$$6H_2O + 6e^- \rightarrow 3H_2 + 6OH^- \tag{5}$$

Overall reactions (in KOH medium):

$$Fe + 2OH^- + 2H_2O \rightarrow FeO_4^{2-} + 3H_2 \tag{6}$$

$$FeO_4^{2-} + 2K^+ \rightarrow K_2FeO_4 \tag{7}$$

Additionally, K_2FeO_4 is a promising chemical oxidant for water and wastewater treatment processes. In several studies, FeO_4^{2-} has been used for the degradation of EDCs and pharmaceuticals in water and wastewater (Jiang et al., 2006, Sharma et al., 2009, Yang et al., 2012). Yu et al. (2008) studied the oxidation of NP in water samples using commercial K_2FeO_4 and found removal efficiencies of 71% and 26% at pH 6 and pH 9, respectively. A few researchers have studied to apply K_2FeO_4 for increasing the dewatering efficiency of the activated sludge (Zhang et al., 2012) However, there is very little literature describing the degradation of NP in sludge samples and NP1EO in water and sludge samples using K_2FeO_4.

2.2. Methodology

2.2.1. Wet chemical synthesis of potassium ferrate

K_2FeO_4 was prepared using the method reported by Li et al. (2005) with some modifications. Briefly, 20 mL of KClO (effective free chlorine: 5%), 9 g of KOH and 3.75 g of $Fe(NO_3)_3 \cdot 9H_2O$ were mixed for 1 h using a magnetic stirrer at a stirring speed of 500 rpm. Under these conditions, Fe(III) was oxidized to Fe(VI) and the color of the mixture turned dark purple as shown in Figure 2.1. Then, 15 mL of saturated KOH was added to the mixture and was further stirred for 2 h. The slurry was filtered using 0.3 μm glass fiber filters (GF-75, Advantec, Japan). The precipitate on the filter was collected, dried at 110 °C for 2 h, and stored in a vacuum desiccator prior to use.

The improvement of the purity of K_2FeO_4 was examined by increasing the amount of agents and changing the drying method. In brief, 40 mL of KClO, 18 g of KOH and 3.75 g of $Fe(NO_3)_3 \cdot 9H_2O$ were mixed for 1 h using a magnetic stirrer at a stirring speed of 500 rpm. Then, 30 mL of saturated KOH was added to the mixture and was further stirred for 2 h. The slurry was filtered using 0.3 μm glass fiber filters (GF-75, Advantec, Japan). The precipitate on the filter was collected and dried by freeze-drying. The precipitate of Fe(VI) was stored in the freezer at -50 °C for 24 hours. Upon removal from the freezer, the precipitate was transferred onto the drum manifold of a freeze-dryer (DC401/800, Yamato, Japan) and was dried under vacuum for 24 h. Then, the dried precipitate was crushed to fine powder and stored in a vacuum desiccator before use.

After the K_2FeO_4 precipitate was dissolved in ultrapure water, the concentrations of total Fe and hexavalent Fe (Fe(VI)) were determined by the method described in Section 2.2.3.

Figure 2.1 Mixing of chemicals (left) and powdered precipitate of K_2FeO_4 after freeze-drying (right).

2.2.2. Electrochemical synthesis of potassium ferrate

The electrosynthesis of ferrate(VI) was conducted using an electrolysis cell with two-separated compartments. The iron and mesh titanium electrodes were separately placed in beakers containing a highly alkaline solution (14.5 M KOH). The electrodes were connected to a DC power supply (A & D, AD-8724D) at a maximum voltage of around 30 V. 10 salt bridges were connected to the separated solutions, allowing ions to migrate to either solution for 6 h. Figure 2.2 shows a diagram of the experiment, and Figure 2.3 shows the operation of the electrosynthesis of ferrate(VI) in 14.5 M KOH. The temperature of synthesis is 55-60 °C (He et al., 2005). After the electrolysis, KOH (5 g / 20 mL) was added to precipitate K_2FeO_4 and was dried by freeze-drying as described above. Then, the concentration of Fe(VI) was determined as described in Section 2.2.3.

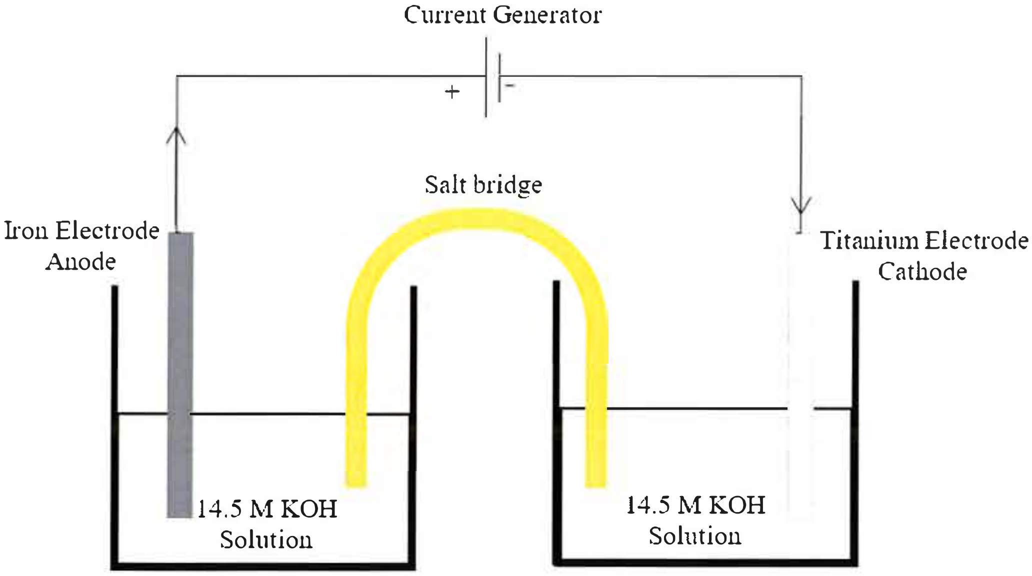

Figure 2.2 Schematic diagram for the electrochemical synthesis of ferrate(VI).

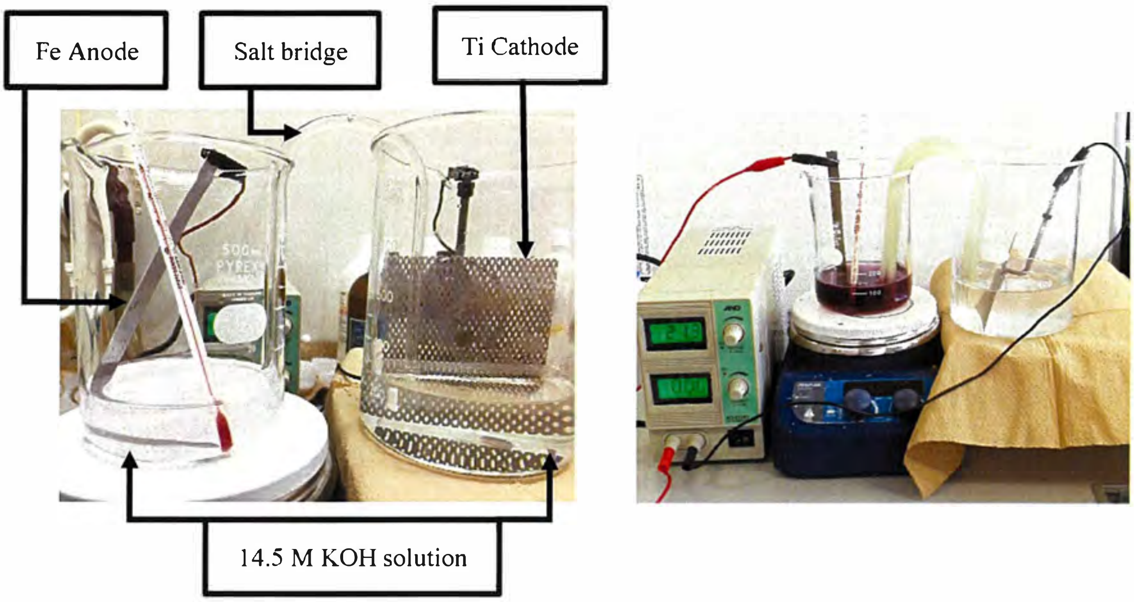

Figure 2.3 Electrochemical synthesis of ferrate(VI).

2.2.3. The concentrations of total dissolved Fe and Fe(VI) ions

For the determination of total Fe concentration, the synthesized K_2FeO_4 precipitate was dissolved in ultrapure water and was digested using hydrochloric acid (HCl) under heating on a hot plate (90 °C). After that, the solutions were allowed to cool down to room temperature and diluted to 100 mL with ultrapure water. The total Fe was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (ICPE-9000, Shimadzu, Japan) after digestion.

The Fe(VI) concentrations were determined using a UV/VIS spectrometer (Jasco V-530, JASCO Corp., Tokyo, Japan) by the ABTS method (Lee et al., 2005). The stock solutions of ABTS reagent were prepared by dissolving 0.1 g 2,2′-Azino-bis (3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (Sigma-Aldrich, Tokyo, Japan) in 100 mL of ultrapure water. A pH 4.1 buffer solution containing 0.6 M acetate and 0.2 M phosphate was prepared by dissolving 3.43mL of acetic acid (CH_3CO_2H), 0.78 g of sodium phosphate dibasic dihydrate ($NaH_2PO_4 \cdot 2H_2O$), and 2.67 g of sodium dihydrogen phosphate monohydrate (Na_2HPO_4 $2H_2O$) in 100 mL ultrapure water. A 5 mM Na_2HPO_4/1 mM borate buffer (pH ≈ 9.1) was prepared for the Fe(VI) standard solutions and synthesized Fe(VI) solutions. A 1 mM borate buffer was prepared by dissolve 0.62 g of boric acid (H_3BO_3) and 0.2 g of sodium hydroxide (NaOH) in 100 mL ultrapure water. A 5 mM Na_2HPO_4/1 mM borate buffer was prepared by dissolving 0.89 g of Na_2HPO_4 $2H_2O$ in 1 L ultrapure water and was mixed with 10 mL of 1 mM borate buffer. The Fe(VI) standard solutions (0-100 μM) were prepared by dissolving the different amounts of commercial K_2FeO_4 (purity > 90%, Sigma-Aldrich Tokyo, Japan) with 5 mM Na_2HPO_4/1 mM borate buffer using a series of 25 mL volumetric flasks. The synthesized Fe(VI) solution was also prepared by dissolving 0.1 g of synthesized Fe(VI) in 100 mL of 5 mM Na_2HPO_4/1 mM borate buffer, then 1 mL of this solution was further diluted to 100 mL of 5 mM Na_2HPO_4/1 mM borate buffer. 5 mL of pH 4.1 buffer containing 0.6 M acetate and 0.2 M phosphate and 1 mL of ABTS reagent were added to 25 mL volumetric flasks. Then, 19 mL of the standard Fe(VI) solutions and the synthesized Fe(VI) solution were added into the series of the flasks, respectively. After checking that no significant decomposition of Fe(VI) occurred in the mixture, the absorbance was measured at a wavelength of 410 nm within 30 min. The calibration curve was illustrated between the absorbances and the concentrations of Fe(VI) standard (Figure 2.4).

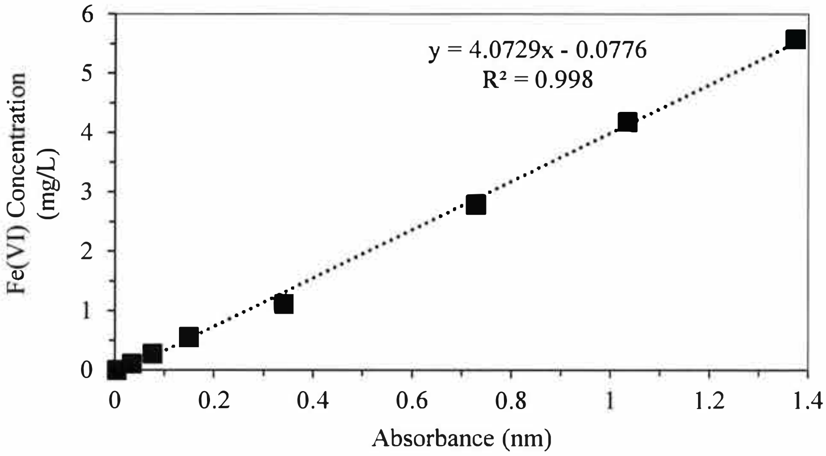

Figure 2.4 Example of calibration curve for the analysis of Fe(VI).

The purity percentage and total iron recovery of the synthesized K_2FeO_4 precipitate were calculated as follows:

$$\text{Purity (\%)} = C \times M_{K_2FeO_4}/M_{Fe} \times 100 \tag{8}$$

$$\text{Recovery of total iron (\%)} = T_p/T_m \times 100 \tag{9}$$

where C is Fe(VI) content (g/g-dried precipitate); $M_{K_2FeO_4}$ is the molar mass of K_2FeO_4 (198.04 g/mol); M_{Fe} is the molar mass of Fe (55.8 g/mol); T_P is the total iron in precipitate (g); and T_m is the total iron (0.52 g) in $Fe(NO_3)_3 \cdot 9H_2O$ added when K_2FeO_4 was prepared.

2.3. Results and discussion

In the wet chemical method, the present preparation procedure increased the purity of K_2FeO_4 from ~30% to ~70% and the recovery of total iron from ~50% to ~80% compared to the previous one. First, the higher volume of hypochlorite in the solution can decrease the impurity of the ferrate(VI) solution (Li et al., 2005). An increase in the amount of KOH could improve the precipitation yield of K_2FeO_4. Moreover, the black color of the synthesized K_2FeO_4 precipitate was strengthened visually and the precipitate became stable for more than a month by changing the drying process to freeze-drying.

The results of ferrate(VI) electrosynthesis showed that the purity of K_2FeO_4 was approximately 27%. Several researchers have reported that the efficiency of ferrate(VI) production by the electrochemical method is related to the intensity of the electric current, the anode electrode material, the type and concentration of the electrolyte, temperature, and pH of solution (Barışçı et al., 2015, Talaiekhozani et al., 2016). Consequently, the further investigation under different conditions is required to improve the purity of ferrate(VI).

2.4. Conclusions

The ferrate(VI) synthesis was carried out using the wet chemical and electrochemical methods. For the wet chemical method, the present preparation procedure increased the purity of K_2FeO_4 from 30% to 70% and the recovery of total iron from 50% to 80% compared to the previous one. In electrochemical method, the purity of K_2FeO_4 was approximately 27%. However, the further work on the electrochemical methods is needed to find out better operating conditions that enhance the current density.

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Chapter 3

Removal of nonylphenol and nonylphenol monoethoxylate using potassium ferrate

3.1. Introduction

NP and NP1EO are EDCs group and present negative impact to human and environment that has been described in Chapter 1. Mainly, sewage sludge can be recycled as a raw material for a fertilizer that might cause an accumulation of micropollutants in soils and plants. Therefore, advanced oxidation processes are an option for the removal of EDCs. As an alternative, Fe(VI) has the potential to remove EDCs (Sharma et al., 2009). Nevertheless, studies for the Fe(VI) reaction with NP and NP1EO are still limited in the Fe(VI) dosage and pH range that are important in treatment of water and sludge sample.

The objective of this Chapter is to clarify the usability of K_2FeO_4 produced by a wet chemical method to degrade NP and NP1EO in water and anaerobically digested sewage sludge samples

3.2. Methodology

3.2.1. Removal of nonylphenol from water samples

3.2.1.1. Experiments on nonylphenol removal from water samples

A stock solution of NP was prepared in methanol with a concentration of 2 g/L and store at 4 °C until use. Water samples with a NP concentration of 1 mg/L were prepared by diluting the stock solution with ultrapure water. The experiments were performed in a 1 L beaker with a magnetic stirrer (700 rpm) at 25 ± 1 °C. The initial pH was adjusted to 6 using 0.1 M H_2SO_4 or 1 M KOH. Reactions were initiated by adding a dried precipitate of K_2FeO_4 (purity 27 - 30%) to the water sample under rapid mixing. The dosages of Fe(VI) were set to 1, 2, and 5 mg/L. Additionally, the initial pH values were adjusted to 2, 2.5, 3, 4 and 5 at a Fe(VI) dosage of 5 mg/L. The water samples were collected from the beakers for the determination of NP concentrations. The reaction between NP and Fe(VI) in the samples was stopped by the addition of methanol and NP was extracted with DCM (Japan Sewage Works Association, 2012). The residual concentrations of NP were analyzed by the gas chromatography mass spectrometry (GC/MS).

3.2.1.2. Analytical method for nonylphenol

The analysis of NP was performed using Agilent 7890A-GC coupled with a 5975C-MS (Agilent Technologies, USA) after derivatization with N,O-Bis(trimethylsilyl)-trifluoroacetamide (Wako, Japan) based on the standard methods for sewage (Japan Sewage Works Association, 2012). The mass to charge (*m/z*) values of 207 and 208 were monitored for the derivatized compounds of NP. Chromatographic separation was conducted using a fused silica capillary column (length 30 m × internal diameters 0.25 mm and film thickness 0.25 μm). The oven temperature was initially set at 50 °C, which was held for 1.5 min, rising to 130 °C at a rate of 50 °C min^{-1}, 210 °C at 5 °C/min, and finally to 280 °C at 50 °C min^{-1}, and held for 5 min. The temperature of the transfer line was set at 280 °C. The injection volume was set to 2 μL in splitless mode at 280 °C. Mass spectrometry was performed using an electron impact (EI) mode of 70 eV. The LOD in this method was 0.25 μg/L.

3.2.2. Removal of nonylphenol from sludge samples

Dewatered sludge after anaerobic digestion was collected from the Tonan sewage treatment plant in Morioka, Japan (Table 3.1), and NP was found in the sample of dewatered sludge (mean 1.2 mg/kg of dry solid). The sample was stored in a refrigerator at 2 °C until use. Dewatered sludge samples were mixed with ultrapure water to adjust the solid concentration to 20 g/L. The pH of 500 mL sludge samples was adjusted to 2 using 1 M H_2SO_4 or 1 M KOH while agitating with a shaker for 24 h at 25 ± 1 °C. Then, the different dosages of K_2FeO_4 synthesized by the wet chemical method were added to the samples. 10 g of the sludge samples were transferred to polytetrafluoroethylene (PTFE) vessels with defined time intervals and mixed with 10 mL of methanol as an extracting agent for NP. The mixture of solid and liquid phases of the samples was subject to a microwave-assisted extraction process, which consisted of heating the samples at 120 °C for 30 min. After the extraction, all samples were allowed to cool to room temperature (25 ± 1°C). The extract was centrifuged at 3,000 rpm for 10 min. The supernatant was decanted into a glass tube and passed through a 0.3 μm glass fiber filter (GF-75, Advantec, Japan). The extraction was repeated twice. NP in the combined extract was diluted with ultrapure water to decrease methanol concentration and was extracted with DCM. The DCM layer was separated from water and concentrated to 5 mL by drying using N_2 gas. The recovery for NP was about 80% during this extraction process. The residual concentrations of NP were analyzed using the GC/MS as described before. All experiments were conducted in triplicate and mean concentration values were calculated.

Table 3.1 Physicochemical characterization of the sludge.

Parameters	**Anaerobically Digested Sewage Sludge**
Water content of dewatered sludge (%)	80.0
pH (Dewatered sludge:ultrapure water, 1:1)	6.8
Phosphorus content of dewatered sludge (g/kg)	8.2
TS after mixing with ultrapure water (g/L)	19.3
VS after mixing with ultrapure water (g/L)	15.0
VS after addition of Fe(VI) (g/L)[a]	13.8

[a] Fe(VI) dosage to sludge sample was 0.5 g/L and reaction time was 3 h.

3.2.3. Removal of nonylphenol monoethoxylate from water samples

3.2.3.1. Experiments on nonylphenol monoethoxylate removal from water samples

The removal of NP1EO from water samples (1 L) using the synthesized K_2FeO_4 was conducted using 1 L beakers with a magnetic stirrer (700 rpm) at 25 ± 1 °C. The initial concentration of NP1EO was set to 100 μg/L, and the initial pH values of the solutions were adjusted to 2, 2.5, 3, 3.5, 4 and 5 using 0.1 M H_2SO_4 or 1 M KOH. The reactions were initiated by adding the dried precipitate of K_2FeO_4 to the samples under rapid mixing, and the Fe(VI) dosages were set to 1, 5 and 10 mg/L, respectively. After 1 h, 50 mL of each sample was taken from beakers and filtered using a 0.3 μm glass fiber filter (GF-75, Advantec, Japan) after adding a thiosulfate solution (5 mM $Na_2S_2O_3$, 1.25 mL) to stop the reaction. NP1EO in each sample was extracted with a Sep-Pak Plus PS2 cartridge preconditioned with 10 mL of MeOH and 10 mL of ultrapure water. After sample loading, the cartridges were dried for 10 min and NP1EO was eluted from the cartridge with 10 mL of MeOH. Then, the samples were evaporated to 0.2 mL with N_2 gas and the final volume was made up to 1 mL using 0.3 mL methanol and 0.5 mL ultrapure water (the final ratio of MeOH to water was 1:1). The NP1EO concentration of each sample was determined using the liquid chromatography tandem mass spectrometry (LC-MS/MS). All experiments were conducted in triplicate, and mean values were calculated.

3.2.3.2. Analytical method for nonylphenol monoethoxylate

NP1EO was determined by the LC-MS/MS. Chromatographic separation was conducted using an Acuity UPLC H-Class (Waters, USA) equipped with an Acuity UPLC BEH C18 column (internal diameters 2.1 × length 50 mm and particle size 1.7 μm) (Waters, USA). The mobile phase consisted of 0.005% formic acid in ultrapure water (Solvent A) and MeOH (Solvent B) using the following gradient as shown in Table 3.2. The column temperature was maintained at 40 °C, and the injection volume was 5 μL. The UPLC was coupled to a Xevo TQD triple quadrupole mass spectrometer (Waters, USA) equipped with an electrospray ionization source. Instrument control, data acquisition, and quantification were performed using Mass Lynx 4.1 software (Waters, USA). Identification of NP1EO was achieved by scanning precursor ion at an *m/z* of 282.2 and product ion at an *m/z* of 127. The capillary voltage was set at 3.50 kV. The source temperature was 130 °C and the desolvation temperature was 400 °C.

Table 3.2 Gradient conditions of the mobile phase.

Time (min)	Flow rate (mL/min)	Solvent A (%)	Solvent B (%)
0.0	0.4	85	15
4.0	0.4	85	15
8.0	0.3	0	100
10.0	0.4	0	100
10.5	0.4	0	100
11.0	0.4	85	85
12.0	0.4	85	85

Calibration curves for NP1EO quantification were generated using linear regression analysis (1 – 100 μg/L), which gave good fits ($R^2 \geq 0.99$). The LOD in this method ranged from 0.07 to 0.15 μg/L.

3.2.4. Removal of nonylphenol monoethoxylate from sludge samples

The concentration of sludge samples was adjusted to 20 g dry solid/L with ultrapure water and was spiked with 10 mg/L NP1EO standard solution (5 mL). The initial pH of sludge suspensions (500 mL) in the shaking flasks was adjusted to 2 and the suspensions were agitated with a shaker for 24 h at 25 ± 1 °C. K_2FeO_4 precipitate was added to the samples and then stirred at 120 rpm. The Fe(VI) dosages were set to 0.05, 0.1, 0.2, 0.3 and 0.5 g/L. After 6 h, 20 mL of the samples were taken from the shaking flasks and centrifuged at 3,000 rpm for 10 min. The supernatant was separated and filtered through a 0.3 μm glass fiber filter (GF-75, Advantec, Japan) followed by the solid phase extraction. The concentrations of NP1EO in the liquid phase were lower than the limit of detection (LOD). Therefore, the concentration of NP1EO in the solid phase only was provided in this study. The sludge sample (0.2 g as dry weight) was extracted with 15 mL of a mixed solvent of DCM/MeOH (70:30, v/v) (Lian et al., 2009) and vortexed for 2 min. Then, the mixture was sonicated for 20 min and the supernatant was taken after centrifugation at 3,000 rpm for 10 min. This procedure was repeated twice. The supernatants were combined, evaporated to a volume of 1 mL using N_2 gas, and redissolved in 200 mL of water. The subsequent solid phase extraction was performed using Sep-Pak Plus PS-2 cartridges connected to a Concentrator (SPC 10-C; Chratec, Kyoto, Japan) at a flow rate of 10 mL/min. Then, samples for analysis by LC-MS/MS were prepared as described above. The recoveries of NP1EO in liquid and solid phases of dewatered sludge ranged from 84% to 92%.

3.2.5. Comparison of nonylphenol and nonylphenol monoethoxylate removal between potassium ferrate and ferric sulfate

NP and NP1EO removals by Fe(VI) and Fe(III) from water samples were investigated. K_2FeO_4 precipitate and aqueous ferric sulfate solution ($Fe_2(SO_4)_3$) were added to the water samples, separately. The initial concentration of NP and NP1EO were set at 1 mg/L and 100 µg/L and the initial pH values of NP and NP1EO solutions were adjusted to 4 and 3, respectively. In NP removal experiments, the dosage of Fe(VI) was set at the optimum dosage of 5 mg/L and the total Fe concentrations were similarly set to 20 mg/L in two different iron sources. In NP1EO removal experiments, the Fe(VI) dosages were set to 1, 5, and 10 mg/L and the total Fe concentrations were set to 4, 20, and 40 mg/L. Immediately after iron addition, the pH values of water samples containing NP and NP1EO were adjusted to 10 and 4 with 0.1 M H_2SO_4 or 1 M KOH to precipitate ions as $Fe(OH)_3$.

After stirring for 1 h, the water samples were partly collected and filtered using a 0.3 μm glass fiber filter (GF-75, Advantec, Japan). Afterwards, the remaining water samples were acidified at a pH of 2.5 to solubilize the precipitate of $Fe(OH)_3$ and filtered using the same filter. NP in filtered samples (5 mL) was extracted with DCM as described in Section 3.2.1.1. NP1EO in filtered sample (10 mL) was extracted with Sep-Pak Plus PS2 cartridges as described above in Section 3.2.3.1. Each filtered sample was digested using HNO_3 and HCl under heating at 90 °C, and diluted to a final volume of 25 mL with ultrapure water. The concentration of dissolved total iron was analyzed using the ICP-AES.

Also, the removals of NP1EO by Fe(VI) and Fe(III) were examined in sludge samples, separately. The concentration of NP1EO spiked to sludge samples was set at 100 μg/L and the initial pH value was adjusted to 2. The dosage of Fe(VI) was set at the optimum dosage of 0.1 g/L and the total Fe concentration was set to 0.4 g/L in two different iron sources. The pH values were immediately adjusted to 3 after iron addition to match the conditions of sludge samples. Each sample was collected after 6 h and NP1EO was extracted from the samples as described in Section 3.2.4.

3.3. Results and discussion

3.3.1. Removal of nonylphenol from water samples

The initial pH and NP concentration in the water phase were 6.0 ± 0.7 and 1.0 ± 0.1 mg/L, respectively. The variations in NP concentrations over time with Fe(VI) dosages of 0, 1, 2 and 5 mg/L are presented in Figure 3.1. The NP concentrations decreased drastically within the first 5 min of reactions, followed by gradual decrease over 60 min. At a lower Fe(VI) dosage of 1 mg/L, the concentration of NP significantly decreased from 1.0 ± 0.1

mg/L to 0.31 ± 0.04 mg/L after 60 min. The concentrations of NP decreased to less than 0.1 mg/L when the dosages of Fe(VI) were increased to 2 and 5 mg/L.

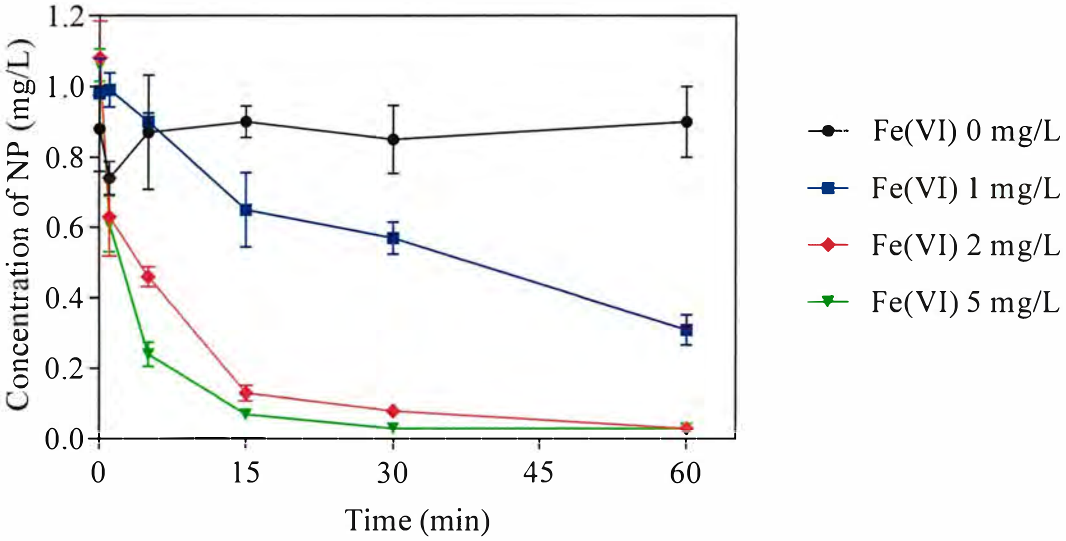

Figure 3.1 Variation in NP concentrations in water samples over time with different Fe(VI) dosages.

In addition, fitting of NP concentrations to the following first order and second order kinetic models (Eqs. (10) and (11)) was examined to obtain the decreasing rates of NP in water samples:

$$\ln (C/C_0) = -k_1 t \quad (10)$$

$$1/C = k_2 t + 1/C_0 \quad (11)$$

where C is the concentration of the target compound (μg/L) at certain time t and C_0 is the initial concentration of the target compound (μg/L). The first and second order kinetic constants (k_1 and k_2) and determination coefficients (r_1^2 and r_2^2) can be obtained from the linear regression analysis. The time variations of ln (C/C_0) and 1/C in water samples with different Fe(VI) dosages are presented in Figure 3.2. Removal of NP from water samples had a better fit with the second order kinetic model (Table 3.3). The value of k_2 increased proportionally with an increase in Fe(VI) dosage from 1 to 5 mg/L (Figure 3.3). Therefore, the optimum Fe(VI) dosage for NP removal in water sample was 5 mg/L with a removal efficiency of 97% after 1 h. In contrast, Toda et al. (2011) reported that the removal of NP was achieved in 6 h by a combination of H_2O_2 (1 g/L) and Fe ion (0.16 g/L). It seems that NP removal by Fe(VI) was faster than that by H_2O_2 and Fe ion. The pH of all solutions after adding K_2FeO_4 sharply increased and then reached about 10; Fe(VI) is reduced into Fe(III) as shown in Eq. (1) and the precipitate of the K_2FeO_4 probably contained potassium hydroxide as an impurity. Ito et al. (2014) have investigated the removal of NP using a commercial K_2FeO_4 and reported that removal efficiency with Fe(VI) dosage of 5 mg/L and an initial pH of 6.0 was higher than 90% with a final pH of 10.

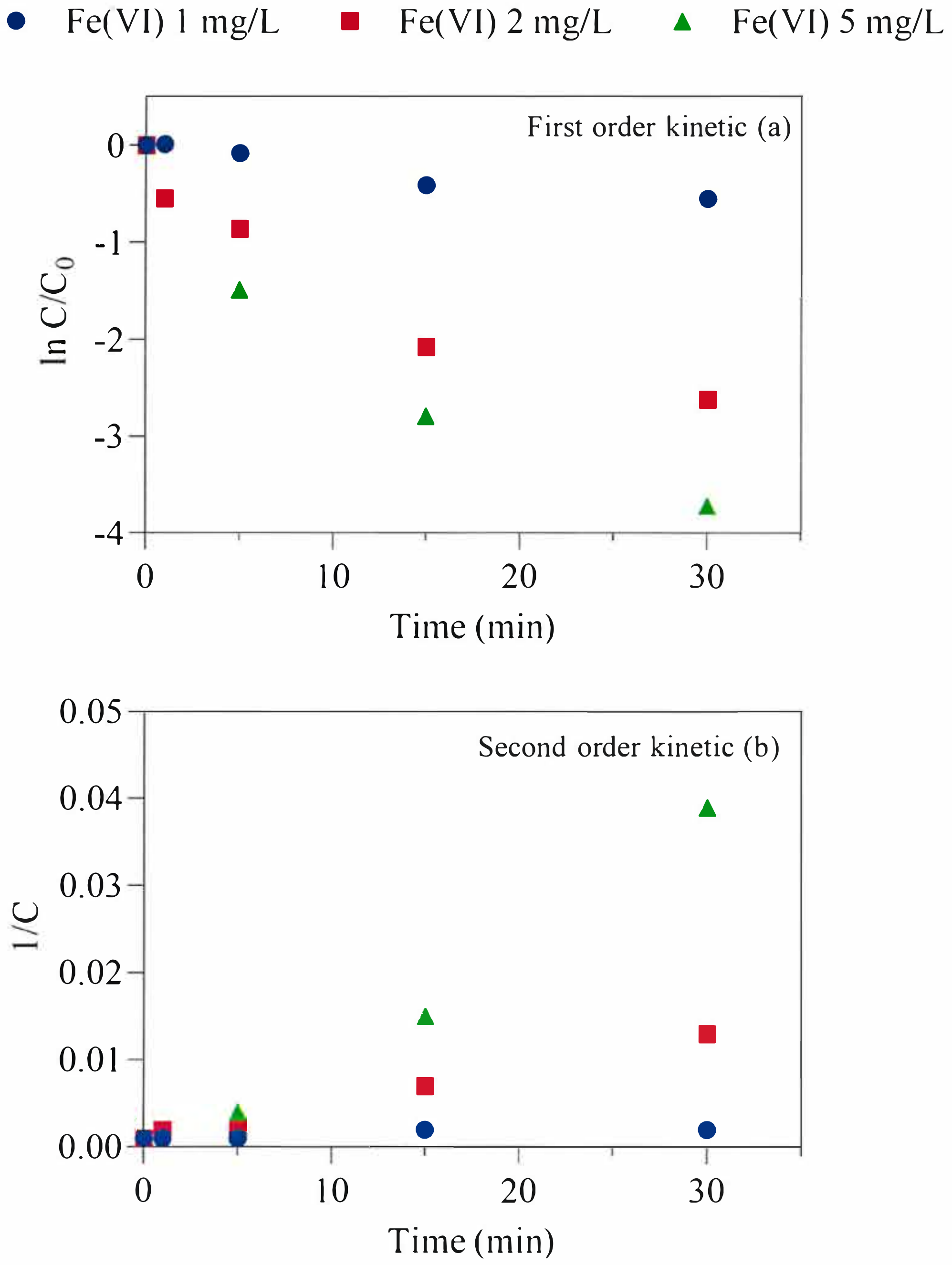

Figure 3.2 Variations of ln (C/C_0) (a) and 1/C (b) in water samples over time with different Fe(VI) dosages. Experimental condition: NP = 1 mg/L, initial pH = 6.

Table 3.3 Kinetic constants for NP removal from water samples using Fe(VI).

Samples	**Fe(VI) dosage**	**First order**		**Second order**	
		k_1 **(1/min)**	r_1^2	k_2 **(L/μg/min)**	r_2^2
Water samples	1 mg/L	1.98×10^{-2}	0.94	3.00×10^{-5}	0.95
	2 mg/L	8.31×10^{-2}	0.91	4.00×10^{-4}	0.99
	5 mg/L	1.18×10^{-1}	0.92	1.30×10^{-3}	0.98

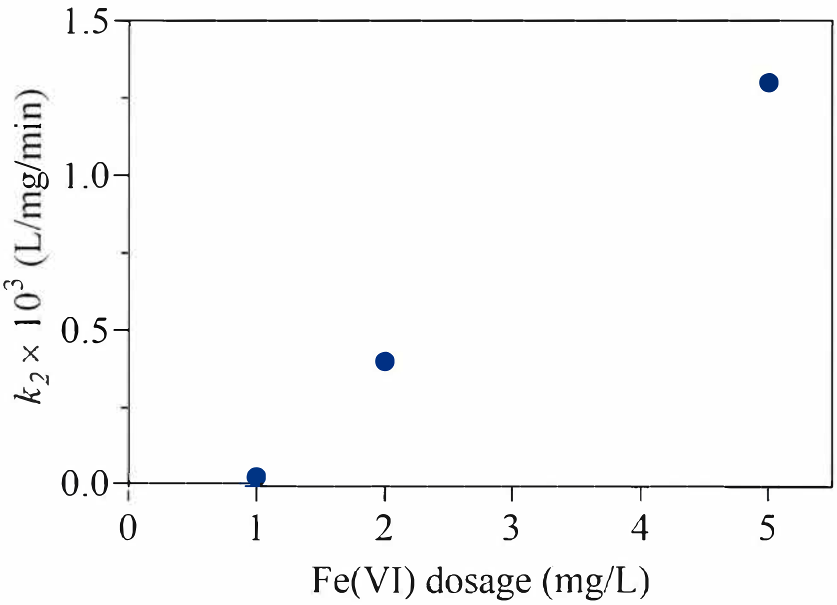

Figure 3.3 Relation between second order rate constant (k_2) for NP removal by Fe(VI) and Fe(VI) dosage in water samples at initial pH of 6.

Sharma et al. (2009) have studied on oxidation of NP by Fe(VI) in water under alkaline conditions (pH 8-11). The results showed that pH value has an influence on NP oxidation by Fe(VI). Nevertheless, there have been limited studies on removal of NP by Fe(VI) under acidic conditions. Consequently, the effect of initial pH on the removal of NP was examined at the optimum Fe(VI) dosage condition in the range of pH from 2 to 5. The time variations of ln (C/C_0) and $1/C$ in water samples at different initial pH values are presented in Figure 3.4. The removal of NP was well expressed by the second order reaction kinetic model (Table 3.4). The values of k_2 increased significantly from 1.00×10^{-6} to 1.50×10^{-3} L/μg/min with an increase in the pH from 2 to 5 (Figure 3.5 (a)). Sharma et al. (2009) reported the k_2 of 2.70×10^2 $M^{-1}s^{-1}$ for NP oxidation by Fe(VI) at pH 8, which is markedly lower than our result (3.83×10^5 $M^{-1}s^{-1}$ at initial pH 5). This might be brought about by different experimental conditions of high Fe(VI) dosage and initial pH under acidic conditions in this study, since Fe(VI) has a higher redox potential (Eq. (1)) under moderately acidic condition (pH 4 - 5) (Li et al., 2005) compared to alkaline condition.

The removal efficiency (R) was calculated using Eq. (12) and the results are shown in Figure 3.5 (a):

$$R\,(\%) = (C_0 - C_t)/C_0 \times 100\% \qquad (12)$$

where C_0 is the initial concentration of NP and C_t is the concentration of NP at time t.

Removal efficiency with initial pH values of 4 and 5 was over 90% (Figure 3.5 (a)) and resulted in higher final pH (approximately 10) compared to the samples with lower initial pH values (Figure 3.5 (b)). However, NP removal efficiency dropped significantly to 78% with an initial pH of 3, and further to 57% with an initial pH of 2, and final pH ranged from 2 to 3. Decreasing the initial pH decreased the removal efficiency of NP by Fe(VI). Al-Abduly and Sharma (2014) reported that Fe(VI) undergoes spontaneous decomposition in water as shown in Eq. (13), and the rate of this reaction at pH 9 – 10 was slower than at lower pH (acidic conditions). Therefore, Fe(VI) probably reacted with water rather than NP under acidic conditions:

$$2FeO_4^{2-} + 5H_2O \rightarrow 2Fe^{3+} + 3/2\,O_2 + 10OH^- \quad (13)$$

Table 3.4 Kinetic constants for NP removal from water samples at different initial pH values with a Fe(VI) dosage of 5 mg/L.

Compounds	**Initial pH**	**Fe(VI) dosage (mg/L)**	**First order**		**Second order**	
			k_1 (1/min)	**r_1^2**	**k_2 (L/μg/min)**	**r_2^2**
NP	2	5	2.00×10^{-3}	0.97	1.00×10^{-6}	0.97
	3		1.21×10^{-2}	0.44	3.00×10^{-5}	0.58
	5		6.17×10^{-2}	0.58	1.50×10^{-3}	0.91

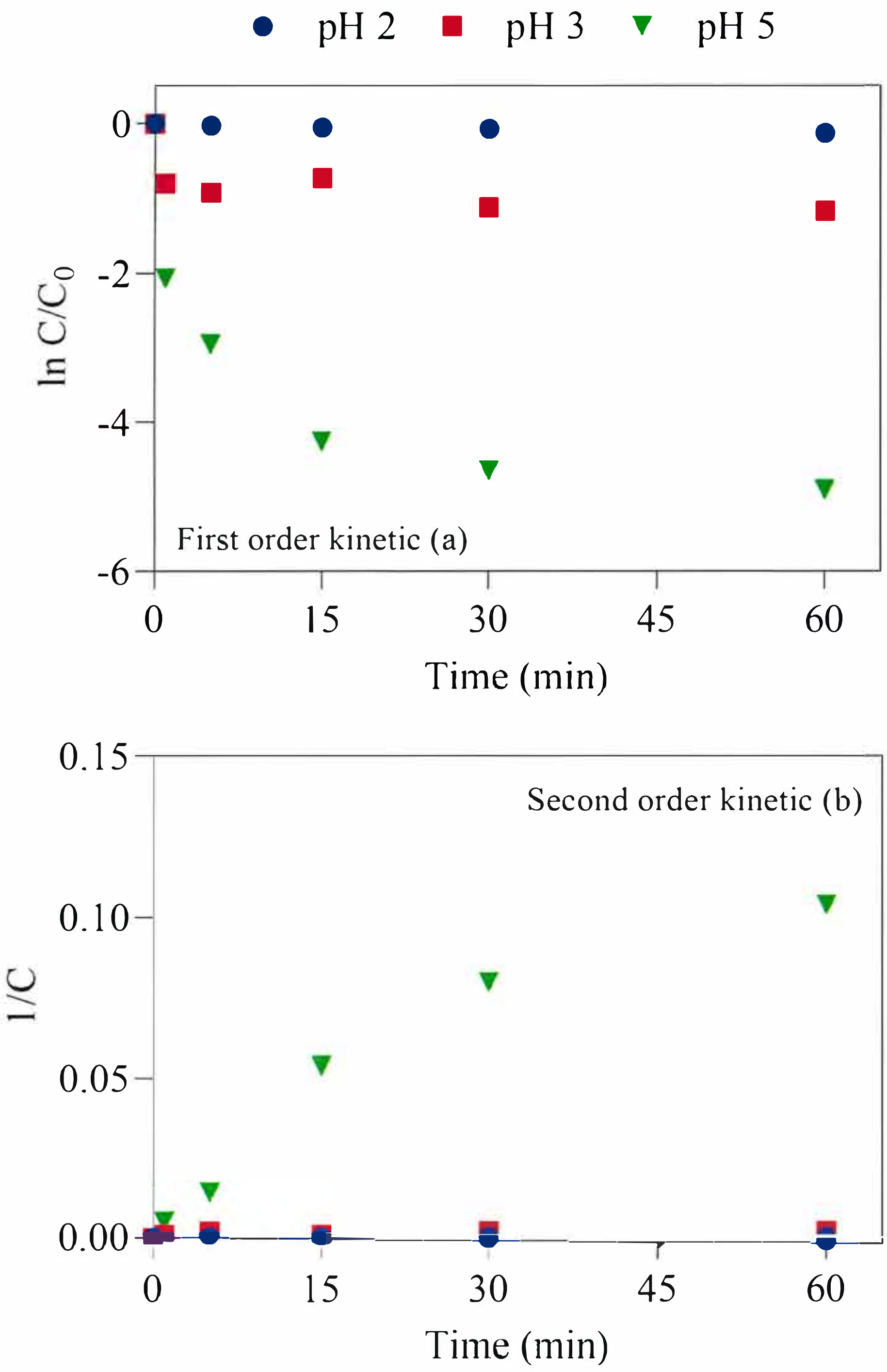

Figure 3.4 Variations of ln (C/C_0) (a) and 1/C (b) over time for NP removal by Fe(VI) at different initial pH values. Experimental condition: NP = 1 mg/L, Fe(VI) = 5 mg/L.

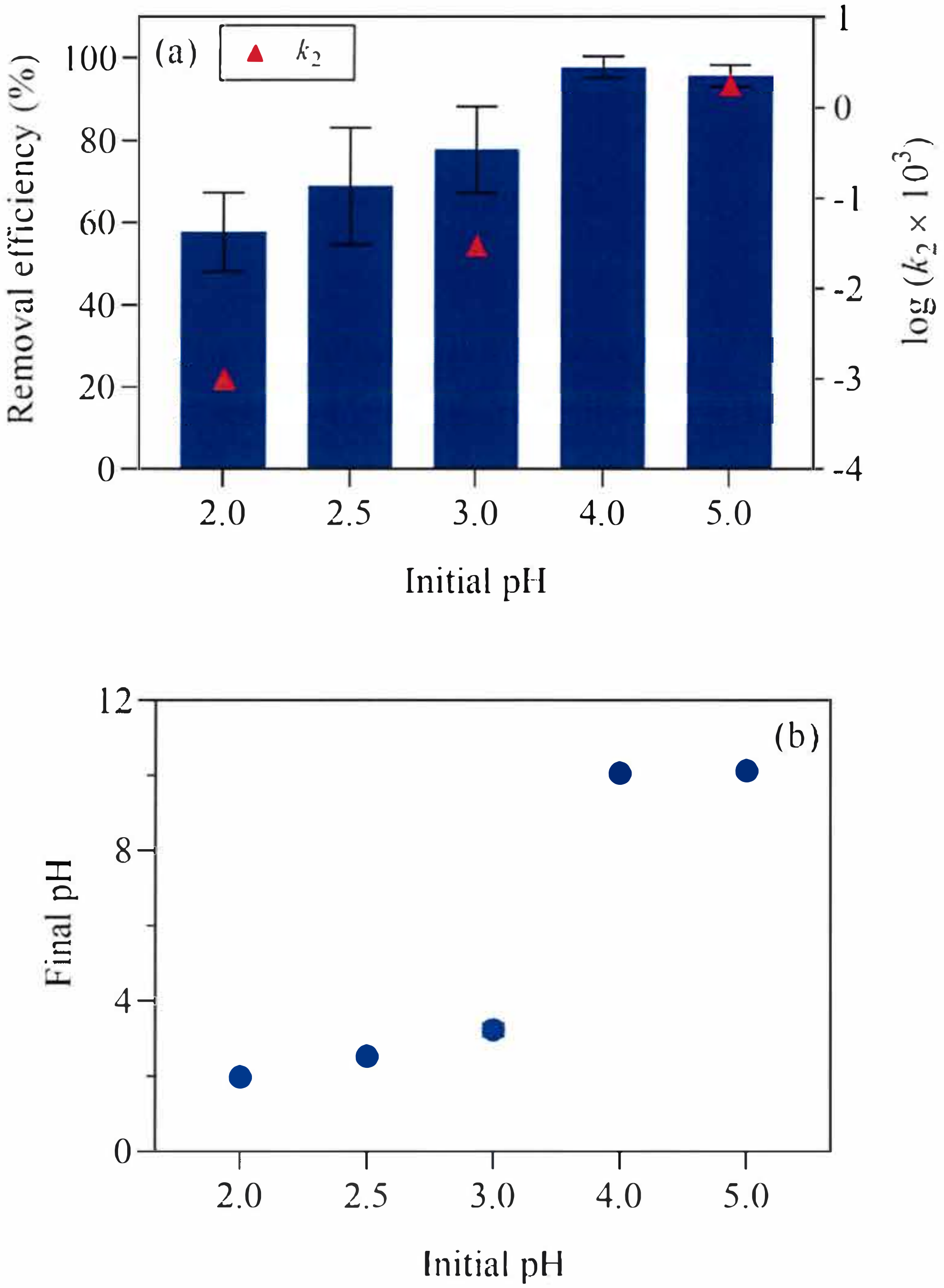

Figure 3.5 NP removal efficiency after 1 h and second order rate constants (k_2, L/μg/min) (a), and final pH (b) in water samples with a Fe(VI) dosage of 5 mg/L at different initial pH values.

3.3.2. Removal of nonylphenol from sludge samples

The initial concentration of NP in sludge sample was 50 ± 6 μg/L. Variations in NP concentrations and pH over time at different Fe(VI) dosages are presented in Figure 3.6. The time variations of ln (C/C_0) and $1/C$ in sludge samples at different Fe(VI) dosages are presented in Figure 3.7. The removal of NP was well fitted with the second order kinetic model (Table 3.5). The k_2 values for NP removal in the sludge samples decreased from 2.00×10^{-4} to 5.00×10^{-5} L/μg/min with an increase in Fe(VI) dosage from 0.5 to 1 g/L. The NP removal efficiency was 58% with a Fe(VI) dosage of 0.5 g/L after 180 min (Figure 3.8). However, by increasing the Fe(VI) dosage to 1 g/L, the NP removal efficiency was reduced to around 40%. These results show that the sludge samples needed more than 200 times the dosage of Fe(VI) to achieve similar k_2 values (10^{-4} L/μg/min) as the water samples.

Moreover, the removal efficiencies of NP in sludge samples were lower than those in the water samples, since sludge sample had a complex matrix with organic and inorganic substances, which may affect NP removal. The concentration of volatile solids (VS) was reduced from 15.0 g/L to 13.8 g/L by addition of Fe(VI) (Table 3.1). This suggested that organic matters as a matrix in the sludge samples might consume Fe(VI) and inhibit NP degradation by Fe(VI). Furthermore, in practice, digested sewage sludge and Fe(VI) should be mixed well to drive contact between NP in sludge and Fe(VI), although more energy will be needed for the sludge because of higher viscosity compared to water samples.

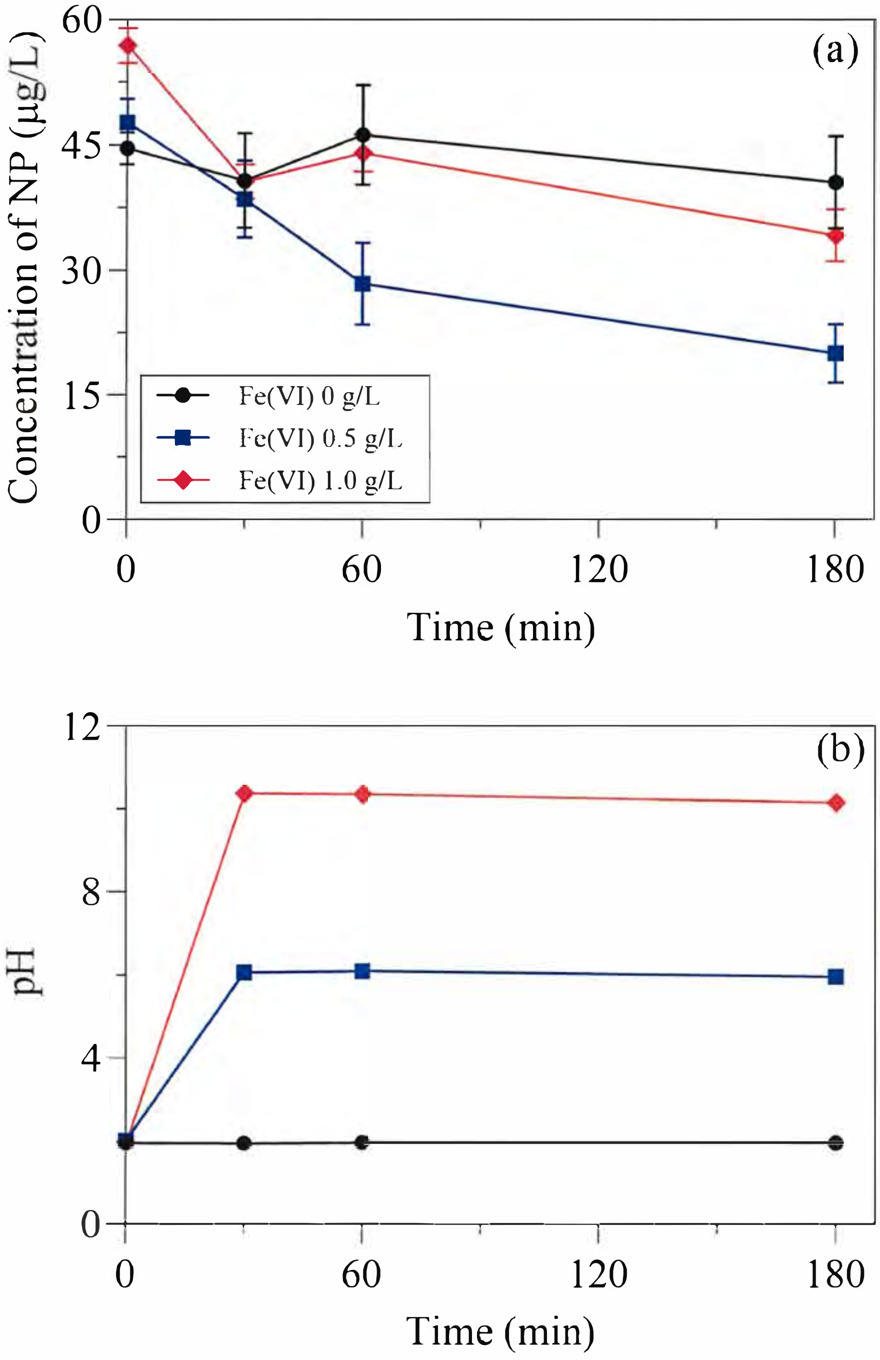

Figure 3.6 Variations in NP concentration (a) and pH (b) in sludge samples over time with different Fe(VI) dosages.

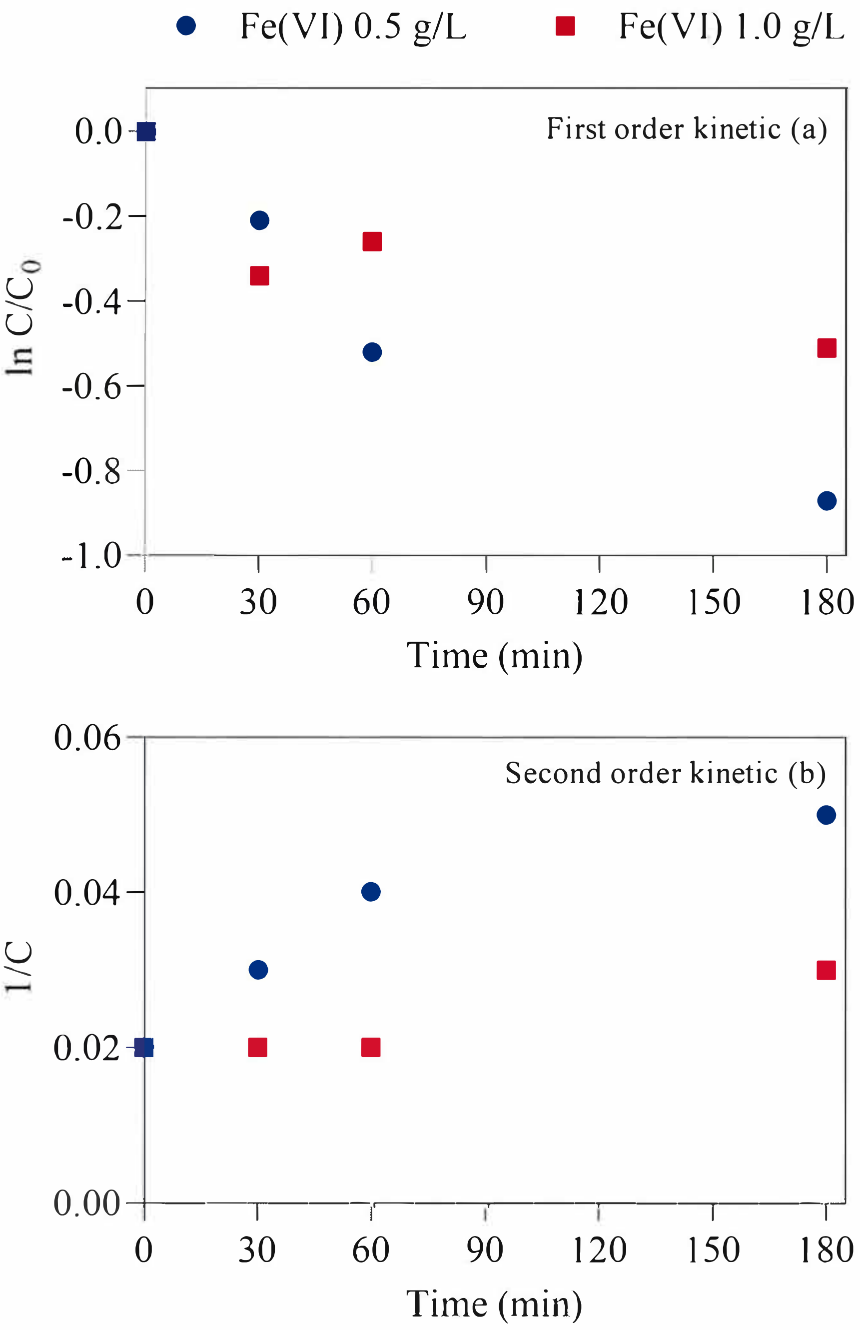

Figure 3.7 Variations of ln (C/C_0) (a) and 1/C (b) over time for sludge samples with different Fe(VI) dosages. Experimental condition: NP = 50 μg/L, initial pH = 2.

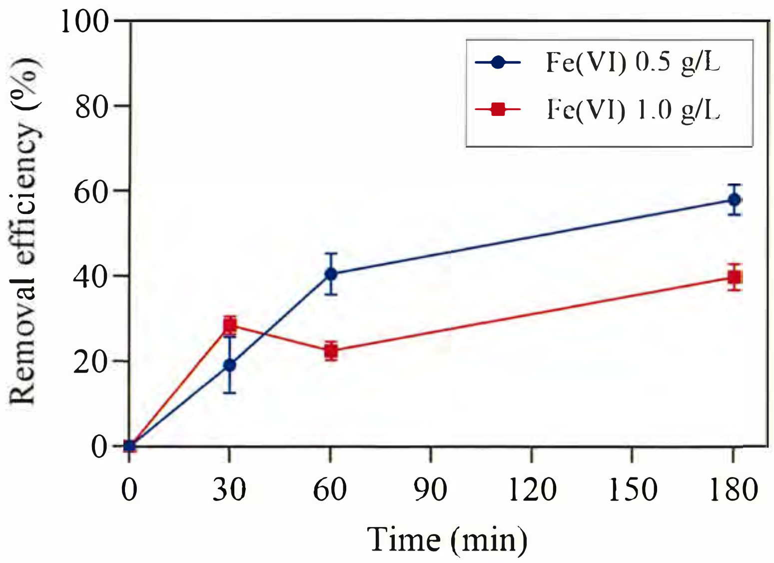

Figure 3.8 Variation in NP removal efficiency from sludge samples over time with different Fe(VI) dosages.

Table 3.5 Kinetic constants for NP removal from sludge samples using Fe(VI).

Samples	**Fe(VI) dosage**	**First order**		**Second order**	
		k_1 **(1/min)**	r_1^2	k_2 **(L/μg/min)**	r_2^2
Sludge samples	0.5 g/L	4.60×10^{-3}	0.92	2.00×10^{-4}	0.97
	1.0 g/L	2.30×10^{-3}	0.73	5.00×10^{-5}	0.78

At Fe(VI) dosages of 0.5 and 1.0 g/L, the concentration of NP slowly decreased over 180 minutes (Figure 3.6 (a)) and the pH increased to 6 and 10.2 (Figure 3.6 (b)), respectively. Therefore, increasing the Fe(VI) dosage did not always improve the removal efficiency of NP from sludge samples. Excessive addition of K_2FeO_4 significantly alkalized the sludge (Figure 3.6 (b)), meaning that NP removal from sludge is ineffective because Fe(VI) ions would probably react with the eluted organic matter at a high pH of 10.2 (Lin et al., 1998).

Generally, it is difficult to eliminate NP in sludge using biological processes such as activated sludge and anaerobic digestion as described previously (Bozkurt and Sanin, 2014). Therefore, some researchers have focused on thermal or chemical NP degradation in the sludge sample. McNamara et al. (2012) showed that no NP in water and anaerobically digested sludge was degraded by the thermal hydrolysis at 150 °C. Zhang and Li (2014) examined the degradation of NP from waste activated sludge by the combined UV/H_2O_2 process and found that 80% of NP was removed within 1 h using UV/H_2O_2 at UV fluence rate of 0.069 mW/cm^2 and H_2O_2 dosage of 0.5 mol/L. However, there are very few reports describing on chemical degradation of NP in anaerobically digested sludge. Our finding suggests that the utilization of Fe(VI) could improve the safety of digested sludge applied to the soil environment.

3.3.3. Removal of nonylphenol monoethoxylate from water samples

The removal of NP1EO from water phase was investigated at an initial NP1EO concentration of 100 μg/L at various Fe(VI) dosages and with initial pH ranging from 2 to 5. As shown in Figure 3.9, the removal efficiencies of NP1EO were less than 30% after 1 h at several Fe(VI) dosages with an initial pH of 2 (Figure 3.9 (a)). This result was similar to the lower removal efficiency of NP from water samples at pH 2. On the other hand, the removal efficiency of NP1EO increased sharply with increasing amounts of Fe(VI) with an initial pH of 3, and attained 92% with an increased final pH of 3.8 (Figure 3.9 (b)) at an Fe(VI) dosage of 10 mg/L. However, NP1EO removal efficiencies with initial pH values of 4 and 5 were below 35% (Figure 3.9 (b)) and the final pH ranged from 9 to 10.5 (Figure 3.10) even though Fe(VI) dosage was 10 mg/L. In addition, the time variations of ln (C/C_0) and 1/C with a Fe(VI) dosage of 10 mg/L at different initial pH values from 2 to 5 are presented in Figure 3.11. The removal rate constants of NP1EO were calculated using the first and second order kinetic models (Table 3.6). The NP1EO removal followed the second order kinetic model well. As seen in Figure 3.9 (a), the k_2 values at initial pH of 2, 3 and 5 were 6.00×10^{-5}, 6.00×10^{-4} and 1.00×10^{-4} L/μg/min, respectively. The k_2 at an initial pH value of 3 was the highest. It is found that there is an optimum acidic condition (initial pH 3) to remove NP1EO efficiently by Fe(VI). This suggests that the degradation of NP1EO in water is more pH dependent than for NP. Other studies also reported that pH has an influence on the degradation of pollutants using Fe(VI), and that the pollutant removal using Fe(VI) dramatically decreased with an increase in pH from 6 to 11 (Sharma et al., 2013, Han et al., 2015, Fan et al., 2018), which supports our result for NP1EO removal.

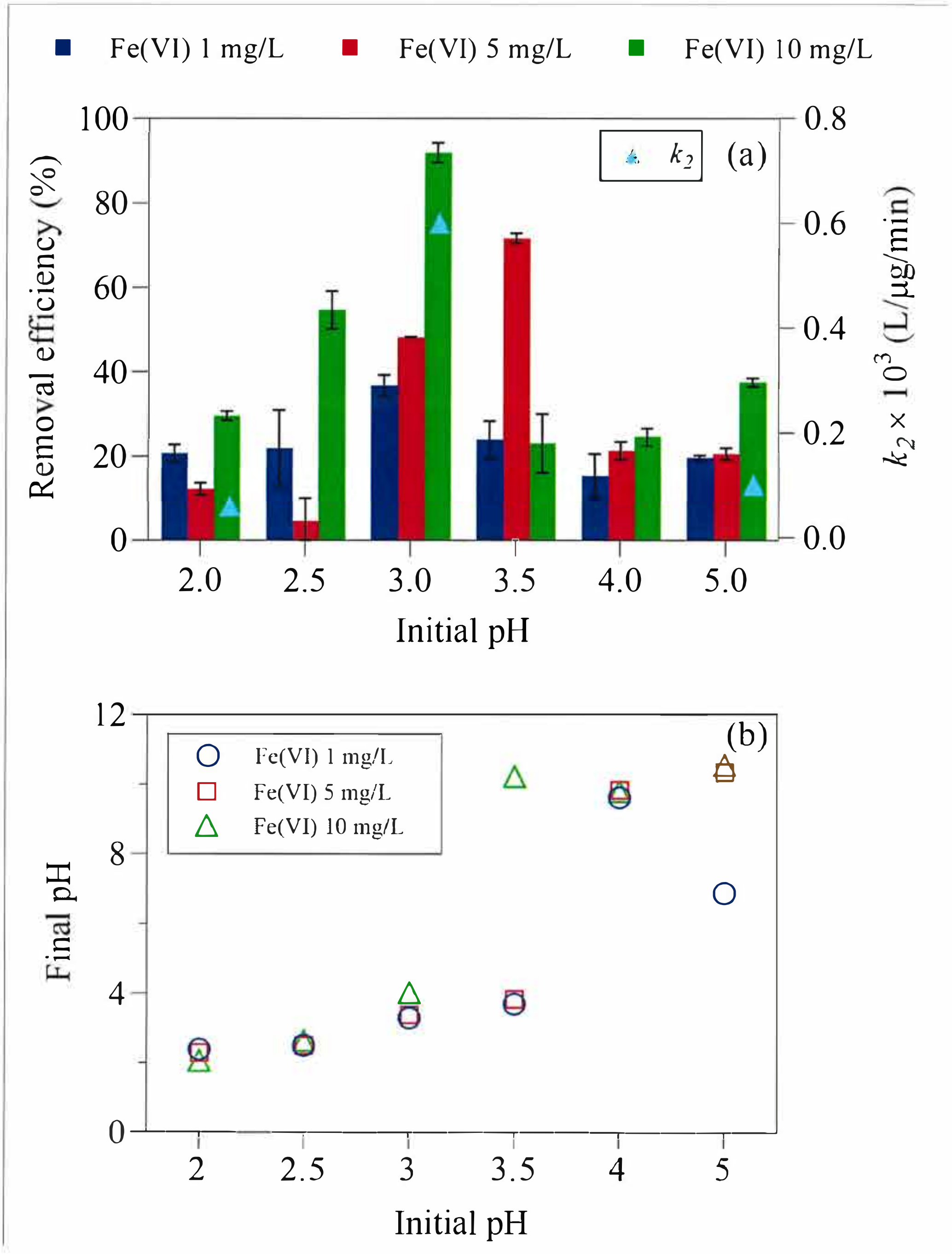

Figure 3.9 NP1EO removal efficiency and second order rate constants (k_2) (a), and final pH (b) from water samples with various Fe(VI) dosages and different initial pH values. Experimental condition: NP1EO = 100 µg/L. The k_2 values for removal of NP1EO are calculated for a Fe(VI) dosage of 10 mg/L.

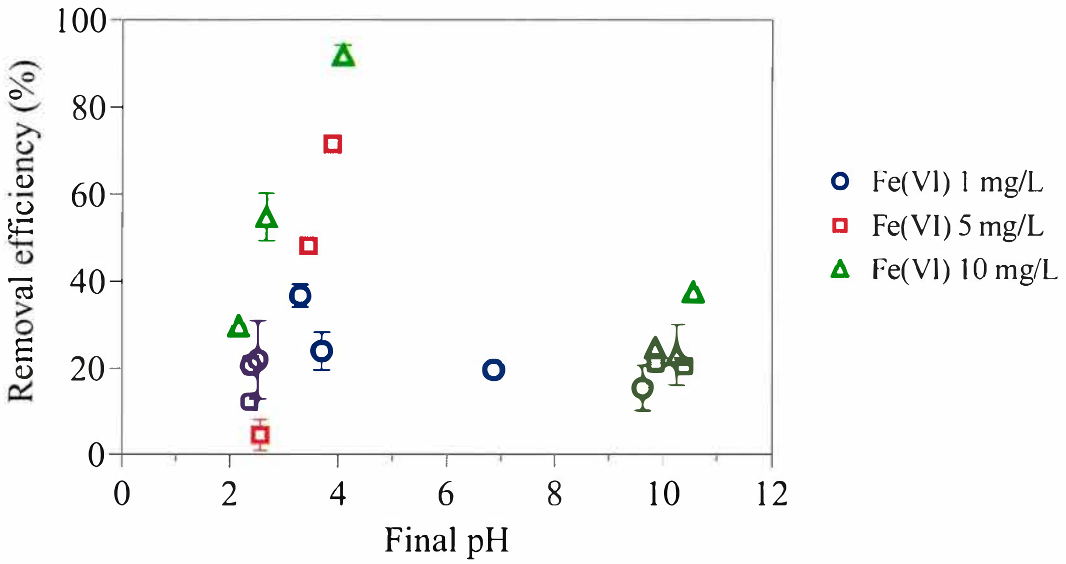

Figure 3.10 Relation between NP1EO removal efficiency and final pH from water samples with different Fe(VI) dosages.

Table 3.6 Kinetic constants for NP1EO removal from water samples at different initial pH values with a Fe(VI) dosage of 10 mg/L.

Compounds	**Initial pH**	**Fe(VI) dosage (mg/L)**	**First order**		**Second order**	
			k_1 (1/min)	**r_1^2**	**k_2 (L/μg/min)**	**r_2^2**
NP1EO	2	10	4.60×10^{-4}	0.82	6.00×10^{-5}	0.86
	3		2.21×10^{-2}	0.94	6.00×10^{-4}	0.99
	5		8.50×10^{-3}	0.84	1.00×10^{-4}	0.86

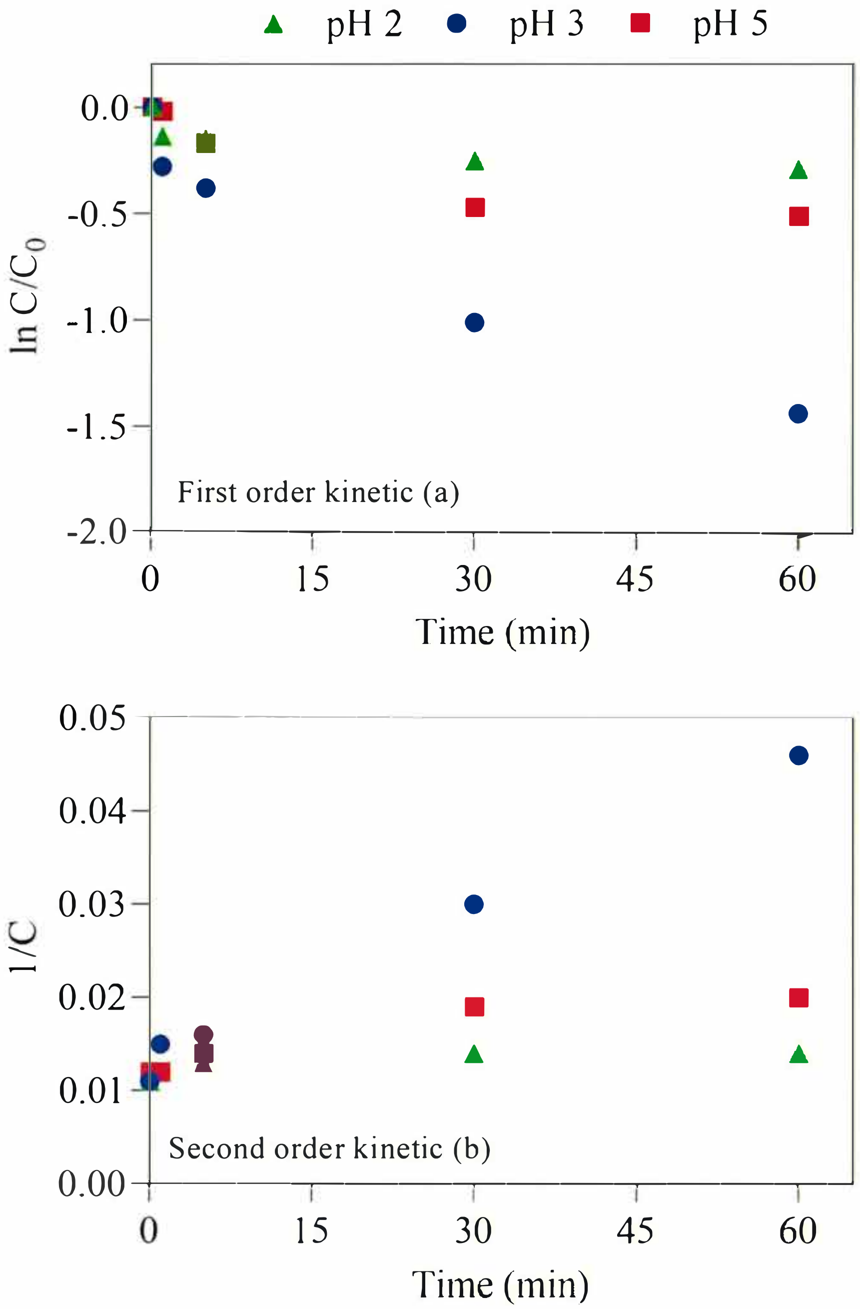

Figure 3.11 Variations of ln (C/C_0) (a) and 1/C (b) over time for NP1EO removal by Fe(VI) at different initial pH values.

Experimental condition: NP1EO = 100 μg/L, Fe(VI) = 10 mg/L.

The concentrations of NP1EO and NP in water samples containing NP1EO before and after the addition of Fe(VI) are presented in Table 3.7 where Fe(VI) dosage was 10 mg/L. The samples were collected after 1 h from the start of the experiment to analyze NP and NP1EO using GC/MS and LC-MS/MS, respectively. NP was not detected in the sample after adding K_2FeO_4. However, NP1EO concentrations decreased from 225 μg/L to 37 μg/L. This result indicated that by-products different from NP were probably generated by the degradation of NP1EO with Fe(VI). Several studies of NP1EO degradation in water samples by AOPs have been conducted (Karci et al., 2014, Priac et al., 2017, Wang et al., 2017); however, there is little information on by-products transformed from NP1EO. Hence, further investigation would be needed to identify by-products from NP1EO degradation.

Table 3.7 Variations in concentrations of NP1EO and NP in water samples before and after K_2FeO_4 addition with initial pH of 3 and Fe(VI) dosage of 10 mg/L.

Compounds	**Concentration (μg/L)**	
	Before adding K_2FeO_4	**After adding K_2FeO_4**
NP1EO	225.1 ± 6.9	37.1 ± 7.3
NP	< LOD	< LOD

3.3.4. Removal of nonylphenol monoethoxylate from sludge samples

As the concentrations of NP1EO in the sludge sample were very low (0.5–28.5 μg/L), the samples were spiked with NP1EO (100 μg/L). Most of the spiked NP1EO was sorbed onto the sludge solid. The removal of NP1EO from the solid phase of sludge samples was investigated with an initial pH value of 2. NP1EO removal using $Fe_2(SO_4)_3$

solution was compared to that with K_2FeO_4 precipitate at the same total iron dosage of 0.4 g/L. The variations in NP1EO concentrations and pH over 6 h are shown in Figure 3.12. NP1EO concentrations decreased to around 5 μg/L with an Fe(VI) dosage of 0.1 g/L and to around 77 μg/L with Fe(VI) dosages of 0.05 and 0.5 g/L. The pH rapidly rose in the first 30 min after adding K_2FeO_4. The final pH after 6 h increased with an increased dosage of Fe(VI) (Figure 3.12 (b)).

The time variations of ln (C/C_0) and 1/C in sludge samples at different Fe(VI) dosages are presented in Figure 3.13. NP1EO removal was well fitted by the second order kinetic model (Table 3.8). The k_2 value dramatically decreased from 3.19×10^{-2} L/μg/min at Fe(VI) dosage of 0.1 g/L to 6.00×10^{-4} L/μg/min at Fe(VI) dosage of 0.5 g/L. In addition, the relation between pH after degradation using Fe(VI) and the removal efficiency of NP1EO after 6 h is shown in Figure 3.14. With an Fe(VI) dosage of 0.1 g/L, pH increased to 2.7 and the removal efficiency of NP1EO reached 96%. On the other hand, only 28% of NP1EO was removed by Fe(III) at the same total Fe dosage of 0.4 g Fe/L. Hence, higher NP1EO removal efficiency was observed in Fe(VI) as compared to Fe(III).

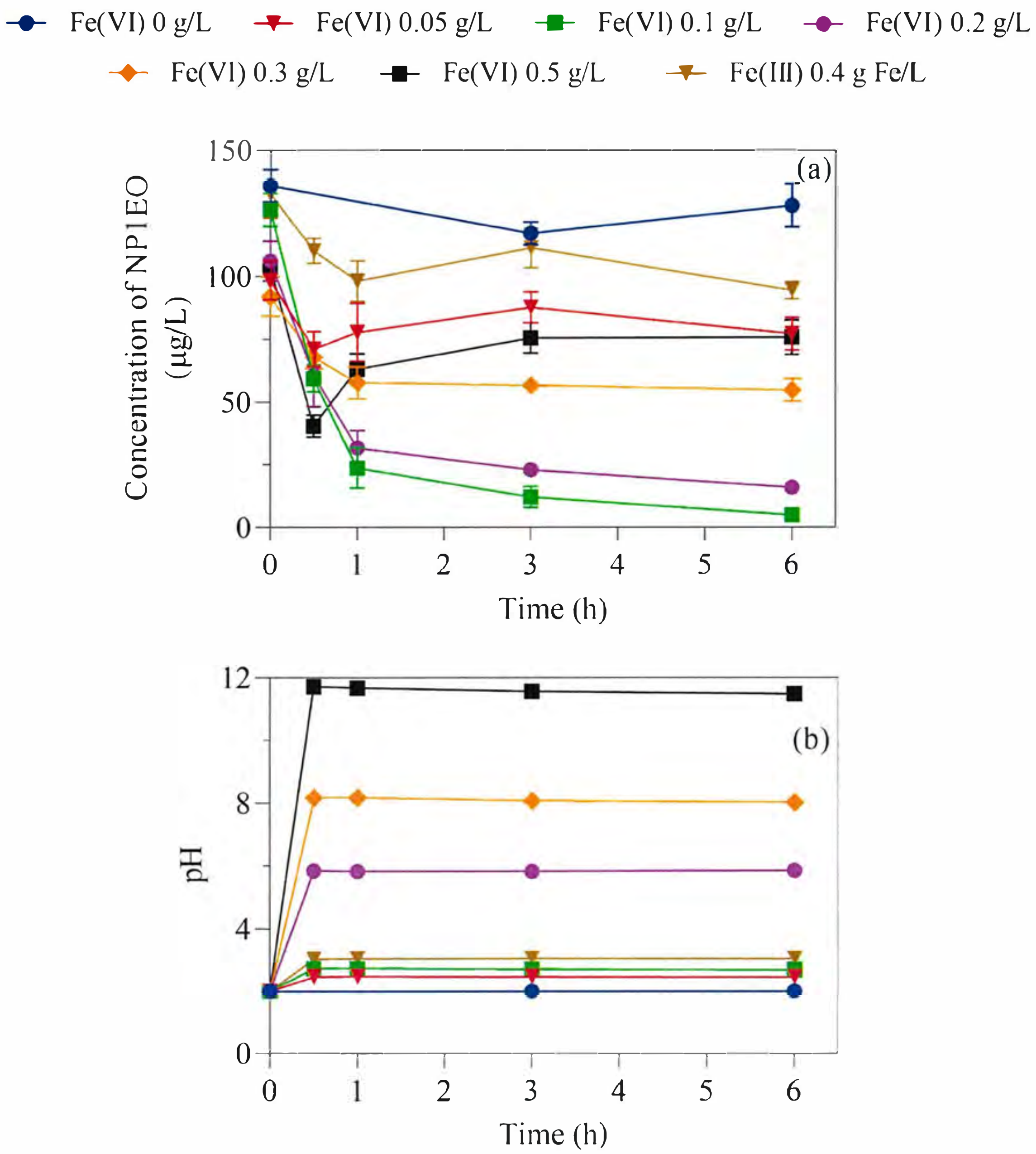

Figure 3.12 Variations of NP1EO concentrations (a) and pH (b) in sludge samples over time with different Fe(VI) dosages.

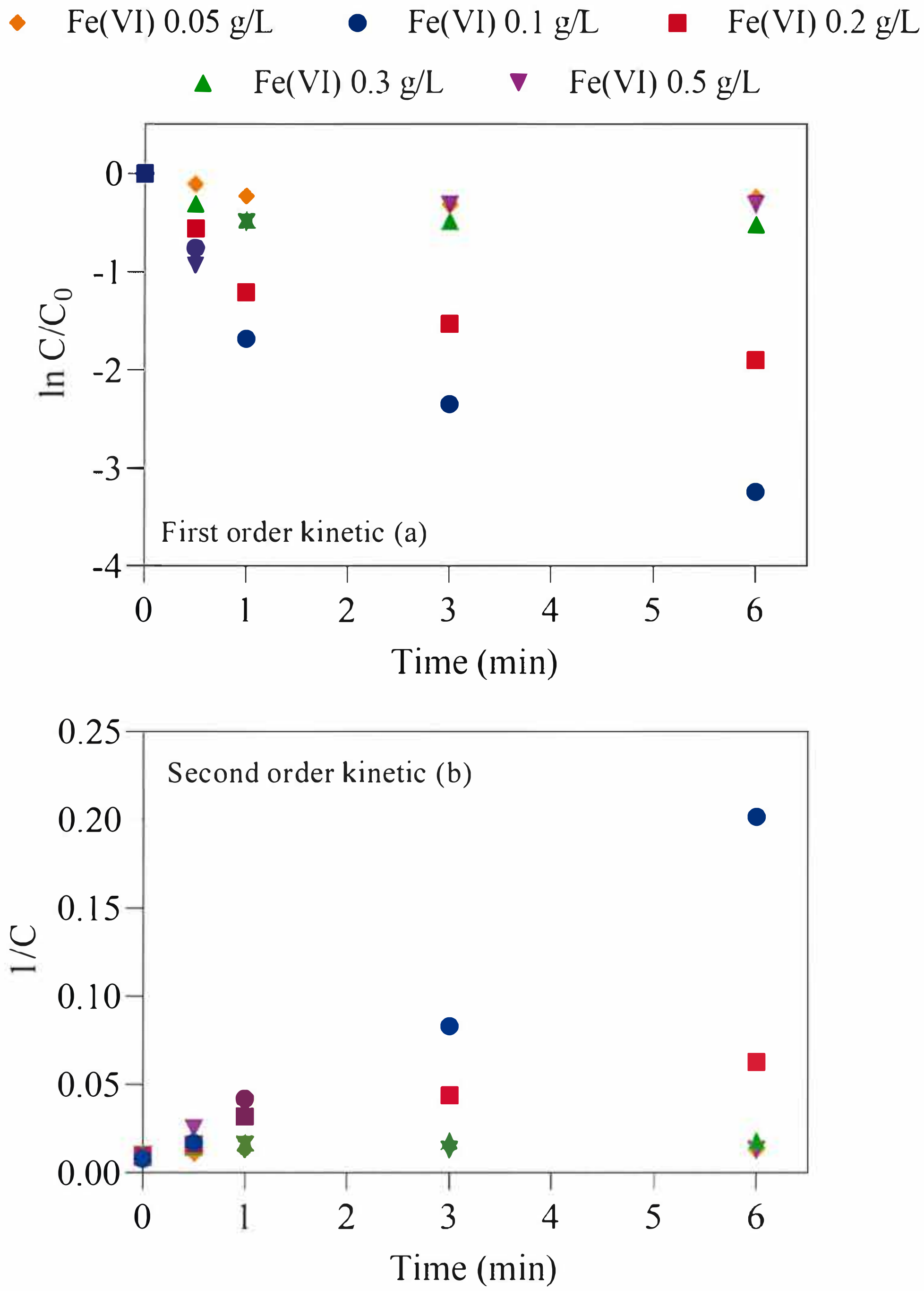

Figure 3.13 Variations of ln (C/C_0) (a) and 1/C (b) over time for sludge samples with different Fe(VI) dosages. Experimental condition: NP1EO = 100 μg/L, initial pH = 2.

Table 3.8 Kinetic constants for NP1EO removal from sludge samples using Fe(VI).

Fe(VI) dosage (g/L)	First order		Second order	
	k_1 (1/min)	r_1^2	k_2 (L/μg/min)	r_2^2
0.05	3.29×10^{-2}	0.41	4.00×10^{-4}	0.40
0.1	4.84×10^{-1}	0.87	3.19×10^{-2}	0.98
0.2	2.71×10^{-1}	0.77	8.40×10^{-3}	0.93
0.3	6.70×10^{-2}	0.48	9.00×10^{-4}	0.52
0.5	2.22×10^{-2}	0.03	6.00×10^{-4}	0.06

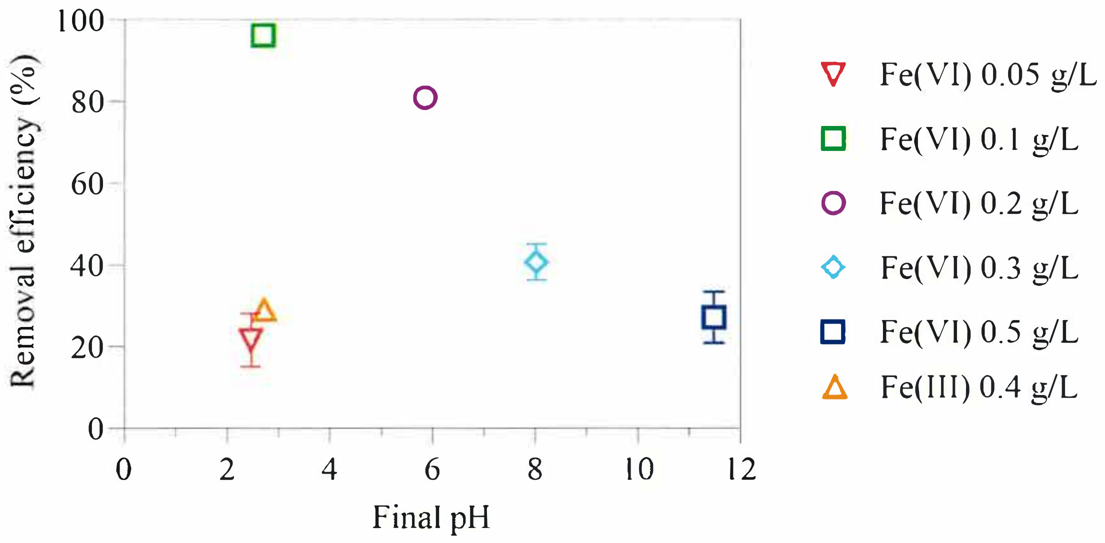

Figure 3.14 Relation between final pH and NP1EO removal efficiency from sludge samples with different Fe(VI) dosages.

Higher Fe(VI) dosages were required in sludge samples than water samples. However, in contrast to water samples, the removal efficiency of NP1EO from sludge samples dramatically increased with an increase in Fe(VI) dosage from 0.05 to 0.1 g/L, even though the initial pH was 2. In comparison, the pH with an Fe(VI) dosage greater than 0.3 g/L increased to above 8 and NP1EO removal efficiency decreased to less than 40%. Hence, the range of pH from 2.5 – 6 after adding Fe(VI) provides higher NP1EO removal efficiencies. This clearly indicates that sludge needs to be preliminarily acidified to remove NP and NP1EO simultaneously by Fe(VI). However, it is necessary to neutralize the acidified sludge for its use as a raw material of fertilizers. So, the additional cost will be required for acidification and neutralization of the treated sludge.

3.3.5. Removal of nonylphenol and nonylphenol monoethoxylate removal using potassium ferrate and ferric sulfate

According to Eq. (1), FeO_4^{2-} decomposes to Fe^{3+} and H_2O in acidic water and then ferric hydroxide precipitates via an increase in pH. This precipitate might act as a coagulant or an adsorbent for NP and NP1EO. The removal of NP and NP1EO using $Fe_2(SO_4)_3$ solutions were compared to that with K_2FeO_4 precipitate. The total Fe concentrations were set to 4, 20, and 40 mg/L in both iron reagents because the purity of K_2FeO_4 precipitate used in this study was about 30%. An increase in Fe(VI) and Fe(III) dosages greatly facilitated the removal of NP1EO (Figure 3.15). For the same iron dosages, the removal efficiencies of NP1EO with K_2FeO_4 precipitate in water and sludge samples were greater than those obtained with $Fe_2(SO_4)_3$ solution.

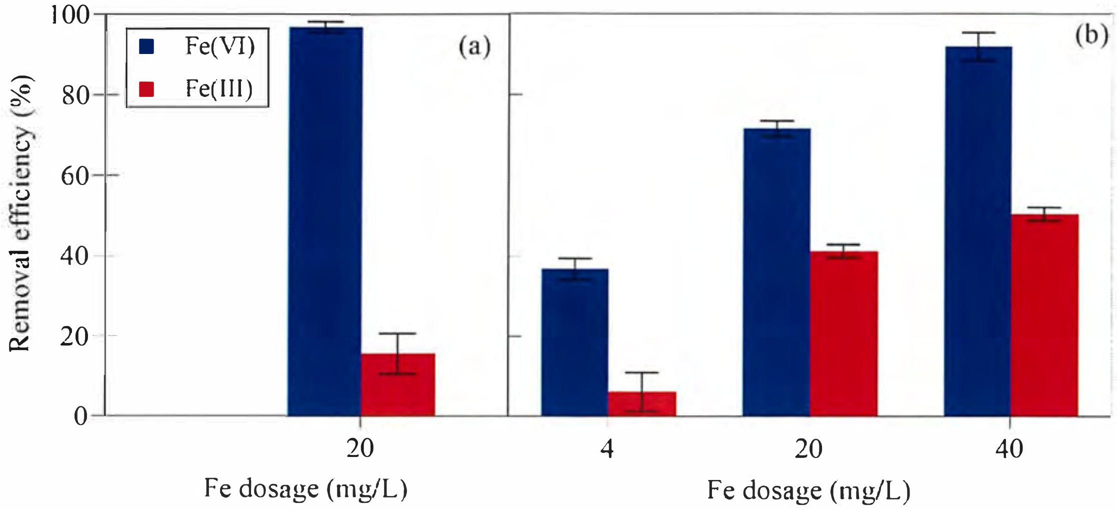

Figure 3.15 Comparison of NP (a) and NP1EO (b) removal between K_2FeO_4 precipitate and $Fe_2(SO_4)_3$ solution. Experimental condition: initial concentration of NP = 1 mg/L and NP1EO = 100 μg/L.

Table 3.9 shows the variations in the concentrations of NP and NP1EO in water samples before and after the addition of K_2FeO_4 precipitate and $Fe_2(SO_4)_3$ solution, and after subsequent pH adjustment to 2.5 to dissolve ferric hydroxide precipitate. At the dosage 20 mg Fe/L of $Fe_2(SO_4)_3$ solution, the concentration of NP was slightly decreased even though the precipitate of $Fe(OH)_3$ was solubilized. It seems that NP is not eliminated by coagulation with ferric hydroxide. On the other hand, the concentrations of NP1EO decreased after the addition of the iron reagents. However, after ferric hydroxide precipitate was dissolved, the NP1EO concentrations with the addition of $Fe_2(SO_4)_3$ solution increased from 39.2 ± 2.7 μg/L to 72.9 ± 3.5 μg/L, which was almost the same as before iron addition. Therefore, this suggested that the removal of NP1EO using $Fe_2(SO_4)_3$ solution occurred due to coagulation with ferric hydroxide. Comparatively, in the case of the addition of K_2FeO_4 precipitate, NP and NP1EO concentrations did not increase after dissolving ferric hydroxide and the removal efficiency was about 97% and 95%, respectively. Therefore, the removals of NP and NP1EO were found to be due to degradation by Fe(VI).

Table 3.9 Variations in NP and NP1EO concentrations before and after addition of iron reagents.

Iron reagents	**K_2FeO_4 precipitate**	**$Fe_2(SO_4)_3$ solution**
NP concentrations (iron reagents as 20 mg Fe/L)		
Before addition of iron reagents with an initial pH of 4	1,098.2 ± 44.5 μg/L	1,098.2 ± 44.5 μg/L
After addition of iron reagents and pH adjustment to 10	34.3 ± 6.5 μg/L	926.7 ± 36.0 μg/L
After pH adjustment to 2.5	32.4 ± 2.5 μg/L	903.1 ± 79.1 μg/L
NP1EO concentrations (iron reagents as 40 mg Fe/L)		
Before addition of iron reagents with an initial pH of 3	72.5 ± 8.2 μg/L	79.0 ± 0.4 μg/L
After addition of iron reagents and pH adjustment to 4	5.8 ± 0.7 μg/L	39.2 ± 2.7 μg/L
After pH adjustment to 2.5	3.7 ± 1.3 μg/L	72.9 ± 3.5 μg/L

3.4. Conclusions

According to the above results, the utilization of K_2FeO_4 could decrease the concentrations of NP and NP1EO in water and sludge samples under different Fe(VI) dosages. The highest removal efficiency of NP was achieved at a mass ratio of 5:1

([Fe(VI)]:[NP]), which is an optimum condition for NP removal with Fe(VI) in water samples. However, the removal efficiency of NP and NP1EO varied with initial pH and final pH, which depended on the Fe(VI) dosage. This study has revealed the possibility of removing NP1EO as well as NP in sludge samples using K_2FeO_4. The sludge treated by K_2FeO_4 could be used as a raw material for safer organic fertilizer. This would mitigate the adverse effects of micropollutants in soil and aquatic environments through the land application of anaerobically digested sewage sludge.

K_2FeO_4 precipitate produced by the wet chemical method exhibited good potential to remove NP and NP1EO from water and digested sewage sludge samples. As the Fe(VI) dosage was increased, NP removal efficiency increased for water samples but decreased for sludge samples, probably due to the reaction of Fe(VI) with organic matter eluted from the sludge by alkalization. Conversely, the highest removal efficiency for NP1EO from water samples was obtained under weakly acidic conditions. A comparison with $Fe_2(SO_4)_3$ revealed that NP and NP1EO removals in the presence of K_2FeO_4 were attributed to the degradation of NP and NP1EO by Fe(VI). The effective removal of spiked NP1EO from the acidified sludge was achieved at an optimum Fe(VI) dosage capable of maintaining weakly acidic conditions, which could simultaneously lower the concentration of NP in the sample. However, the organic matter as a matrix in sludge would consume Fe(VI) and inhibit NP and NP1EO degradation by Fe(VI). The optimum pH range differed between NP and NP1EO for water samples. An initial pH of 4 was the optimum for NP removal from water sample using Fe(VI). In the case of NP1EO, the final pH should be between 3 and 6 for optimal NP1EO removal from water and sludge samples. Therefore, it is necessary to adjust the initial pH to acidic conditions before adding the Fe(VI) precipitate. The pathways for the degradation of NP and NP1EO by Fe(VI) must be evaluated further.

3.5. References

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Chapter 4

Characterization of nonylphenol degradation products with potassium ferrate

4.1. Introduction

The biodegradation of NP in sewage sludge occurred through the action of microorganisms under aerobic conditions, with the half-lives range from 1.1 to 99.0 days. NP was degraded rapidly during incubation with a mixture of digested sludge and sawdust at low concentrations, but it was more persistent at higher concentrations (Mao et al., 2012). The anaerobic biodegradation of NP has been reported by Chang et al. (2005), indicating that NP was slowly degraded within 84 days in sewage sludge. Zhang et al. (2008) reported that NP was hardly degraded under anaerobic conditions and large amounts of NP accumulated in the sludge. Therefore, many researchers have attempted to degrade or mineralize these compounds completely by advanced oxidation processes (AOPs).

NP degradation by UV/TiO_2 was degraded efficiently after 30 min. Furthermore, the degradation of NP by the combination of biological and ozonation treatment has been studied by Bertanza et al. (2011), which resulted in estrogenic activity decline and reduction of NP concentration. In addition, Dulov et al. (2013) studied the comparison of NP degradation in water samples by UV, H_2O_2/UV, and Fenton/photo-Fenton processes. The optimum condition for complete NP degradation was H_2O_2/UV (250 µmol/L H_2O_2) at pH 11 for 12 min.

Xin et al. (2014) investigated NP degradation by photoelectrocatalytic (WO_3/TiO_2) and studied the degradation mechanism and products of NP. The degradation rate and TOC removal rates of NP were 98% and 60%, respectively, after 120 min under neutral conditions. The TOC removal rates were obviously lower than the degradation rates of NP. The results indicated that many intermediates emerged in the decomposition of NP. Furthermore, Karci et al. (2014) investigated NPEOs degradation by H_2O_2/UV-C and Photo-Fenton treatment and suggested that incomplete mineralization occurs with photochemical oxidation processes and oxidation of these compounds yields a variety of transformation products. Therefore, it is essential not only to estimate the degradation products but also to assess their biodegradability and estrogenic activity.

In Chapter 3, the effectiveness of Fe(VI) on NP degradation in water and sludge samples was clarified. NP in the oxidation process by Fe(VI) would be transformed into degradation products including water (H_2O), CO_2, and other compounds. If the degradation products besides H_2O and CO_2 are formed as a result of incomplete mineralization of NP, the chemical structure, biodegradability, and endocrine disrupting activity of the degradation products need to be investigated to evaluate their fate and potential risk. Although the investigation on estrogen removal by other treatments, such as chlorination and ozonation, has been well studied (Guedes Maniero et al., 2008), there has been no report regarding the estrogenic activity of degradation products from NP with Fe(VI). Furthermore, there is little information on the biodegradability of degradation products from NP with Fe(VI).

In this Chapter, firstly, the degree of mineralization of NP with Fe(VI) and the biodegradability of degradation products from NP were assessed using NP with benzene labelled with ^{14}C as a tracer, because the disappearance of ^{14}C from the system would indicate the transformation of benzene to $^{14}CO_2$ and/or more volatile organic compounds than NP. Secondly, the chemical structure of the degradation products from NP with Fe(VI) was estimated based on the mass spectrometry. Thirdly, the estrogenic activity of degradation products from NP with Fe(VI) was investigated by yeast estrogen assay (YES).

4.2. Methodology

4.2.1. Biodegradability of nonylphenol and its degradation products

The non-radioactive stock solution of NP was prepared in methanol at the concentration of 5 g/L. The radioactive stock solution of NP consisting of the benzene ring labeled uniformly with ^{14}C (Figure 4.1) was also prepared and its radioactivity was 500 Bq/mL. The biodegradability of NP and its degradation products with Fe(VI) was examined based on the OECD guidelines 310 (OECD, 1992) with some modifications. The preparation of mineral salts medium (MSM) is shown in Table 4.1. The activated sludge taken from the Tonan sewage treatment plant in Morioka, Japan, was used as an inoculum for biodegradation. The total solid of the activated sludge ranged from approximately 5,000 to 6,000 mg/L. Each bottle was inoculated with activated sludge (5 g/L of suspended solids).

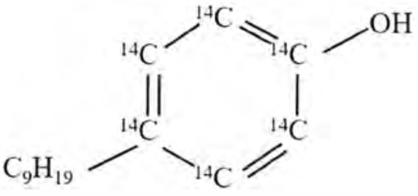


Figure 4.1 Chemical structure of ^{14}C-labeled NP

Table 4.1 Preparation of Stock solutions for mineral medium

	Stock solutions for mineral medium	**Amount (g)**
(a) pH7.4	Potassium dihydrogen orthophosphate (KH_2PO_4)	0.850
	Dipotassium hydrogen orthophosphate (K_2HPO_4)	2.175
	Sodium dihydrogen phosphate dodecahydrate ($Na_2HPO_4 \cdot 12H_2O$)	6.718
	Ammonium chloride (NH_4Cl)	0.050
(b)	Calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$)	2.750
(c)	Magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$)	2.250
(d)	Iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$)	0.025

Reagents (a) to (d) were dissolved in ultrapure water and the volume of the solutions was made up to 100 mL. 10 mL of solution (a) was added in 80 mL of ultrapure water, then 1 mL of solutions (b), (c), and (d) were added and the solution was made up to the final volume of 100 mL.

The water sample with a volume of 100 mL at an NP concentration of 1 mg/L was prepared by diluting the non-radioactive NP stock solution with ultrapure water. Figure 4.2 shows a schematic diagram of the experimental procedure for the biodegradability of NP and its degradation products. 75 μL of the ^{14}C-labeled NP stock solution was added to the water sample to mix with non-labeled NP, and the mass concentration of ^{14}C-labeled NP in the mixture was equivalent to 6.3×10^{-6} mg/L. 30 mL of the mixture was allocated to three glass bottles, respectively. Then, the potassium ferrate solution was added to the mixture at a Fe(VI) dosage of 1 mg/L, and the samples were agitated at 25 ± 1 °C on a rotary shaker (125 rpm) for 24 hours for NP degradation. After that, the samples were weakly acidified by HCl solution to prevent activated sludge microorganisms from being inhibited by the alkaline conditions. Furthermore, 1 mL of the sample taken from two different bottles with and without addition of Fe(VI) was allocated to multiple glass vials with a volume of 20 mL. Then, 0.2 mL of the mineral medium and 0.5 mL of the activated sludge were added to the vials containing the samples with and without addition of Fe(VI) to evaluate the degree of biodegradation of NP and its degradation products. The control samples without inoculation of activated sludge were also prepared for the comparison. The vials were tightly capped and agitated at 25 ± 1 °C on a rotary shaker (125 rpm) for 10 days. The radioactivity of the samples in the vials was determined by a liquid scintillation counter (LSC-5100; Aloka, Tokyo, Japan) after adding 17 mL of scintillation cocktail (PerkinElmer, Hionic-Fluor) to the samples. The decreasing rate of ^{14}C was calculated as follows:

$$\text{Decreasing rate (\%)} = (A_0 - A_i) / (A_0) \times 100 \tag{14}$$

where A_0 is radioactivity of the original sample (Bq/g), A_i is radioactivity of sample on the day i (Bq/g).

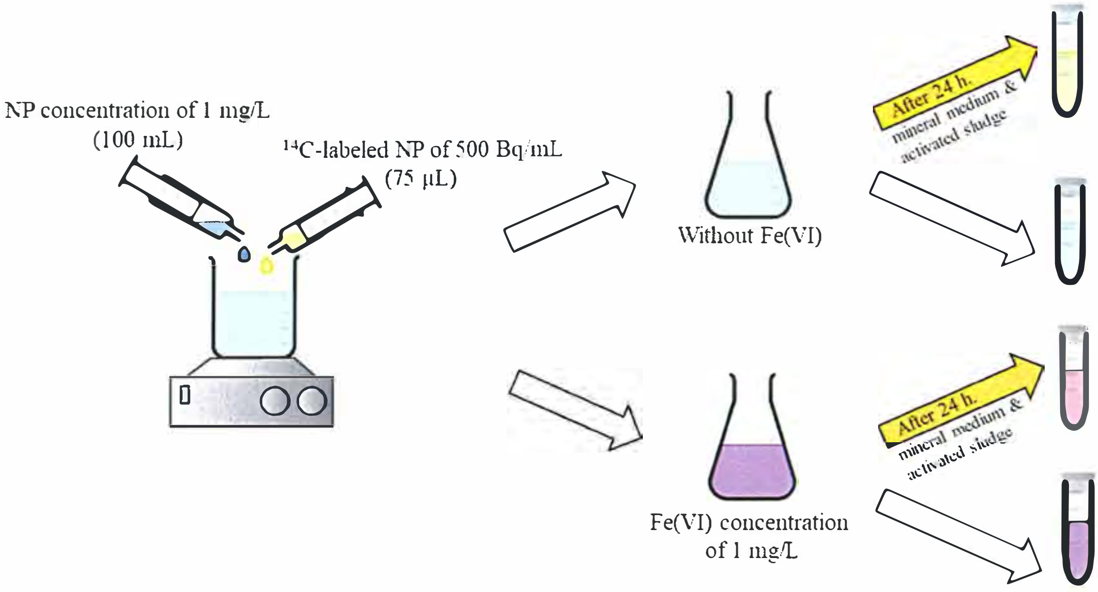


Figure 4.2 Schematic diagram of the experimental procedure for the biodegradability of NP and its degradation products.

The reduction of radioactivity could be interpreted as abiotic volatilization of NP and its degradation products with Fe(VI) and/or biotic volatilization of CO_2 and other metabolites produced by metabolizing NP and its degradation products with activated sludge microorganisms. Statistical analyses including one-way ANOVA with Tukey–Kramer HSD were all carried out using the SPSS software to assess significant differences among different conditions. Statistically significant results were depicted by p values < 0.05.

Furthermore, the spontaneous degradation and/or volatilization of non-labeled NP in the water sample with a concentration of 1 mg/L was investigated for longer time. The water sample was agitated at 25 ± 1 °C and 120 rpm on a rotary shaker (NR-150, Taitec

Co., Ltd., Japan) for 14 days. The samples were collected and the NP concentrations were analyzed by GC/MS as described in Section 3.1.1.2

4.2.2. Estimation of nonylphenol degradation products

The result in Chapter 3 showed that the removal of NP was more than 90% when the mass ratios of Fe(VI) to NP was 5:1. Therefore, this condition was set to assess degradation products from NP. The estimation of NP degradation products was performed on three samples separately, including the K_2FeO_4 solution and the NP solutions before and after the addition of K_2FeO_4. Consequently, the solutions of Fe(VI) (500 mg/L) were prepared by dissolving K_2FeO_4 precipitate in ultrapure water. For the NP solution without K_2FeO_4 addition, the initial concentration of NP was set to 100 mg/L in ultrapure water. The degradation of NP with Fe(VI) was carried out at an initial NP concentration of 100 mg/L and an Fe(VI) dosage of 500 mg/L. The initial pH was adjusted to 3 using 0.1 M H_2SO_4 or 1 M KOH. The experiments were conducted using 1 L beakers with a magnetic stirrer (700 rpm) at 25 ± 1°C. The reaction mixtures were left for 1 h to allow the oxidation reactions. Then, the samples were filtered through a 0.3 μm glass fiber filter (GF-75, Advantec, Japan). The concentration of NP was determined using GC-MS according to section 3.1.1.2.

For mass spectrum analysis, each sample was injected directly to MS/MS at the flow rate of 0.5 mL/min and the mobile phase of the mixture of methanol and water at a volumetric ratio of 1 to 1 was supplied at a temperature of 30 °C. The flow injection analysis was conducted at an injection volume of 3 μL. Full-scan mass chromatograms of three samples were obtained by scanning the *m/z* from 0 to 500 in the negative ionization

(NI) mode at a capillary voltage of 3.5 kV and a cone voltage of 55 V. The appearance of the peaks different from ones monitored in two samples containing K_2FeO_4 only or NP only was checked in the sample containing both NP and K_2FeO_4 to estimate the presence of degradation products from NP.

4.2.3. Estrogenic activity of nonylphenol degradation products

Variations in the estrogenic activities before and after treating water samples containing NP with Fe(VI) were determined using the yeast estrogen assay (YES). The effects of the initial NP concentration and Fe(VI) dosage on the NP degradation were examined in water sample. The initial concentrations of NP in the water sample varied from 5 to 20 mg/L. The initial pH of the samples was adjusted to 3 using 0.1 M H_2SO_4 or 1 M KOH and the Fe(VI) dosage was set to 25 to 100 mg/L. The mass ratio of Fe(VI) to NP was 5:1, which is consistent with the result in Chapter 3. In addition, NP degradation was conducted under the different Fe(VI) dosages at 5 to 50 mg/L with an initial NP concentration of 10 mg/L. The samples were filtrated through a 0.3 μm glass fiber filter (GF-75, Advantec, Japan). NP concentrations in the filtrate were determined by GC-MS as described in section 3.1.1.

The yeast estrogen screen (YES) assay was performed according to the method reported by Sasaki and Terasaki (2018). Briefly, 1.25 μL of the samples and 17β-estradiol (E2) standard solutions were put in a sterile 96-well flat-bottom microplate and serially diluted 5-fold from rows 1 to 7. The assay medium was prepared by mixing 2% glucose medium lacking tryptophan and leucine for 18 h at 30 °C under shaking conditions. Then, the preincubated cell suspension was inoculated into a 0.1% glucose medium lacking tryptophan and leucine. 100 µL of the assay medium was added to each well. The microplates were then sealed, homogenized using a shaker, and incubated for 18 h at 30°C. The cells were digested by the addition of 50 µL of Z buffer containing 1.5 mg/mL Zymolyase 20 T and incubated at 30 °C for 1 h. Then, 50 µL of 0.5 M phosphate buffer containing 0.5 mg/mL chlorophenol red-β-galactopyranoside (CPRG) was added, and the samples were reacted at 30 °C for 1 h; the colorimetric reaction was stopped by addition of 40 µL of 2 M Na_2CO_3. After incubation, the absorbance was read at 540 nm and 690 nm.

4.3. Results and discussion

4.3.1. Biodegradability of NP and its degradation products with Fe(VI)

The variations in the decreasing rate of ^{14}C over time under different conditions is shown in Figure 4.3. The initial ^{14}C concentration and pH value of the solutions were 109 Bq/g and 7.3 ± 0.4, respectively. The decreasing rate of ^{14}C in control without both addition of Fe(VI) and inoculation of activated sludge microorganisms was increased to 13% for 1 day and slightly raised to 28% after 10 days. Additionally, the concentration of non-labelled NP in the water sample was gradually decreased from 1.04 mg/L to 0.8 mg/L when water sample was agitated for 14 days (Figure 4.4). These results suggested that a part of NP was volatilized from water samples into the atmosphere over time, which is consistent with the results of Lalah et al. (2003). They investigated that 64.4% loss of ^{14}C-labeled NP was found in an open system, while 33.9% of ^{14}C-labeled NP was declined in the close system after 28 days.

The decreasing rate at a Fe(VI) dosage of 1 mg/L was increased to 15% after 1 hour. As shown in Figure 3.1, 70% of NP in water sample with a Fe(VI) dosage of 1 mg/L would be degraded during the first 1 hour. These results would indicate that about 15% of NP was released into the atmosphere via transformation to highly volatile substances such as CO_2 during the first 1 hour and at least 55% of NP was transformed to other degradation products and they remained in water sample. The decreasing rates of ^{14}C after 10 days showed no statistically significant difference between two conditions of the control and the Fe(VI) dosage of 1 mg/L ($p > 0.05$).

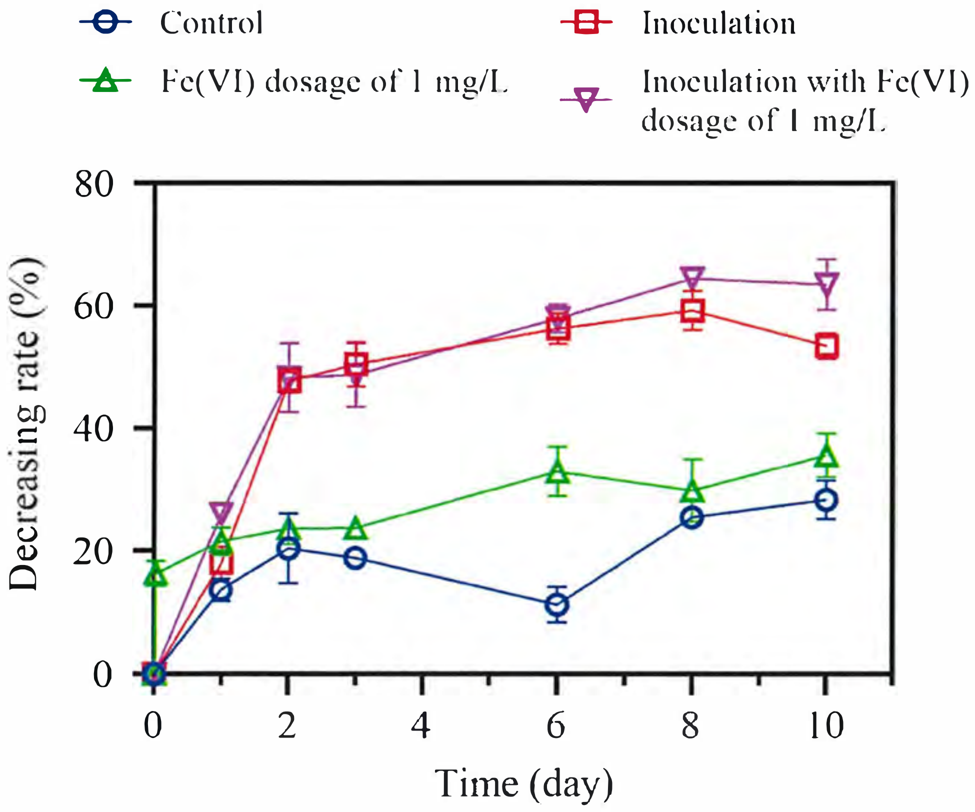


Figure 4.3 Variations in decreasing rate of ^{14}C over time under different conditions.

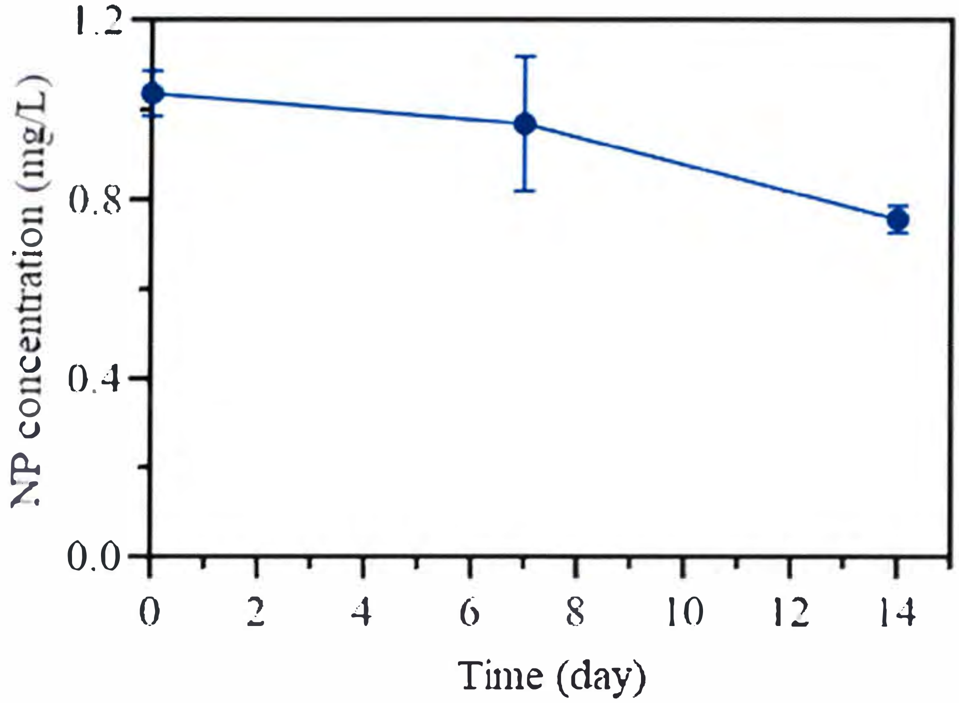


Figure 4.4 Variation in non-radioactive NP concentration in water sample for 14 day.

Conversely, when the water sample without the addition of Fe(VI) was inoculated with activated sludge microorganisms, the decreasing rate of ^{14}C was increased to 48% on day 2, which was higher than those in the control and no inoculation after Fe(VI) addition. This result suggested that a part of the benzene ring in NP was converted to more volatile substances such as CO_2 by the microbiological reaction of activated sludge microorganisms because six carbon atoms constituting benzene ring in NP are labelled with ^{14}C. In two cases with and without the Fe(VI) addition, the inoculation of activated sludge microorganisms resulted in an increase in the decreasing rates of ^{14}C to almost the same level (about 58%) for 6 days. After 10 days, the decreasing rate of ^{14}C with Fe(VI) addition was slightly higher than that without Fe(VI) addition ($p < 0.05$). This result suggests that biodegradability of the degradation products from NP with Fe(VI) is higher than or equal to that of the parent NP. The maximum biodegradation rate was higher than 60% under inoculation and Fe(VI) dosage of 1 mg/L in 10 days that satisfies the criteria for ready biodegradability (OECD, 1992). The following readily biodegradable according to OECD test guidelines, degree of biodegradation has to be reached to 60% CO_2 in 10 days within the 28 days test period.

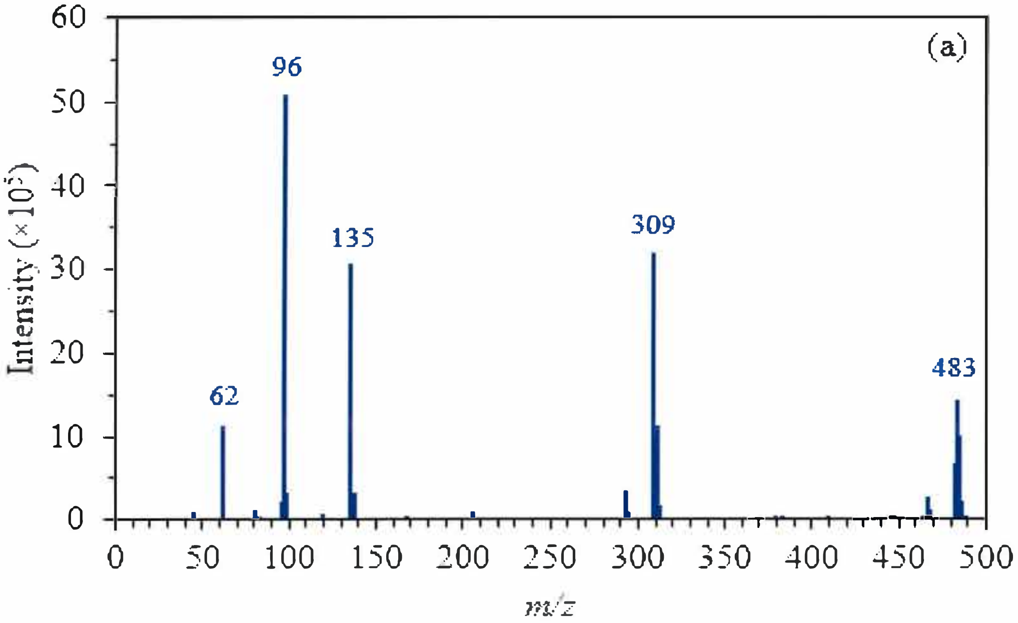
4.3.2. Estimation of NP degradation products

Variation in NP concentration in the water samples before and after the addition of Fe(VI) are presented in Table 4.2. The NP concentration was decreased from 116 mg/L to 1.69 mg/L for 1 h at an Fe(VI) dosage of 500 mg/L. Although most of NP was degraded, the result in section 4.3.1 suggested that degradation products would be formed during the oxidation process with Fe(VI). Therefore, the mass spectrum of the water samples were monitored using a mass spectrometer to estimate the chemical structure of the degradation products.

Table 4.2 Variation in concentration of NP in water samples before and after K_2FeO_4 addition with initial pH of 3 and Fe(VI) dosage of 500 mg/L.

Concentration (mg/L)	
Before adding K_2FeO_4	**After adding K_2FeO_4**
116.2 ± 15.4	1.69 ± 0.3

The mass spectrum of the Fe(VI) solution and NP water samples before and after Fe(VI) addition are shown in Figure 4.5. All samples were measured on the same day as the degradation experiment since the sensitivity is affected by the condition of the analytical instrument depending on the day. 5 major peaks of the intensity were detected in the Fe(VI) solution (Figure 4.5 (a)). The peak at *m/z* 96 was detected at all samples. Therefore, the peak at *m/z* 96 can be ignored. The peak at *m/z* 219 in the NP water sample before Fe(VI) addition (Figure 4.5 (b)) indicates the presence of molecular ions from NP. The peaks at *m/z* 62, 135, 309 and 483 were detected in both Fe(VI) solution and NP water sample after the addition of Fe(VI) (Figure 4.5 (a) and (c)). Therefore, these peaks can also be ignored. The peak at *m/z* 219 disappeared and a new peak with low intensity at *m/z* 223 was detected in the NP water sample after Fe(VI) addition (Figure 4.5 (c)), which possibly indicates the presence of degradation products from NP with Fe(VI). However, the intensities of NP degradation products were lower than those of NP. The difference of peak intensities between the Fe(VI) solution and NP water sample after Fe(VI) addition is shown in Figure 4.6. Xin et al. (2014) also reported that many intermediates emerged in the decomposition of NP by photoelectrocatalysis because of incomplete mineralization of NP. The mass spectrum of degradation products from NP by photoelectrocatalysis have revealed six products with *m/z* of 95, 112, 137, 193, and 239. However, product *m/z* 223 has not previously been reported by Xin et al.



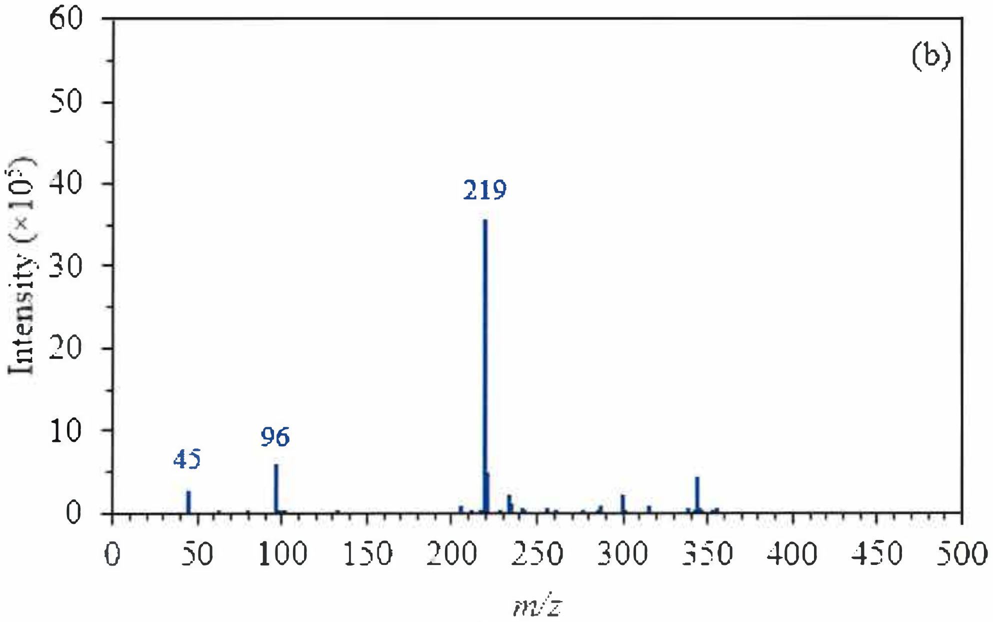


Figure 4.5 Mass spectrum of Fe(VI) solution (a), NP before (b), and after (c) addition of Fe(VI).

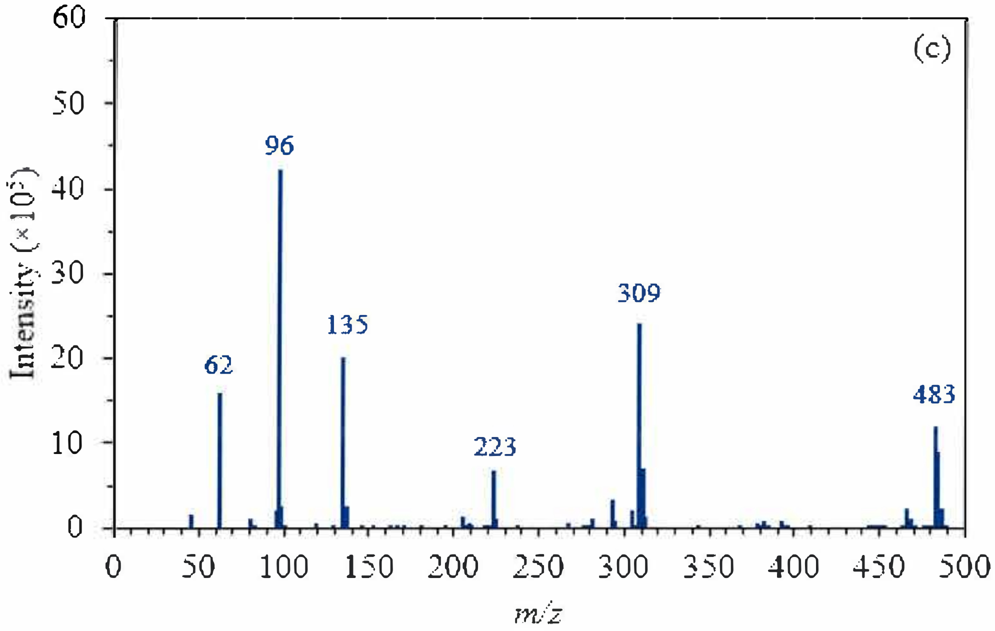


Figure 4.5 (cont.) Mass spectrum of Fe(VI) solution (a), NP before (b), and after (c) addition of Fe(VI).

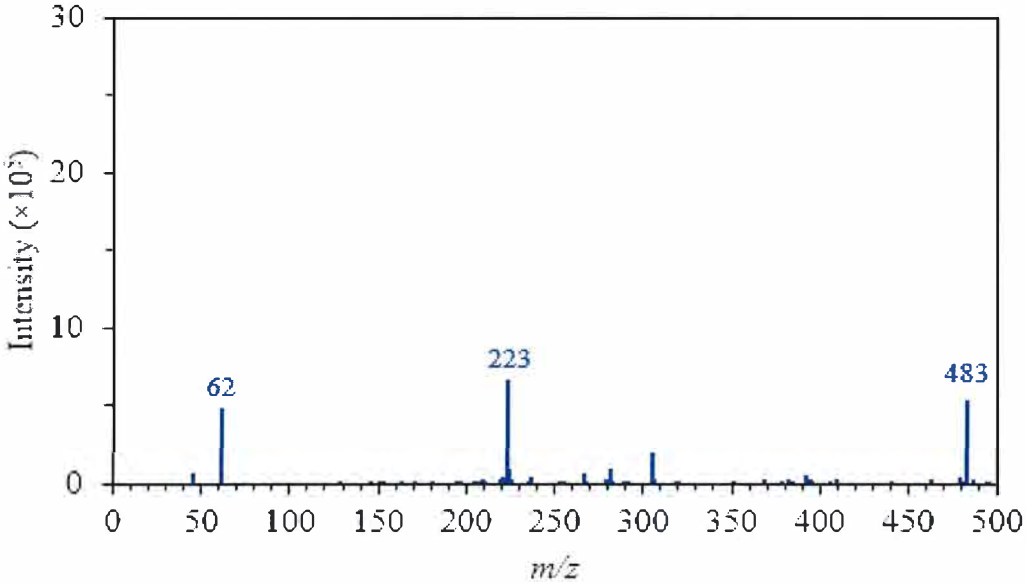


Figure 4.6 Difference of mass spectrum on NP in water sample after the addition of Fe(VI).

4.3.3. Estrogenic activity of NP degradation products

Figure 4.7 shows the variations in the estrogenic activity and NP concentration of the water samples before and after Fe(VI) addition at a mass ratio (Fe(VI):NP) of 5:1 under different NP concentrations (from 5 to 20 mg/L). The estrogenic activity of NP was expressed in β-galactosidase activity. Although NP has much less estrogenic activity than E2 under the same molar concentration, the estrogenic activity was detected in water sample before Fe(VI) addition and increased with an increase in NP concentration as shown in Figure 4.7 (a). After Fe(VI) addition, the estrogenic activities were significantly decreased to almost zero and had no apparent difference among different NP concentrations as well as those of NP (Figure 4.7 (b)). These results demonstrated that NP degradation with Fe(VI) removed the estrogenic activity from degradation products.

The effect of Fe(VI) dosage on the estrogenic activity of water sample was investigated under the same NP concentration. The initial concentration of NP was set at 10 mg/L and the dosage of Fe(VI) varied from 5 to 50 mg/L. Figure 4.8 shows the variations in estrogenic activity and NP concentration at different Fe(VI) dosages. Although significant levels of residual estrogenic activity were observed at Fe(VI) dosages of 5 and 10 mg/L, the estrogenic activity was reduced significantly with a further increase in Fe(VI) dosage. At a low Fe(VI) dosage of 5 mg/L, NP concentration and estrogenic activity were 5.7 mg/L and 1.5 U (Figure 4.8). On the other hand, the concentration of NP and estrogenic activity was decreased to almost zero at Fe(VI) dosages of 25 and 50 mg/L. Thus, at least mass ratio of 2:1 ([Fe(VI):[NP]) is required for removal of estrogenic activity of NP.

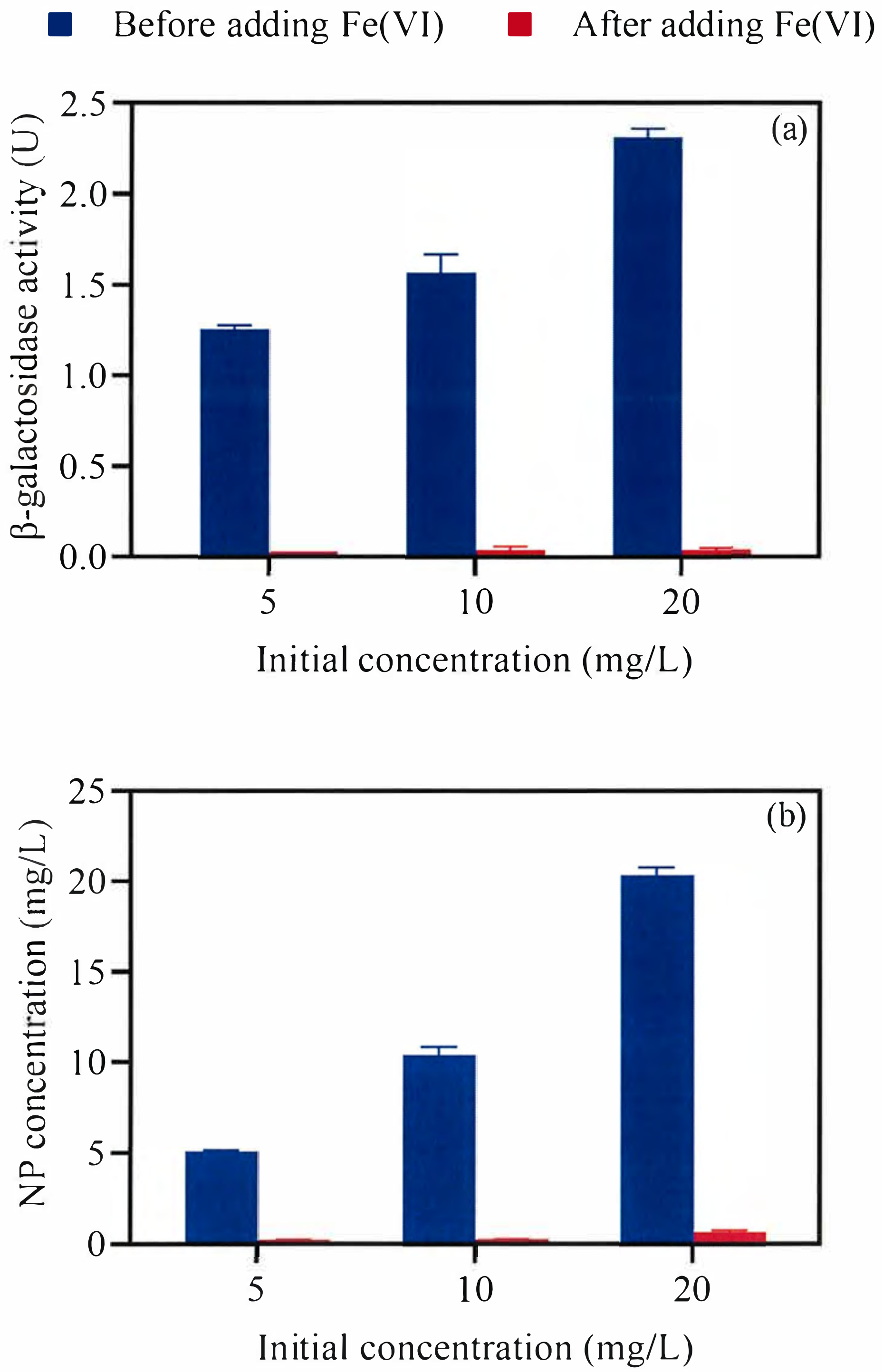


Figure 4.7 Variations in estrogenic activity (a) and NP concentration (b) of water samples before and after addition of Fe(VI) at Fe(VI): NP = 5:1 with different initial NP concentrations.

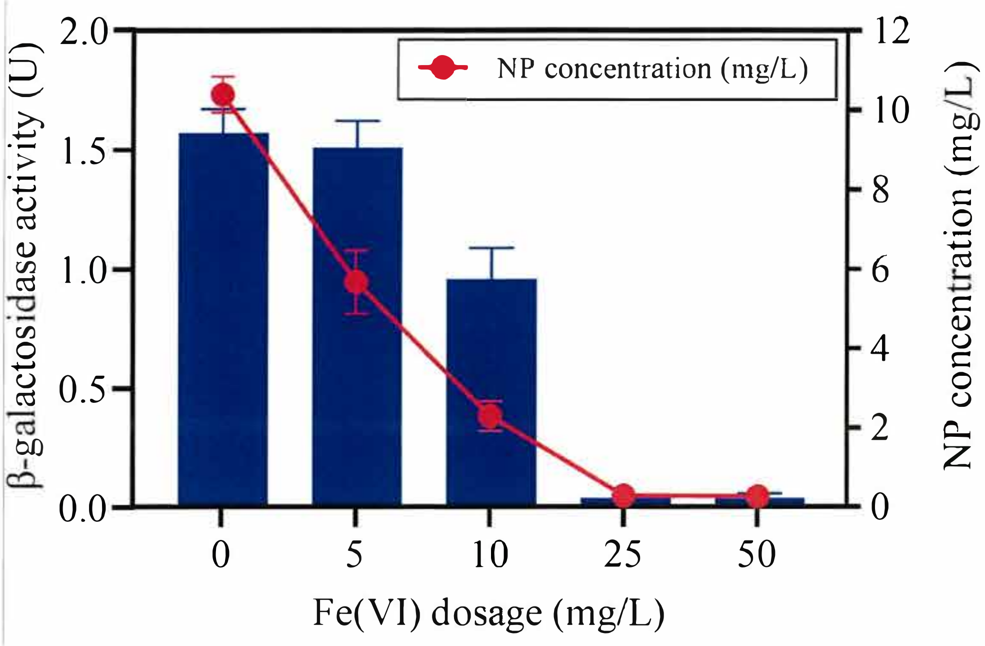


Figure 4.8 Variations in estrogenic activity and NP concentration in water samples at different Fe(VI) dosages. The initial NP concentration was 10 mg/L.

It is reported that two active sites of NP causing estrogenic activity are phenolic hydroxy group and nonyl group (Preuss et al., 2006). A remarkable reduction in estrogenic activity with Fe(VI) was observed regardless the incomplete mineralization of NP as shown in Fig. 4.3. This might suggest that phenolic hydroxy group was altered by the treatment with Fe(VI). In the mass spectrum analysis, a unique peak was detected at *m*/*z* 223 after the treatment with Fe(VI) (Fig. 4.5 (c)). If NP is transformed to degradation products forming molecular ion with *m*/*z* 223, phenol constituting NP might be transformed to cyclohexanone and/or cyclohexanol with a double bond between two carbon atoms, involving addition of four hydrogen atoms. However, further study is needed to identify the chemical structure of NP degradation products.

4.4. Conclusions

In this Chapter, the biodegradability of NP and its degradation products with Fe(VI) was evaluated using ^{14}C-labeled NP as a radioactive tracer and activated sludge microorganisms as an inoculum. The results demonstrated that the addition of Fe(VI) to the NP solution spiked with the tracer resulted in a slight decrease in the concentration of ^{14}C, which indicates incomplete mineralization of NP and formation of degradation products. The concentration of ^{14}C was gradually dropped by the microbial inoculation without Fe(VI). The combination of inoculation and Fe(VI) enhanced an increase in the decreasing rate of ^{14}C. These results suggested that NP was transformed to more biodegradable products through the treatment with Fe(VI).

Based on the analysis of mass spectrum, a peak undetectable in the water samples containing K_2FeO_4 precipitate only or NP only was detected at *m/z* 223 in the water sample after the treatment with Fe(VI). Moreover, the effect of Fe(VI) dosage on the estrogenic activity of water sample containing NP was studied using a yeast estrogen screen (YES). The results showed that the estrogenic activity of water sample was decreased with an increase in Fe(VI) dosage and was significantly lowered as well as NP at the mass ratios of Fe(VI) to NP greater than or equal to 2.

4.5. References

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Chapter 5

Evaluation of bioavailability of phosphorus in sludge treated with ferrate

5.1. Introduction

The utilization of sewage sludge as fertilizers seems to be the practical option since sewage sludge becomes a valuable source of organic matters and major nutrients such as nitrogen and phosphorus required for plant growth, which contributes to the improvement of physical and chemical properties of the soils. However, recycling sewage sludge to the green and agricultural lands presents some contaminants that could accumulate in plants. Therefore, the direct application of sewage sludge involves the potential risk for humans and environment. In Chapter 3, the removal of micropollutants such as NP and NP1EO in anaerobically digested sewage sludge sample was examined using the K_2FeO_4 precipitate. The results showed that Fe(VI) can degrade these micropollutants. During degradation, Fe(VI) is reduced to Fe(III) and the formation of Fe(III) is expected to coagulate colloidal particles and flocculate suspended solids. In general, anaerobically digested sewage sludge contains several hundred mg/L of dissolved phosphate phosphorus (PO_4-P). Therefore, Fe(III) generated by Fe(VI) reduction would react with phosphates in the sludge to precipitate ferric phosphates ($FePO_4$) compounds (Kralchevska et al., 2016). Wilfert et al. (2015) reported that several studies debated that the occurrence of Fe in biosolids might reduce or improve the bioavailability of P.

The usability of the sludge treated with Fe(VI) as a raw material for organic fertilizer containing phosphate compounds should be evaluated based on P bioavailability using chemical extraction methods. Total P content is not an indicator of the agronomic effectiveness of sludge treated with Fe(VI), but the P solubility from sludge plays an important role in the agronomic performance in different extractants (Chien, 1993). According to the European regulation on fertilizers (European Commission, 2003), it requires information on P solubility either in water (H_2O), 2% citric acid (2% CA), 2% formic acid (2% FA), or neutral ammonium citrate (NAC). Therefore, the objective of this study was to evaluate the potential bioavailability of phosphorus compounds precipitated in the sludge treated with Fe(VI).

5.2. Methodology

5.2.1. Sample preparation

Digested sewage sludge was collected from the Tonan sewage treatment plant in Morioka, Japan. 500 mL of digested sewage sludge was placed into 1 L shaking flasks. The experiment was conducted for both untreated and treated sludge with the K_2FeO_4. The initial pH of sludge sample was adjusted to 2 and the samples were agitated with a shaker (120 rpm) for 24 h at 25 ± 1 °C. After that, the samples were collected to measure the total and dissolved P concentrations. Also, the samples were used to evaluate P extractability.

After acidifying the samples for 24 h, the samples were treated with the K_2FeO_4 precipitate under the same conditions as described in Chapter 3. Briefly, the K_2FeO_4 precipitate was added to the samples at an Fe(VI) dosage of 1 g/L and then stirred at 120 rpm. After 3 h, the pH of samples was adjusted to 7 and then 40 mL of the samples were taken from the shaking flasks. The total and dissolved P concentrations in the samples were measured. Phosphorus in the sludge samples before and after Fe(VI) addition was extracted with various extraction reagents as described in Section 6.2.2. All the experiments were performed in triplicate.

5.2.2. Extraction of phosphorus from treated sludge samples

The preparation of extraction solutions are as follows: the 2% citric acid solution was prepared by dissolving 20 g of citric acid ($C_6H_8O_7 \cdot H_2O$) in ultrapure water. For 2% formic acid solution, 16.4 mL of formic acid (concentration 99%; density at 20 °C = 1.22 g/mL) was diluted with 1 L of ultrapure water. The NAC solution was prepared by dissolving 185 g of citric acid in 750 mL of ultrapure water and adding 172.5 mL of ammonium hydroxide solution (28% of NH_3). The pH of solutions was adjusted to 7 at 20 °C using an ammonium hydroxide solution, and then the solution volume was diluted to 1 L with ultrapure water.

0.4 g dry weight of untreated and treated sludge samples was collected and centrifuged at 4,000 rpm for 10 min. The supernatant was decanted into a centrifuge tube and passed through a 1 μm membrane filter (Mixed cellulose ester, Advantec, Japan). Phosphorus in the solid phase was extracted with H_2O, 2% CA, 2% FA, and NAC, respectively. P extractions were performed according to EN 15958:2011 (H_2O soluble P), EN 15920:2011-08 (2%(w/v) citric acid-soluble P), EN 15919:2011-08 (2%(w/v) formic acid-soluble P), and EN 15957:2011 (neutral ammonium citrate-soluble P).

40 mL of the respective solution was mixed with the solid phase in 50 mL centrifuge tube. The extractions were conducted by shaking for 30 min at 40 rpm and 20 - 25 °C for

H_2O, 2% CA and 2% FA, and for 1 h at 65 °C in water bath for NAC. Then, the NAC extracts were immediately cooled and diluted with ultrapure water at a volumetric ratio of 1:5 (extract:water). After extraction, the samples were centrifuged at 4,000 rpm for 10 min. The supernatants were passed through a 1 μm membrane filter (Mixed cellulose ester, Advantec, Japan). All extracts were analyzed the dissolved P concentrations by ICP-AES.

5.2.3. Analytical methods

5.2.3.1. Total P concentration

40 mL of untreated and treated sludge without centrifugation were collected in 100 mL beaker without filtration and acidic digestion. 1.25 mL of HNO_3 (61%) was added to the beaker containing samples, which were then placed on a hotplate (90 °C) in a fume hood until the volume was decreased to 10-15 mL by evaporation. After cooling, 1.25 mL of HNO_3 and 1.25 mL of HCl (36%) were added to each digested sample and followed by heating on a hotplate. Next, the digestion was performed by adding 2.5 mL of HNO_3, evaporated to dryness, and was allowed to cool to room temperature. The sample after digestion was transferred to 25 mL volumetric flasks, diluted with ultrapure water, and kept in plastic bottles until analysis with ICP-AES. The total P concentrations of the samples were measured by ICP-AES after digestion and were used to calculate the extraction efficiency of P from digested sludge ($P_{soluble}$ / P_{total}). Calibration working standards of P in the range from 0 to 50 mg/L were prepared by diluting the stock calibration standards.

5.2.3.2. Dissolved P concentration

40 mL of samples were filtered through a 1 μm membrane filter (Mixed cellulose ester, Advantec, Japan). The filtrate was measured by ICP-AES after digestion as described above.

5.3. Results and discussion

The total and dissolved P contents of untreated and treated sludge are shown in Table 5.1. The total P concentrations in untreated sludge were similar to that in sludge treated with Fe(VI). The dissolved P concentration of the treated sludge was lower than that of the untreated sludge. This decrease might be a result of the formation of $FePO_4$ via reaction between phosphate and ferric ions (Li et al., 2018). The pH of sludge samples after adding Fe(VI) sharply increased from 2 to 10. After 3 h, the pH was adjusted to 7 before extraction. The contents of P extracted from the sludge solid phase with H_2O, 2% FA, 2% CA and NAC are shown in Table 5.2. The content of P extracted with H_2O was low before (2.7 g/kg) and after Fe(VI) addition (1.9 g/kg). In 2% FA and 2% CA, the P content before Fe(VI) addition was almost the same, while sludge after Fe(VI) addition had different P contents. However, the content of P extracted with NAC was increased after Fe(VI) addition.

The extraction efficiencies of phosphorus from sludge solid phase with H_2O, 2% FA, 2% CA and NAC before and after Fe(VI) addition are reported in Figure 5.1. The extraction efficiencies of P in sludge before Fe(VI) addition was higher than that of sludge after Fe(VI) addition in the case of H_2O and 2% FA, while P extraction efficiencies with 2% CA were similar in sludges before and after Fe(VI) addition. The extraction efficiency from the treated sludge sample with H_2O showed 4% of total P. Conversely, the other extracts presented a variety of P extraction efficiencies of 13% and 46% and 72% for 2% FA, 2% CA and NAC, respectively, which suggests that 72% of P in the treated sludge is bioavailable for plant uptake. Therefore, the treated sludge containing $FePO_4$ compound could be applied to a raw material of fertilizer. However, the amount of $FePO_4$ in treated sludge is related to Fe(VI) dosage for removing nonylphenolic compounds, which is perceived as a negative point. Thus, it would be essential to investigate the optimum Fe(VI) dosage on micropollutant removal and P retention when this process is applied practically.

Table 5.1 Total P and dissolved P contents of sludge samples.

Sample	**Total P**	**Dissolved P**
	(g/kg TS)	
Before addition of Fe(VI)	42.1	13.7
After addition of Fe(VI)	45.5	3.2

Table 5.2 P content extracted from sludge solid phase with H_2O, 2% CA, 2% FA and NAC.

Sample	**Water**	**2% FA**	**2% CA**	**NAC**
		(g/kg TS)		
Before addition of Fe(VI)	2.7	13.0	13.2	9.2
After addition of Fe(VI)	1.9	5.8	20.8	32.9

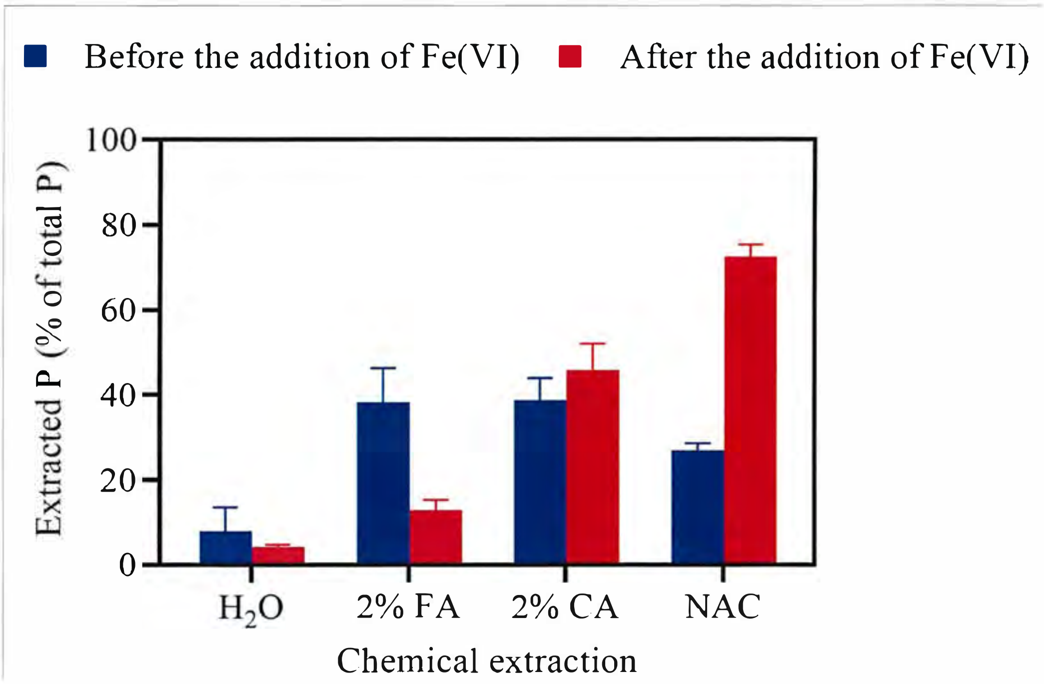

Figure 5.1 Extraction efficiencies of phosphorus from sludge solid phase with H_2O, 2% CA, 2% FA and NAC before and after Fe(VI) addition.

5.4. Conclusions

The bioavailability of P in the sludge after the treatment with Fe(VI) was evaluated using different extraction reagents. The results suggested that the sludge treated with Fe(VI) improved P bioavailability. The sludge treated with Fe(VI) can be utilized as a raw material of organic fertilizer including bioavailable P, although the treated sludge needs to be neutralized.

5.5. References

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Chapter 6

Conclusions and future recommendations

1) Preparation of potassium ferrate

The electrochemical method to synthesize K_2FeO_4 was examined using iron plate and KOH solution. The purity of K_2FeO_4 was approximately 30%. Therefore, further work is needed to find out better electrolytical conditions to decrease the electrical resistance and promote the electrolysis of iron plate for improving the production and purity of synthesized K_2FeO_4.

2) Removal of nonylphenol and nonylphenol monoethoxylate using potassium ferrate

The utilization of K_2FeO_4 produced by the wet chemical method could decrease the concentrations of NP and NP1EO in water and anaerobically digested sewage sludge samples under different Fe(VI) dosages. The optimum mass ratio of Fe(VI) to NP was 5:1 for removal of NP. The removal efficiency of NP and NP1EO varied with the initial and final pH values depending on the Fe(VI) dosage because the K_2FeO_4 contains KOH as impurity and consumes acid when Fe(VI) is reduced to Fe(III). The optimum pH range differed between NP and NP1EO for water samples. The optimum initial pH values for the removal of NP and NP1EO were 4 and 3 in water samples, respectively. The final pH should be between 3 and 6 for the optimal NP1EO removal from water and sludge samples. The mechanism of NP and NP1EO degradations using Fe(VI) are presented in Figures 6.1 and 6.2, respectively. Besides, the degradation products from NP with Fe(VI) was estimated in Chapter 4. However, the pathways for the degradation of NP and NP1EO with Fe(VI) need to be investigated further.

The effective removal of spiked NP1EO from the acidified sludge was achieved at an optimum Fe(VI) dosage capable of maintaining weakly acidic conditions, which could simultaneously lower the concentration of NP in the sample. Therefore, it is necessary to adjust the initial pH to acidic conditions before adding the Fe(VI) precipitate. However, the organic matter as a matrix in sludge would consume Fe(VI) and inhibit NP and NP1EO degradation by Fe(VI). The sludge treated with Fe(VI) could be used as a raw material for safer organic fertilizer, which would decrease micropollutants loaded with sludge fertilizer to agricultural lands and mitigate the adverse effects of the sludge application on soil and surrounding aquatic environments.

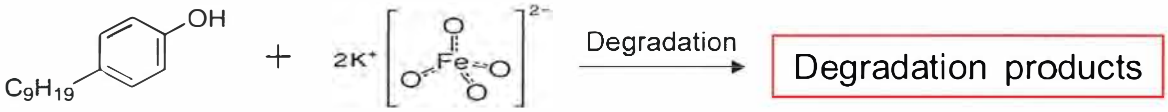

Figure 6.1 Degradation mechanism of NP using Fe(VI)

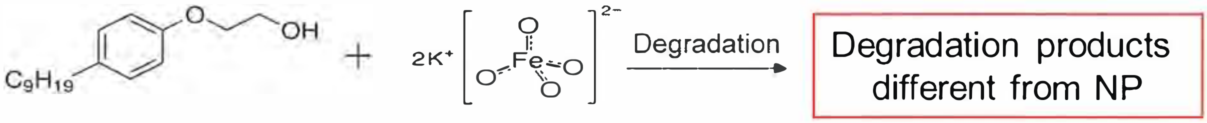

Figure 6.2 Degradation mechanism of NP1EO using Fe(VI)

3) Characterization of nonylphenol degradation products with potassium ferrate

Firstly, the biodegradability of degradation products from NP with Fe(VI) was investigated using NP consisting of benzene ring labeled with ^{14}C as a tracer. The addition of Fe(VI) to the NP water sample spiked with the tracer resulted in a slight decrease in the concentration of ^{14}C, which indicates incomplete mineralization of NP and formation of degradation products. The concentration of ^{14}C was gradually decreased in both inoculation of activated sludge microorganisms only and inoculation with addition of Fe(VI). The biodegradability of NP degradation products with Fe(VI) was slightly higher than that of NP. These results suggested that NP was transformed into more biodegradable products through the treatment with Fe(VI).

Secondly, the estimation of degradation products from NP with Fe(VI) was examined based on mass spectra of water samples containing K_2FeO_4 precipitate only, NP only and both of them. In water sample containing both K_2FeO_4 precipitate and NP, the peak at *m*/*z* 219 representing the presence of NP disappeared and a unique peak with a low intensity was detected at *m*/*z* 223. There might be a possibility that four hydrogen atoms were added to NP through the degradation with Fe(VI) as shown in Figures 6.3.

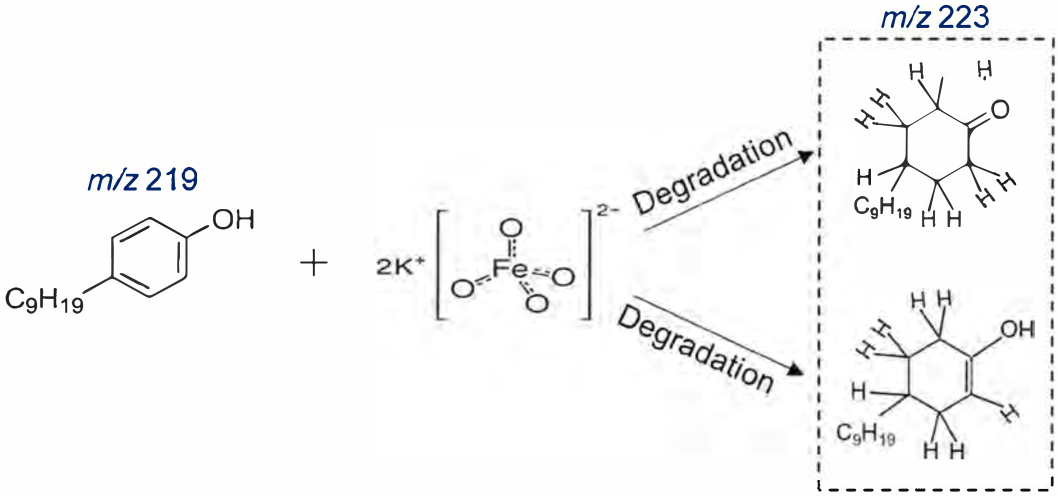

Figure 6.3 Estimated degradation mechanism of NP using Fe(VI)

Thirdly, the estrogenic activity of the NP water sample treated with Fe(VI) was investigated using the yeast bioassay. An increase in Fe(VI) dosage decreased estrogenic activity and NP concentration. Moreover, estrogenic activity was significantly decreased at a mass ratio of Fe(VI) to NP more than 2. This result indicates that chemical structure of estrogenically active sites of NP was altered by the treatment with Fe(VI).

4) Evaluation of bioavailability of phosphorus in treated sludge

Bioavailability of phosphorus in the sludge treated with Fe(VI) was evaluated using different extraction reagents. The addition of Fe(VI) to the acidified sludge at a pH of 2 increased the pH to 10 and decreased dissolved P concentration due to the precipitation of phosphate with ferric ion and ferric hydroxide formed via Fe(VI) reduction. The extraction efficiency of phosphorus from the solid phase of the treated sludge after pH adjustment to 7 were about 40% in 2% citric acid and about 70% in neutral ammonium citrate, respectively, which were higher than those before the treatment with Fe(VI). These results suggested that the treated sludge could be utilized as a raw material of organic fertilizer containing bioavailable phosphorus, although it is necessary to adjust the pH of the sludge treated with Fe(VI) to around neutral value before the utilization as fertilizers. However, further investigation should be required to clarify the effect of Fe(VI) dosage on simultaneous NP and NP1EO degradation and phosphorus precipitation in the sludge sample.

5) Recommendations for Fe(VI) technology to apply in the sludge treatment process

This research was aimed to develop new knowledge for removing nonylphenolic compounds and mitigate the toxic effects of water and sewage sludge using Fe(VI). Moreover, the potential of phosphorus bioavailability in treated sludge was evaluated. Our findings showed that the treatment using Fe(VI) could be applied to a real sludge treatment process. The treatment process using Fe(VI) could be installed after anaerobic sludge digestion process as shown schematically in Figure 6.4. The pH values of anaerobically digested sewage sludge should be adjusted to acidic conditions before being added to the reactor. Ferrate synthesized by the wet chemical method would be directly added to an oxidation reactor to oxidize, neutralize and flocculate acidified sludge before it enters the dewatering process. However, the information about practical application of Fe(VI) treatment remains unclear. Consequently, the pilot-scale trials for sludge treatment using Fe(VI) are needed to clarify the treatment performance in the future.

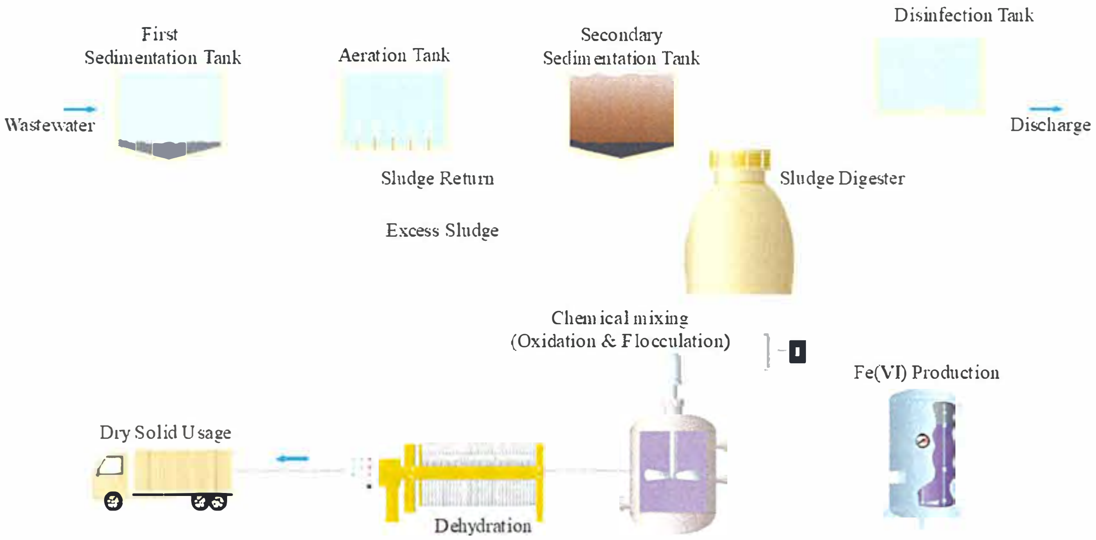

Figure 6.4 Schematic of the possible Fe(VI) oxidation in the sludge treatment process.

Curriculum Vitae

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PUBLICATIONS

Limmun, W., Ito, A., Ishikawa, N., Momotori, J., Kawamura, Y., Majima, Y., Sasamoto, M. and Umita, T. (2019) Removal of nonylphenol and nonylphenol monoethoxylate from water and anaerobically digested sewage sludge by Ferrate(VI). Chemosphere 236.

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