Journal of Hazardous Materials 165 (2009) 540–547

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Reaction kinetics and transformation products of 1-naphthol by Mn oxide-mediated oxidative-coupling reaction

Hyun-Sang Shin[a], Dong-Min Lim[a], Doo-Hee Lee[a], Ki-Hoon Kang[b,*]

[a] Dept. of Environmental Engineering, Seoul National University of Technology, Seoul, 139-743, Republic of Korea
[b] Technology Research Institute, Daelim Industrial Co., Ltd., Seoul, 110-732, Republic of Korea

ARTICLE INFO

Article history:
Received 29 February 2008
Received in revised form 6 October 2008
Accepted 7 October 2008
Available online 15 October 2008

Keywords:
1-Naphthol
Birnessite
Mn oxide
Oxidative-coupling reaction

ABSTRACT

In this study, the transformation of 1-naphthol *via* oxidative-coupling reaction was investigated using Mn oxides. 1-Naphthol was transformed completely by birnessite, which is one of the natural Mn oxides present in soil. The surface area-normalized specific rate constant, k_{surf}, for 1-naphthol was determined to be 9.66×10^{-4} L/m^2 min using observed pseudo-first-order rate constants with respect to birnessite loading. The transformation of 1-naphthol was dependent on the solution pH, and the pseudo-first-order rate constants increased from 0.028 at pH 11 to 0.075 at pH 2 at a birnessite loading of 0.625 g/L. GC and LC mass spectroscopic analysis of the supernatants were performed after separating the reaction solution into hydrophobic and hydrophilic fractions by solvent extraction. The major transformation products were found to be 1,4-naphthoquinone(1,4-NPQ) and naphthol polymerized products with a molecular weight (m/z) ranging from 400 to 2000. Transformation of 1,4-NPQ, to the polymerized products by an additional birnessite loading was also verified. The DOC concentrations of the supernatants before and after the reaction were analyzed and the rate of oligomeric precipitate formation was measured.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants that originate mainly from the incomplete combustion of fossil fuels, oil refineries, chemical production, and coal to heavy oil conversion processes, etc. [1]. PAHs consist of nonpolar hydrophobic naphthalene, anthracene and pyrene as well as their polar ionic degradation derivatives with similar toxicity and enhanced mobility [2]. These compounds are generally categorized as major contaminants on account of their toxicity even at low concentrations and carcinogenicity [3]. Effective control measures for wastewater and soil contaminated with PAHs have long been studied due to their high resistance to degradation and their potential for bioaccumulation.

1-Naphthol, which is one of major degradation by-products of naphthalene, is discharged from many industries, such as dye, plastics, synthetic rubber and asbestos production, and is known to have similar toxicity to naphthalene [4]. In addition, due to the substituted hydroxyl group, it has a much higher solubility in water than naphthalene, which can result in a high levels of contamination in aquatic and soil environments through enhanced mobility. Table 1 shows the chemical structure of 1-naphthol along with its typical properties.

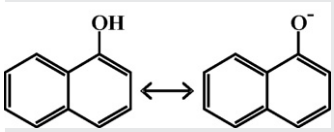
Metal (hydr)oxides and oxidoreductive enzymes can transform phenols and anilines into humic-like polymers through an oxidative-coupling reaction [5–7]. In many cases, the transformed products precipitate from the aqueous phase due to the increased molecular weight, which makes them much easier to separate [8]. In addition, oxidative coupling is one of the natural processes that immobilizes (or binds) organic contaminants in terrestrial environments. Organic compounds oxidized by oxidoreductive catalysts are covalently bound to soil organic matter to form the most persistent complexes. These complexes are often referred to as 'bound residues', which are difficult to decompose by microbial activity or chemical treatments [9]. Many studies have provided direct evidence for the formation of covalent bonds using ^{13}C- or ^{15}N-labeled chemicals in combination with ^{13}C- or ^{15}N-NMR spectroscopy [10,11]. This immobilization of contaminants in soil is of considerable importance because it can lead to a substantial decrease in the bioavailability of contaminants and restrict their leaching into the groundwater [5,11]. The oxidative-coupling reaction can also be considered to be a natural detoxification process because a decrease in toxicity has been confirmed by several research groups [12,13].

Like phenolic compounds, hydroxylated PAHs may be transformed through an oxidative-coupling reaction in the presence

* Corresponding author. Tel.: +82 2 2011 8291; fax: +82 2 2011 8068.
E-mail address: khkang@daelim.co.kr (K.-H. Kang).

0304-3894/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2008.10.027

Table 1
Selected physical and chemical properties of 1-naphthol.

Structural formula	Chemical and physical property	
	M_w (g/mol)	144.17
	S_w (mol/L)	666
	$\log K_{ow}$	2.85
	pK_a	9.34

of enzymes or metal oxides. Aktas et al. [14] performed a kinetic examination of the transformation of 1-naphthol by an oxidative-coupling reaction in the presence of laccase, one of oxidoreductive enzymes, and suggested the possibility of oxidative-coupling for the removal of hydroxylated PAHs. However, most studies on oxidative-coupling reaction have focused mainly on the utilization of enzymes due to their significance in natural detoxification processes and the carbon cycle. This process is uneconomical for mass production and unsuitable for maintaining the activity of the enzymes during storage and distribution. Therefore, maintaining the activity of the enzymes during application to expand their life-time is a major technical challenge.

On the other hand, Mn(III/IV) oxides, which are commonly present in soil particles, can act as oxidants due to their relatively high oxidizing capacity, as indicated below [6–8,15–17].

$$Mn^{III}OOH(s) + 3H^+ + e^- \rightarrow Mn^{2+}(aq) + 2H_2O \qquad E^0 = +1.50\,V$$

$$(1/2)Mn^{IV}O_2(s) + 2H^+ + e^- \rightarrow (1/2)Mn^{2+}(aq) + H_2O$$
$$E^0 = +1.29\,V$$

Oxidation by Mn oxide is selective for phenolic and aniline compounds. Therefore, these compounds are well known abiotic mediators for oxidative coupling, which can result in the formation of humic substances in natural environments [16,18]. Shindo and Huang [6] examined a variety of metal oxides commonly present in soil, and concluded that the abiotic formation of humic substances in the environment was largely due to Mn oxides.

This study examined the oxidative-coupling reaction of 1-naphthol using birnessite (δ-MnO_2), which is one of the common Mn oxides found in natural soil. The kinetics of the reaction by birnessite was measured by evaluating the transformation efficiency as a function of time. The effects on the birnessite loading and pH were also examined. For the reaction products, UV–vis spectroscopy was carried out to confirm that the removal of 1-NP was caused by oxidative polymerization. The reaction products present in the liquid phase were separated by solvent extraction into hydrophilic and hydrophobic fractions. Each fraction was analyzed by GC and LC mass spectroscopy to determine the molecular weight and structure. The DOC concentrations of the supernatants before and after the reaction were also analyzed to quantify the formation of oligomeric precipitates from the oxidative coupling of 1-NP. The transformation of one major reaction by-product (1,4-naphthoquinone) as well as its ability to cross-couple with 1-NP and/or 1-NP reaction products *via* Mn oxide were also investigated. Overall, these results may contribute to a better understanding of the reaction with Mn oxide, and provide a good method for removing PAHs in field applications.

2. Methods and materials

2.1. Materials

1-Naphthol (1-NP) and 1,4-naphthoquinone (1,4-NPQ) were obtained in high purity (>99%) from Sigma–Aldrich (St. Louis, MO) and used as received. All other chemicals were of high purity and purchased from Sigma–Aldrich. Stock solutions of 1-NP and 1,4-NPQ were prepared by dissolving the chemicals in deionized water in a N_2 atmosphere for 24 h followed by filtration through a PTFE membrane filter (0.2 μm, Pall Co., NY). The resulting concentrations were determined by HPLC analysis. Standard solutions were prepared using these stock solutions, and the pH was adjusted to 5.0 ± 0.1 with either 0.1N HCl or NaOH. In preliminary experiments using buffered standard solutions, it was found that the buffer compounds could significantly affect the rate and degree of the 1-NP transformation, probably due to a change in solution chemistry, i.e. ionic strength, adsorption to oxide particles, etc. Therefore, a buffer was not used to adjust the pH of the standard solutions in order to minimize any possible effects on the reaction.

Birnessite was prepared by boiling potassium permanganate in hydrochloric acid as described by McKenzie [19]. The resulting oxide particles were filtered and washed repeatedly with deionized water to ensure the removal of excess reagents, then freeze-dried. The FT/IR spectrum (Bomen MB154) of birnessite showed characteristic peaks at 930, 1630 and 3450 cm^{-1} [20]. XRD (Rigaku, Japan) also confirmed the major crystalline structure of birnessite. The BET surface area of the prepared birnessite was determined to be 44.37 m^2/g using a Micromeritics surface area analyzer (Model ASAP 2010, Norcross, GA).

As a standard natural humic substance for the comparison with the 1-NP transformation products, soil fulvic acid was extracted using the standard procedure proposed by the International Humic Substances Society (IHSS). The extracted fulvic acid was fractioned with an ultrafiltration membrane of MWCO of 1000 Da, and the filtered subfraction was used.

2.2. Batch experiments

The individual transformation experiments were carried out in a sealed batch systems prepared in 20-mL serum bottles. The serum bottles were filled with 20 mL of the 1-NP standard solutions (40 mg/L, pH 5, unless otherwise stated) with a certain amount of birnessite added (12.5–50 mg). The bottles were crimp-sealed using a Teflon-lined rubber septum. Each bottle prepared was wrapped with aluminum foil to prevent exposure to light, and loaded on an end-over-end rotary shaker at 30 rpm at 20 ± 2 °C. The decrease in 1-NP concentration was determined by periodically analyzing a 500-μL reaction solution samples by HPLC.

After the reaction, the reaction solutions were centrifuged at $10{,}000 \times g$ for 15 min, and the reaction products present in the supernatants were separated into hydrophobic and hydrophilic fractions by solvent extraction with CH_2Cl_2. The hydrophobic fraction was concentrated using a vacuum rotary evaporator for further GC/MS analysis, while the hydrophilic fraction was used for LC/MS analysis without pretreatment.

The effect of the solution pH on the transformation was evaluated using the same experimental setup with a 20-mL serum bottle containing 20 mL of the 1-NP standard solutions (30 mg/L) and 12.5 mg of birnessite as described above. The initial pH was adjusted to 2–11 with either 0.1N HCl or NaOH. Samples were taken from the bottles and the remaining 1-NP concentrations were analyzed by HPLC as a function of time.

Since 1,4-NPQ is one of the major reaction by-products from the birnessite-induced transformation of 1-NP, its conversion by

Mn oxide was also evaluated. The above described experimental setup was employed for this experiment using 20 mL of a 1,4-NPQ standard solution (10.8 mg/L) and 25 mg of birnessite. The cross-coupling reactions of 1,4-NPQ with 1-NP and/or 1-NP reaction products were also evaluated by carrying out the experiment in the presence of 1-NP (10 mg/L).

2.3. Analyses

The 1-NP and 1,4-NPQ concentrations were determined by HPLC (Shimadzu, Tokyo, Japan) with a UV absorbance detector operated at 254 nm using a Waters C18 4.6 mm × 150 mm (5-μm particle size) reverse-phase column (Milford, MA). The mobile phase, which was composed of 50/50 acetonitrile and water, was delivered at a flow rate of 1.0 mL/min. The samples taken from the reaction bottle were filtered through a 0.45 μm PTFE syringe filter. A preliminary test confirmed there was minimal loss caused by adsorption to the membrane (<0.02%). Twenty microliters of the filtered sample was analyzed by HPLC.

In order to confirm that the decrease in 1-NP concentration was caused by the birnessite-mediated oxidative-coupling reaction, UV–vis spectroscopy was carried out on the reaction solutions at different times using a Shimadzu UV-1601 system with a 10 mm quartz cell over the wavelength range 200–800 nm.

GC/MS analyses were carried out on the hydrophobic fraction of the reaction solution using an Agilent 6890 GC system equipped with an Agilent 5973 mass selective detector and an Agilent 7683 series injector. A DB-5MS, 30 m × 0.25 mm, ID 0.25 μm capillary column (J&W 122-5532) and ultra-high purity helium carrier gas (10.50 psi, 1.0 mL/min) were used with an injection volume of 1 μL. A column temperature gradient was used, which was started at 55 °C, maintaining at that temperature for 1 min, gradually increased to 275 °C at a rate of 10 °C/min, and finally increased to 300 °C at a rate of 5 °C/min. The temperature of the injector port was 270 °C.

For the hydrophilic fraction of the reaction solution, LC/MS analyses were carried out using a LCQ DECA XP mass spectrometer (ThermoElectron Inc., Woburn, MA) with an electrospray interface used in negative ion mode. The samples were run on a Shiseido HPLC system (Nanospace SI-2, Japan) using a Luna® C18 1.0 mm × 250 mm (5-μm particle size) column (Phenomenex Inc., Torrance, CA). The mobile phase was 5% (A) and 95% (B) acetonitrile in gradient mode (A:B = 100:0 (5′) ~ 0:100 (40′)).

The oligomeric precipitates formed from the reaction were quantified by measuring the DOC concentrations of the supernatants before and after the reaction using a TOC analyzer (Formacs^{HT}, Skalar, Netherlands).

3. Results and discussion

3.1. Oxidative-coupling reaction of 1-naphthol by birnessite

In order to examine the transformation of 1-NP by birnessite, the reaction solutions (containing 25 mg of birnessite in 20 mL of 1-NP standard with pH 5.0) were analyzed by HPLC. Fig. 1(a) shows chromatograms at different times. As indicated in the chromatograms, the peak intensity of 1-NP with a retention time of 4.6 min decreased with time and finally disappeared after 40 min. On the other hand, of the peak at 1.1 min for the reaction products increased as the peak for 1-NP decreased. In addition, new peaks were observed at a retention time of 2.6 and 3.9 min, which might have been generated from the 1-NP transformation. However, there was no definite trend for the increase or decrease in these peaks because they were probably generated by intermediates of the transformation or by reaction products also involved in the further transformation by birnessite.

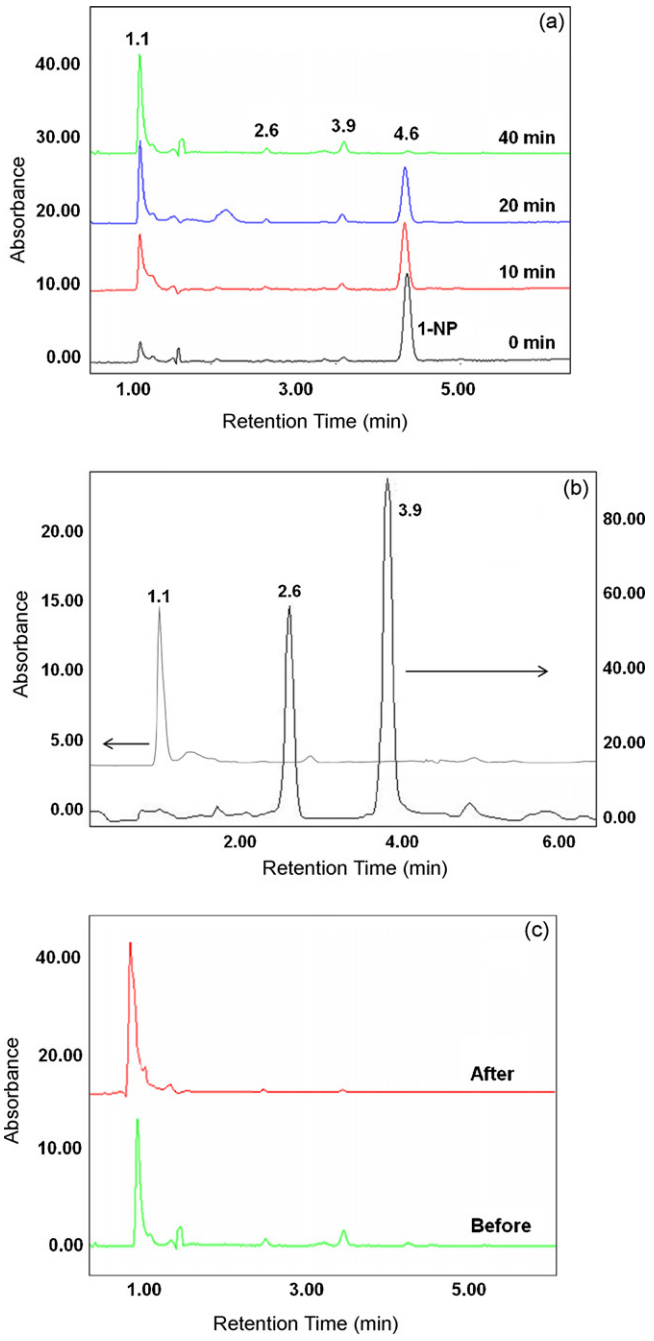


Fig. 1. HPLC chromatograms of (a) 1-NP and its reaction products by birnessite at different times (experimental conditions: 40 mg/L 1-naphthol, 1.25 g/L Mn oxides, pH 5.0 ± 0.1, and 20 °C in the dark), (b) hydrophobic and hydrophilic fractions of the reaction solution (after 40 min), and (c) hydrophobic reaction products before and after the reaction by additional birnessite (25 mg/20 mL).

As a reverse phased HPLC column was used in this study, the more polar compounds exhibit a shorter retention time [21]. Therefore, the reaction products shown in Fig. 1(a) may be more polar than 1-NP and possess lower octanol-water partition coefficients (K_{ow}) than 1-NP (2.85) [22]. For a more detailed examination of the reaction products with respect to polarity, the sample was separated into hydrophobic and hydrophilic fractions by solvent extraction using methylene chloride. HPLC analysis of the hydrophobic fraction (methylene chloride extracts) revealed two

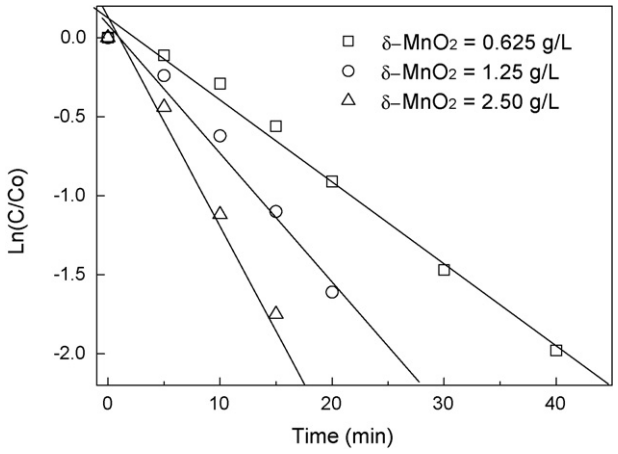


Fig. 2. Pseudo-first-order disappearance of 1-NP at different birnessite loadings (experimental conditions: 40 mg/L 1-NP, pH 5 at 20 °C).

Table 2
Observed kinetic constants and half-lives for the oxidative transformation of 1-NP (40 mg/L) at various birnessite loadings and pH.

	Birnessite loading		
	0.625 g/L	1.25 g/L	2.5 g/L
k (min^{-1})	0.052	0.082	0.13
r^2	0.994	0.991	0.993
$t_{1/2}$ (min)	13.30	8.49	5.30
k_{surf}[a] (L/m^2 min)	9.66×10^{-4} (r^2 = 0.998)		

	Solution pH					
	pH 2	pH 3	pH 5	pH 7	pH 9	pH 11
k (min^{-1})[b]	0.075	0.066	0.055	0.046	0.036	0.028
r^2	0.998	0.997	0.999	0.999	0.999	0.996
$t_{1/2}$ (min)[b]	9.2	10.6	12.7	15.0	19.0	24.8

[a] Normalized to a birnessite surface area of 44.37 m^2/g.
[b] Amounts of birnessite added is 0.625 g/L.

peaks at 2.6 and 3.9 min, while only one peak at 1.1 min was observed in the remaining aqueous phase (hydrophilic fraction) (Fig. 1b). This suggests that the reaction products formed from the oxidative-coupling reaction of 1-NP have various solubility and polarity, which is similar to the reaction of phenols reported by Majcher et al. [23]. In the experiments of oxidative coupling of ^{14}C-labeled catechol by Mn oxide, they confirmed the same results by extracting the reaction solution using a variety of solvents with different polarity and pH.

Upon the addition of a certain amount of birnessite into the reaction solution (25 mg/20 mL), the peaks for the hydrophobic reaction products disappeared after 40 min, while those for the hydrophilic products increased (Fig. 1c). This suggests that the hydrophobic products are intermediates of the oxidative-coupling reaction and are subject to a further transform to more stable hydrophilic compounds [13,24].

3.2. Kinetics of 1-NP transformation by Mn oxide-mediated oxidative-coupling reaction

3.2.1. Reaction kinetics with respect to Mn oxide loadings

In order to examine the reaction kinetics of the oxidative transformation of 1-NP by birnessite, the transformation rate was evaluated as a function of time at various birnessite loadings. As shown in Fig. 2, the transformation rate increased with increasing birnessite loading. With a birnessite loading of 0.625 g/L, approximately 40 min was needed for a 99% transformation, while only 15 min was required with a birnessite loading of 2.5 g/L. Fig. 2 also shows that the transformation follows pseudo-first-order kinetics with r^2 = 0.991–0.994. Table 2 summarizes the rate constants, k, and half-lives with respect to the birnessite loading. When the birnessite loading was increased from 0.625 to 2.5 g/L, the rate constants increased approximately 2.5-fold from 0.052 to 0.13 min^{-1}, and the half-life decreased from 13.3 to 5.3 min.

Since the transformation occurs on the surface of birnessite, the quantity of available birnessite surface area might be a more important variable in the reaction kinetics than the birnessite mass. Therefore, a more meaningful interpretation of the kinetic data can be obtained by normalizing the observed rate constants to the birnessite surface area [25]. The observed rate constants showed a linear correlation with the birnessite surface area, assuming a constant specific surface area of 44.37 m^2/g. The slope of the line of best fit is the specific rate constant, k_{surf} (L/m^2 min), where the rate constants obtained were normalized to 1 m^2/L birnessite (Table 2). This surface area-normalized rate constant is a variable that is independent of the birnessite loadings. Therefore, it can provide more generalized information for a quantitative evaluation of the reactivity of certain compounds.

3.2.2. Reaction kinetics with respect to pH

pH is an important reaction variable that determines the surface charge of birnessite as well as the degree of protonation of 1-NP. According to the reaction model of oxidative coupling, it was assumed that the reaction was initiated by the surface complexation of the hydroxyl group of a reactant to the manganese atom on the oxide surface [26,27], which is affected by the pK_a of the reactant, the surface charge of Mn oxide and the solution pH [28]. The effect of the solution pH was examined by carrying out a series of batch experiments at different solution pHs ranging from 2 to 11. Table 2 summarizes the pseudo-first-order rate constants obtained along with the corresponding half-lives. The rate constant decreased with increasing pH from 0.028 min^{-1} at pH 11 to 0.075 min^{-1} at pH 2. This shows that a lower solution pH is more favorable for the transformation. An effect of the solution pH can be anticipated considering that the pK_a value of 1-NP is 9.34 and the point of zero charge (PZC) of birnessite is 2.4–2.7 [29]. At a pH higher than the PZC, the surface of birnessite was negatively charged while the amount of negatively charged ions of 1-NP increased with increasing pH. Therefore, as the pH increases, physical contact between the reactants is inhibited by electrostatic repulsion, which reduced the reaction rate. This result is typical for the reaction of metal oxide with a low PZC value with weak acidic organic compounds [30].

The rate constants were correlated with pH in order to quantify the effect of the solution pH on the reaction rate, as shown in Fig. 3. As shown in the figure, there was a strong high linear relationship (r^2 = 0.994) between the rate constant and pH. This strong dependence of the rate constants can be attributed to the effect of pH on the electron transfer reaction as well as the electrostatic interaction mentioned above. For electron transfer, protons are needed to reduce MnO_2 to release Mn^{2+} ions, and the reduction potential of MnO_2 increases with decreasing pH [31]. The higher rate constant at pH 2 might be due to the higher rate of electron transfer for the oxidant, MnO_2, and protonation of the oxide surface at a pH less than the PZC of MnO_2, which also facilitates the electron-transfer reaction. Similar results showing the effect of pH on the rate constants of the oxidative transformation of phenolic compounds by Mn oxide have been reported [32].

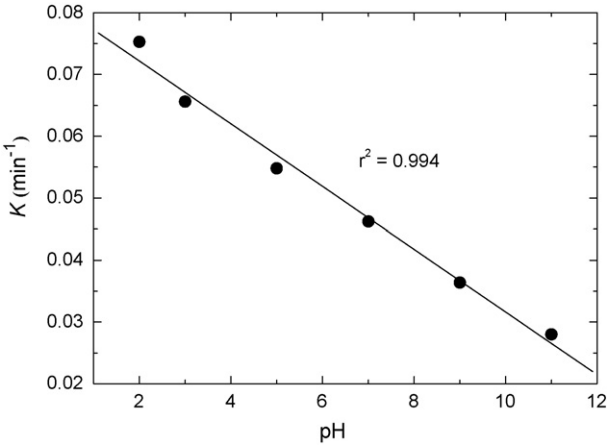


Fig. 3. Correlation between the pseudo-first-order rate constants and solution pH (experimental conditions: 30 mg/L 1-NP, 0.625 g/L birnessite loading at 20 °C).

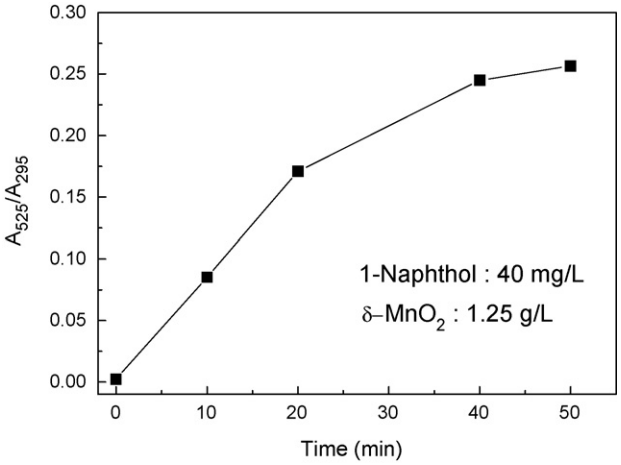


Fig. 5. UV–vis absorption ratios (A_{525}/A_{295}) of 1-NP and its reaction products by Mn oxide as a function of the reaction time (experimental conditions: 40 mg/L 1-NP, 1.25 g/L birnessite, pH 5 at 20 °C).

3.3. Characterization of the reaction products by UV–vis spectrometric analysis

In order to confirm that the reaction products identified by HPLC were the oligomeric products of 1-NP formed by the oxidative-coupling reaction, the 1-NP standard (40 mg/L, pH 5.0) and reaction solution were scanned with a UV–vis spectrometer after 40 min, and the results are shown in Fig. 4. The UV–vis absorption spectrum of soil fulvic acid (20 mg/L, pH 5.0) is also shown for comparison. The absorbance maximum (λ_{max}) in the spectrum of the 1-NP standard was 295 nm, which was caused by the primary absorption band (E_2-band) of the benzene ring of 1-NP molecule [33]. This absorbance maximum decreased as the 1-NP transformation progressed, while there was an increase in absorbance at around 450–600 nm. This increase in the absorption maximum in this wavelength region suggests the production of reaction products that absorb light in the visible wavelength region. Although reduced Mn(II) might cause an increase in the absorption maximum in the wavelength region, the experimental evaluation confirmed that the Mn(II) present in the reaction solution (<0.02 mg/L) had a negligible effect on the absorption characteristics. This increase in absorption in the visible region is a phenomenon caused by the conjugation of benzene rings [33], which provides evidence of oligomer formation through the birnessite-mediated oxidative-coupling reaction.

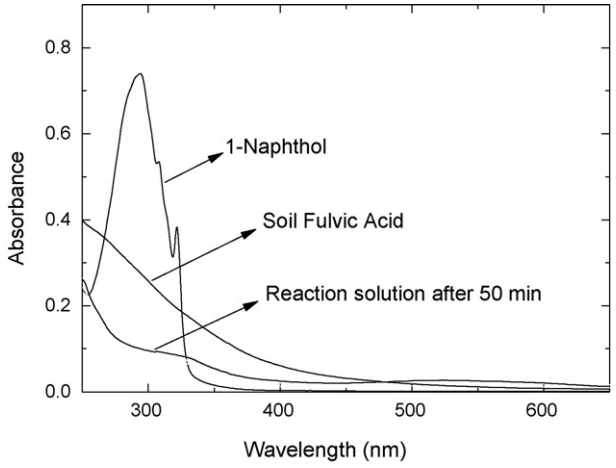


Fig. 4. UV–vis absorption spectra of the 1-NP standard (40 mg/L, pH 5) and its reaction solution after 50 min, shown with the spectrum of soil fulvic acid (20 mg/L, pH 5).

The transformation of 1-NP to oligomers may be explained quantitatively, as shown in Fig. 5. In the figure, the absorbance ratios (A_{525}/A_{295}), absorbance maxima of 1-NP and reaction products, were correlated with the reaction time. The absorption ratio of the 1-NP standard was 0.002. During the reaction, the absorption ratio increased to approximately 0.25 after 50 min, which corresponds to an increase of approximately two orders of magnitude. In addition, the increase in ratio was linear during the initial phase of the reaction, while the rate decreases when the reaction was complete. Shindo and Haung [6] examined the transformation of polyphenols with Mn oxide, and also observed this "browning effect" in the reaction solution. They suggested this to be one of the major processes generating humic substances in the natural environment.

3.4. GC/MS and LC/MS analyses of reaction products

In order to determine the molecular structure of the hydrophobic reaction intermediates, the reaction solution was solvent-extracted with dichloromethane, and analyzed by GC/MS. Three major peaks were detected at 9.96, 11.27 and 11.39 min (Fig. 6a). According to the mass spectra, the peak at 11.39 min was caused by the remaining 1-NP (m/z = 144, Fig. 6b), while the peak at 9.96 min was identified as 1,4-naphthoquinone (1,4-NPQ, Fig. 6c). This was later confirmed using 1-NP and 1,4-NPQ standards, i.e. the patterns of the m/z ratios of the fragment ions were identical (>95%). The retention times of the standards by HPLC analysis were also identical. This confirms the previous supposition of comparable polarity of 1-NP and its reaction products based on the HPLC chromatogram because $\log K_{ow}$ of 1,4-NPQ is 1.71 [21]. A plausible reaction pathway on the oxidative transformation of 1-NP to 1,4-NPQ by Mn oxide can be explained by the oxidation of 1-NP to 1,4-dihydroxynaphthalene, which becomes further oxidized to 1,4-naphthoquinone as shown in Fig. 7. Wu et al. [34] proposed the same pathway for the formation of 1,4-NPQ as a metabolite of 1-NP in mammals through cytochrome P450-dependent monooxygenase enzymes (CYP).

On the other hand, the compound at 11.27 min appears to be a dimer formed from the oxidative coupling of 1-NP, as indicated by the molecular ion (m/z = 281) and the fragment ion peaks of the mass spectrum (Fig. 6d). Karthikeyan and Chorover [35] also reported that the naphthoquinone-type monomers (i.e.

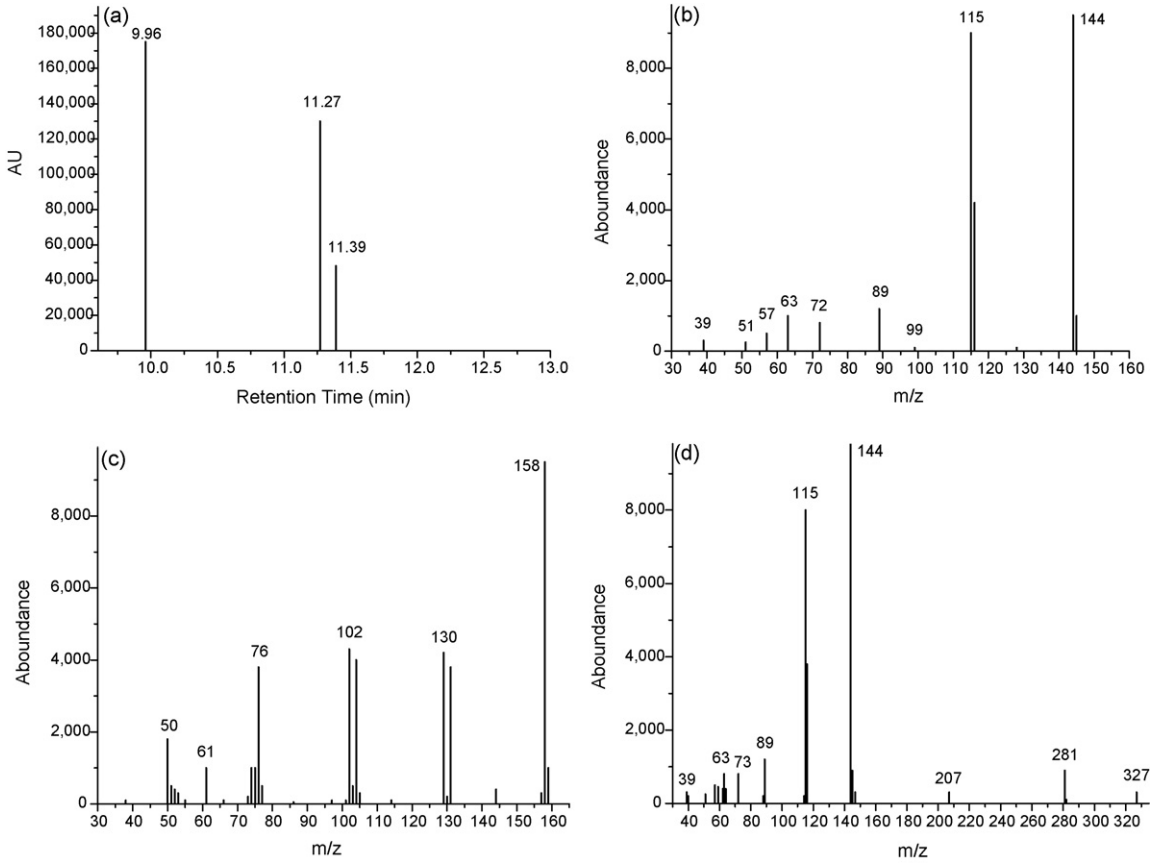


Fig. 6. (a) GC/MS chromatogram of the CH_2Cl_2-extracted reaction products and (b–d) mass spectra of 1-NP and its reaction products.

1,2-NPQ, 1,4-NPQ and 2-hydroxy-1,4-NPQ, etc.) and their coupled reaction products such as naphthol–naphthol (m/z = 286), naphthol–naphthoquinone (m/z = 300, 316) were formed from the photolytic transformation of 1-NP.

LC/MS analysis was performed on the hydrophilic reaction products remaining after solvent extraction, and the results are shown at Fig. 8. As shown in the mass spectrum, the hydrophilic products comprise a wide range of oligomers with molecular weights (m/z) ranging from 400 to 2000. This may have been caused by self-coupling of the oxidized 1-NP products (quinone and radicals with various resonance structures) at various bonding sites and from cross-coupling between quinone, radicals and various oligomer products [10,22]. On the other hand, peaks with a molecular weight lower than 1-NP (m/z = 144) may have been generated from partial ring cleavage and the release of functional groups, as reported elsewhere [23,36,37].

In general, the oligomer products remaining in the aqueous phase after the oxidative-coupling reaction are quite soluble and have low molecular weights. In their experiments using horseradish peroxidase (HRP), Xu et al. [13] also analyzed the 1-NP reaction products using size exclusion chromatography (SEC) and mass spectroscopy, and reported that the molecular weights of the soluble oligomers ranged from 400 to 600 m/z, which corresponds to the naphthol trimer and tetramer, while those of the oligomeric precipitates were 853 Da, which corresponds to a naphthol hexamer. However, in this study using Mn oxide, soluble (hydrophilic) reaction products with a higher molecular weight were produced from the reaction. This discrepancy with HRP might have been caused by several side reactions with Mn oxide, such as partial ring cleavage and the removal of substituents, as mentioned above. The major peaks in the mass spectrum (m/z = 684.9, 757.8) might be oligomers formed from 4 to 5 molecules of 1-NP. Due to these

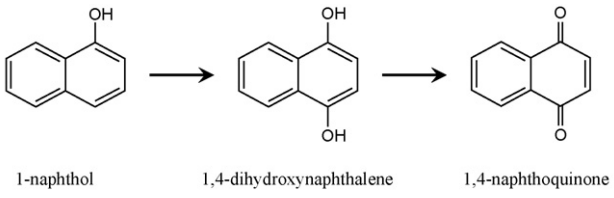


Fig. 7. Possible reaction pathway of 1-NP to 1,4-NPQ *via* Mn oxide.

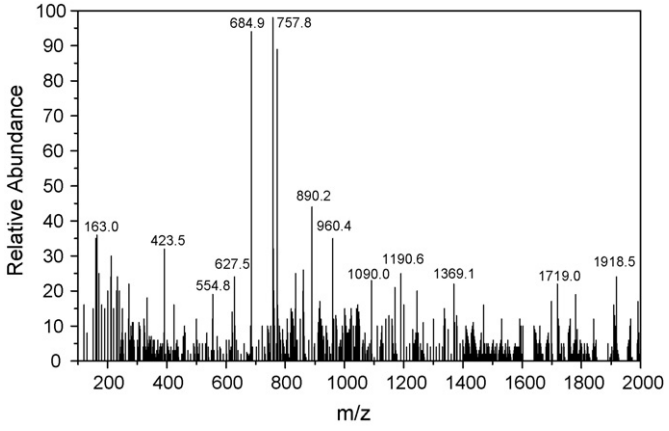


Fig. 8. LC/MS spectrum of CH_2Cl_2 non-extractable reaction products produced at pH 5 with 40 mg/L 1-NP and 1.25 g/L birnessite.

Table 3
DOC analysis results for the supernatants before and after the birnessite-mediated transformation reaction of 1-NP.

		Initial concentration of 1-NP	Birnessite loading (g/L)		
			0.625	1.25	2.5
DOC in supernatants	mg/L	20.5	13.2	12.0	10.6
	%	100	64.3	58.5	51.7
mg DOC removed/g birnessite	–		11.7	6.8	4.0

side reactions, a clear oligomerization pattern of the molecular weight distribution could not be obtained, as in the enzymatic reaction.

3.5. Distribution of DOC concentrations

The oligomers formed from the oxidative-coupling reaction may form precipitates as the molecular weights increase or become irreversibly incorporated into the soil organic matter to form bound residues [38,39]. Therefore, for a better understanding of the fate of the reaction products, it is important to examine the fraction of insoluble reaction products formed from the 1-NP oxidative-coupling reaction by Mn oxide. In this study, the distribution of soluble and insoluble reaction products was determined by analyzing the DOC concentration before and after the reaction at different birnessite loadings. Table 3 shows the analysis results of the initial 1-NP standards and soluble reaction products remaining in the aqueous phase after the reaction with different birnessite loadings. 1,4-NPQ and hydrophilic oligomers were the major reaction products remaining in the supernatant, as described earlier, and the DOC concentrations of the supernatants ranged from 13.2 to 10.6 mg/L (or 64.3–51.7%) at a birnessite loading ranging from 0.625 to 2.5 g/L. This suggests that the 1-NP contents removed by precipitation (and possibly adsorption onto Mn oxide and oligomers) ranged from 35.7 to 48.3%. In addition, the DOC removal rate per unit Mn oxide decreased with increasing birnessite loading (11.7 mg DOC removed/g birnessite at 0.625 g/L to 4.0 mg DOC removed/g birnessite at 2.5 g/L loading). Considering that stoichiometrically, an excess of birnessite had been injected, the result suggests that the increased birnessite loading had minimal effect on the degree of coupling. On the other hand, the main effect of the increased loading is the greater likelihood of contact between the reactants, which enhances the reaction rate.

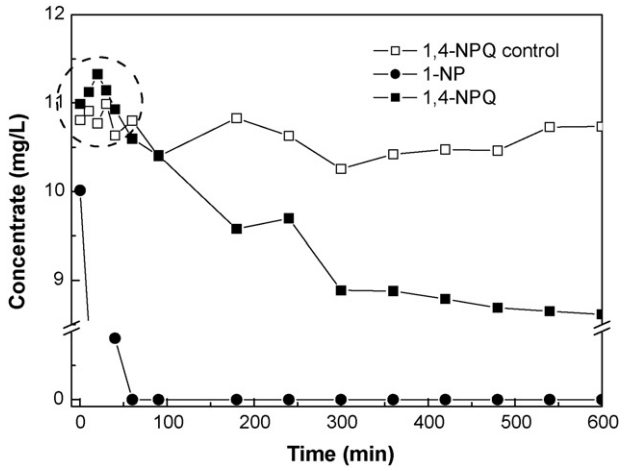


Fig. 9. Transformation of 1,4-NPQ in the absence (□) and presence (■) of 1-NP (●) (experimental conditions: 10.8 mg/L 1,4-NPQ, 1.25 g/L birnessite, and 10.0 mg/L 1-NP at pH 5.0, 20 °C).

3.6. Cross-coupling reaction of 1,4-NPQ with 1-NP and/or 1-NP reaction products

1,4-NPQ generated from the 1-NP oxidative-coupling reaction is known to be tumorigenic due to its binding capacity to macromolecules including DNA and proteins [40]. Therefore, its ultimate fate can be an important factor in engineering applications. As described earlier, 1,4-NPQ was removed completely upon the injection of additional birnessite in the reaction solution. In the reaction, 1,4-NPQ may have been transformed directly through birnesite-mediated oxidative coupling. One possible explanation is that the kinetics of 1,4-NPQ oxidative coupling by Mn oxide are much lower than those of 1-NP. On the other hand, a cross-coupling reaction with 1-NP or 1-NP oligomers may be another explanation. Therefore, in order to identify the transformation pathway of 1,4-NPQ, it was reacted with birnessite in the presence or absence of 1-NP, and the results are shown in Fig. 9. As shown in the figure, 1,4-NPQ was not transformed significantly by birnessite in the absence of 1-NP over a 10 h period. Although the concentration was varied to some extent with reaction time, it may have been caused by reversible sorption onto birnessite particles. However, in the presence of 1-NP (10 mg/L), the 1,4-NPQ concentration increased during the initial phase of the reaction (to approximately 30 min), and then decreased continuously thereafter, while 1-NP had disappeared almost completely within 60 min. The increase in 1,4-NPQ concentration during the reaction resulted from the oxidation of 1-NP by birnessite. On the other hand, the cross-coupling of 1,4-NPQ with 1-NP and its oligomer products is the most plausible explanation for the continuous decrease in 1,4-NPQ concentration. In the presence of a reactive mediator, the cross-coupling or binding reactions of compounds non-reactive to Mn oxide (or other oxidoreductive enzymes) have been reported [8,17,24]. However, since the transformation rate of 1,4-NPQ is relatively slower than that of 1-NP, the information provided from these experiments should be considered for actual applications of 1-NP clean-up processes using Mn oxide.

4. Conclusions

This study examined the potential of Mn oxide to transform (and eventually remove) 1-naphthol, a typical PAHs degradation derivative, and provided basic information for a novel solution for removing PAHs from various environmental media. These results demonstrate the high susceptibility of hydroxylated PAHs (1-NP) oxidation by Mn oxides and the rapid reaction rates under mild acidic conditions, which are common in natural water and soil. The Mn oxide-mediated oxidative polymerization of 1-NP in an aqueous solution produces hydrophilic oligomers with a wide range of molecular weights ranging from several hundred to several thousand, as well as insoluble precipitates. 1,4-NPQ generated from the oxidative-coupling reaction could also be removed *via* a birnessite mediated-cross coupling reaction in the presence of 1-naphthol. Overall, it is believed that the use of Mn oxide in engineered humification processes is a promising technology for remediating soils and water contaminated with hydroxylated PAHs. Studies on the

hydroxylation of PAHs through partial degradation as a pretreatment method and the applicability of Mn oxide in the field are currently underway.

Acknowledgements

This study was supported by the Korea research Foundation Grant by the Korean Government (MOEHRD) (KRF-2004-D00379). This work was also supported by Environmental Technology Education Innovation Program (2006) of the Ministry of Environment in Korea.

References

[1] WHO, IPCS Environmental Health Criteria 202. Selected Non-heterocyclic Polycyclic Aromatic Hydrocarbons, World Health Organization, Geneva, 1998.
[2] R.P. Schwarzenbach, P.M. Gschwend, D.M. Imboden, Environmental Organic Chemistry, John Wiley & Sons, New York, 1993.
[3] US EPA, http://www.epa.gov/ttn/atw/hlthef, 2003.
[4] S.J. Stohs, S. Ohia, D. Bagchi, Naphthalene toxicity and antioxidant nutrients, Toxicology 180 (2002) 97–195.
[5] J.-M. Bollag, Decontaminating soil with enzymes: an *in situ* method using phenolic and anilinic compounds, Environ. Sci. Technol. 26 (1992) 1876–1881.
[6] H. Shindo, P.M. Huang, Role of Mn(IV) oxide in abiotic formation of humic substances in the environment, Nature 298 (1982) 363–365.
[7] H. Shindo, P.M. Huang, Significance of Mn(IV) oxide in abiotic formation of organic nitrogen complexes in natural Environment, Nature 308 (1984) 57–58.
[8] K.-H. Kang, J. Dec, H. Park, J.-M. Bollag, Transformation of the fungicide cyprodinil by a laccase of *Trametes villosa* in the presence of phenolic mediators and humic acid, Water Res. 36 (2002) 200–208.
[9] T.R. Roberts, W. Klein, G.G. Still, P.C. Kearney, N. Drescher, J. Desmoras, H.O. Essen, N. Aaharonson, J. Vonk, Non-extractable pesticide residues in soils and plants, Pure Appl. Chem. 56 (1984) 945–956.
[10] K.A. Thorn, P.J. Pettigrew, W.S. Goldenberg, E.J. Weber, Covalent binding of aniline to humic substances. 2. ^{15}N-NMR studies of nucleophilic addition reactions, Environ. Sci. Technol. 30 (1996) 2764–2775.
[11] J. Dec, K. Haider, A. Benesi, V. Rangaswamy, A. Schäffer, U. Plücken, J.-M. Bollag, Analysis of soil-bound residues of the ^{13}C-labeled fungicide cyprodinil by NMR spectroscopy, Environ. Sci. Technol. 31 (1997) 1128–1135.
[12] J.-W. Jung, S.H. Lee, H. Ryu, K.-H. Kang, K. Nam, Detoxification of phenol through bound residue formation by birnessite in soil: transformation kinetics and toxicity, J. Environ. Sci. Health A 43 (2008) 255–261.
[13] F. Xu, D.E. Koch, I.C. Kong, R.P. Hunter, A. Bhandari, Peroxidase-mediated oxidative coupling of I-naphthol: characterization of polymerization products, Water Res. 39 (2005) 2358–3236.
[14] N. Aktas, H. Cicek, A.T. Unal, G. Kibarer, N. Kolankaya, A. Tanyolac, Reaction kinetics for laccase-catalyzed polymerization of 1-naphthol, Bioresour. Technol. 80 (2001) 29–36.
[15] J.-M. Bollag, K.L. Shuttleworth, D.H. Anderson, Laccase-mediated detoxification of phenolic compounds, Appl. Environ. Microbiol. 54 (1988) 3086–3091.
[16] J.-M. Bollag, C. Myers, S. Pal, P.M. Huang, The role of abiotic and biotic catalysts in the transformation of phenol compounds, in: P.M. Haung, J. Berthelin, J.-M. Boallg, W.-B. McGill, A.L. Pake (Eds.), Environmental Impact of Soil Components Interactions: Natural and Anthropogenic Organics, CRC Press, Boca Raton, FL, 1995, pp. 299–310.
[17] K.-H. Kang, D.-M. Lim, H. Shin, Oxidative-coupling reaction of TNT reduction products by manganese oxide, Water Res. 40 (2006) 903–910.
[18] D.L. Sparks, Environmental Soil Chemistry, Academic Press Inc., California, 1995, pp. 99–139.
[19] R.M. McKenzie, The synthesis of birnessite, cryptomelane, and some other oxides and hydroxides of manganese, Miner. Mag. 38 (1971) 493–502.
[20] M.B. McBride, Oxidation of dihydroxybenzenes in aerated aqueous suspensions of birnessite, Clay Clay Miner. 37 (1989) 341–347.
[21] D.C. Hansch, Quantitative Chemical Analysis, Fifth ed., W.H. Freeman and Company, New York, NY, 1999.
[22] W.D. Burgos, D.F. Berry, A. Bhandari, J.K. Novak, Reversible sorption and irreversible binding of naphthalene and α-naphthol to soil: elucidation of processes, Environ. Sci. Technol. 30 (1996) 1205–1211.
[23] E.H. Majcher, J. Chorover, J.-M. Bollag, P.M. Huang, Evolution of CO_2 during birnessite-induced oxidation of ^{14}C-labeled catechol, Soil Sci. Soc. Am. J. 64 (2000) 157–163.
[24] K.-H. Kang, J. Dec, H. Park, J.-M. Bollag, Effect of phenolic mediators and humic acid on cyprodinil transformation in presence of birnessite, Water Res. 38 (2004) 2737–2745.
[25] A. Agrawal, P.G. Tratnyek, Reduction of nitro aromatic compounds by zero-valent iron metal, Environ. Sci. Technol. 30 (1996) 153–160.
[26] M.B. McBride, Adsorption and oxidation of phenolic compounds by iron and manganese oxides, Soil Sci. Soc. Am. J. 51 (1987) 1466–1472.
[27] A.T. Stone, J.J. Mogan, Reduction and dissolution of Mn(III) and Mn(IV) oxides by organics. 2. Survey of the reactivity of organics, Environ. Sci. Technol. 18 (1984) 617–624.
[28] M.B. McBride, Oxidation of 1,2- and 1,4-dihydroxybenzens by birnessite in acidic aqueous suspension, Clay Clay Miner. 37 (1989) 479–486.
[29] H. Shindo, P.M. Huang, Catalytic effect of manganese(IV), iron(III), Al, and Si oxides on the formation of phenolic polymers, Soil Sci. Soc. Am. J. 48 (1984) 927–934.
[30] M.S. Odziemkowski, R.W. Gillham, Surface redox reactions on commercial grade granular iron (steel) and their influence on the reductive dechlorination of solvent. Micro Raman Spectroscopic Studies, in: Proceedings of the 213th ACS National Meeting, San Francisco, CA, 1997, pp. 13–17.
[31] H. Zhang, C.H. Huang, Oxidative transformation of triclosan and chlorophene by manganese oxides, Environ. Sci. Technol. 37 (2003) 2421–2430.
[32] W. Stumm, J. Morgan, Aquatic Chemistry, 3rd ed., Wiley, New York, 1996, pp. 425–490.
[33] R.M. Silvertein, F.X. Webster, Spectrometric identification of organic compounds, 6th ed., John Wiley & Sons, New York, 1997.
[34] R. Wu, S. Waidyanatha, A.P. Henderson, B. Serdar, Y. Zheng, S.M. Rappaport, Determination of dihydroxynaphthalenes in human urine by gas chromatography-mass spectrometry, J. Chromatogr. B 826 (2005) 206–213.
[35] K.G. Karthikeyan, J. Chorover, Effect of solution chemistry on the oxidative transformation of 1-naphthol and its complexation with humic acid, Environ. Sci. Technol. 34 (2000) 2933–2945.
[36] M.C. Wang, P.M. Huang, Significance of Mn(IV) oxide in the abiotic ring cleavage of pyrogallol in natural environments, Sci. Total Environ. 113 (1992) 147–157.
[37] J. Dec, K. Haider, J.-M. Bollag, Release of substituents from phenolic compounds during oxidative coupling reactions, Chemosphere 52 (2003) 549–556.
[38] H. Seling, T.M. Keinath, W.J. Weber, Sorption and manganese-induced oxidative coupling of hydroxylate aromatic compounds by natural geosorbents, Environ. Sci. Technol. 37 (2003) 4122–4127.
[39] S.J. Parikh, J. Chorover, W.D. Burgos, Interaction of phenanthrene and its primary metabolite(1-hydroxy-2-naphthoic acid) with estuarine sediments and humic fractions, J. Contam. Hydrol. 72 (2004) 1–22.
[40] M.A. Troester, A.B. Lindstrom, S. Waidyanatha, L.L. Kupper, S.M. Rappaport, Stability of hemoglobin and albumin adducts of naphthalene oxide 1,2-naphthoquinone, and 1,4-naphthoquinone, Toxicol. Sci. 68 (2002) 314–321.