

A novel solution for hydroxylated PAHs removal by oxidative coupling reaction using Mn oxide

Ki-Hoon Kang, Dong-Min Lim and Hyun-Sang Shin

ABSTRACT

In this study, removals of 1-naphthol by oxidative-coupling reaction using birnessite, one of the natural Mn oxides present in soil, was investigated in various experimental conditions (reaction time, Mn oxide loadings, pH). The removal efficiency of 1-naphthol by birnessite was high in all the experimental conditions, and UV-visible and mass spectrometric analyses on the supernatant after reaction confirmed that the reaction products were oligomers formed by oxidative-coupling reaction. Pseudo-first order rate constants, k , for the oxidative transformation of 1-naphthol by birnessite was derived from the kinetic experiments under various amounts of birnessite loadings, and using the observed pseudo-first order rate constants with respect to birnessite loadings, the surface area normalised specific rate constant, k_{surf} , was also determined to be 9.3×10^{-4} (L/m²·min) for 1-naphthol. In addition, the oxidative transformation of 1-naphthol was found to be dependent on solution pH, and the pseudo-first order rate constants were increased from 0.129 at pH 10 to 0.187 at pH 4.

Key words | birnessite, Mn oxide, 1-naphthol, oxidative-coupling reaction

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INTRODUCTION

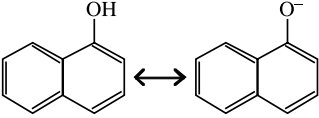
Polycyclic aromatic hydrocarbons (PAHs), aromatic compounds possessing more than two benzene rings, are known to distribute in watercourses, soil and atmosphere from various sources such as cigarette smoke, incomplete combustion of fossil fuel, oil refinery, chemical production, coal to heavy oil conversion process, and other various industries (WHO 1998). PAHs comprise from non-polar hydrophobic naphthalene, anthracene and pyrene to their polar ionic degradation derivatives with similar toxicity and enhanced mobility (Schwarzenbach *et al.* 1993). These compounds are generally categorised as major contaminants due to their toxicity even at low concentrations and carcinogenicity (US EPA 2003). Effective control measures for PAHs contaminated wastewater and soil have long been studied due to their high resistance to degradation and potential for bioaccumulation.

1-naphthol, one of the major degradation by-products of naphthalene, is discharged from dye, plastics for medical

purpose, synthetic rubber and asbestos industries, and is known to have toxicity similar to naphthalene (Stohs *et al.* 2002). In addition, due to the substituted hydroxyl group, its solubility is extremely high compared to naphthalene which, in turn, results in a high readiness of contamination to aquatic and soil environments by the enhanced mobility. Table 1 presents the chemical structure of 1-naphthol with several typical properties.

Metal (hydr)oxides and oxidoreductive enzymes can transform phenols and anilines to humic-like polymers via oxidative coupling reaction (Shindo & Huang 1982, 1984; Bollag 1992). In many cases, the transformed products are precipitated out from the aqueous phase due to the increased molecular weight, which makes it much easier to separate (Kang *et al.* 2004). Since oxidative coupling reaction is believed to be responsible for the formation of natural organic matters, i.e. humic substances, which can be considered as a natural detoxification process, the drastic

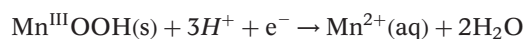
Table 1 | Selected physical and chemical properties of 1-naphthol

| 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 |

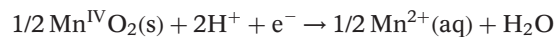
reduction of toxicity has also been confirmed by several research groups (Xu *et al.* 2005; Jung *et al.* 2007).

Like phenolic compounds, hydroxylated PAHs may be transformed through oxidative coupling reactions in the presence of enzymes or metal oxides. Aktas *et al.* (2001) performed kinetic examination of 1-naphthol transformation through oxidative coupling reactions in the presence of laccase, one of the oxidoreductive enzymes, suggesting the possibility of oxidative-coupling for the removal of hydroxylated PAHs. Most researches concerning oxidative coupling reaction, however, have focused mainly on the utilisation of enzymes, probably because of their significance in a natural detoxification process and carbon cycle. It is still uneconomic for mass production and for maintaining their activity during the period of storage and distribution. In addition, how to maintain their activity during application to expand the life-time of the enzymes is one of the main technical challenges.

On the other hand, Mn(III/IV) oxides, commonly present in soil particles, can act as oxidants due to their relatively high oxidising capacity as indicated below (Shindo & Huang 1982, 1984; Bollag *et al.* 1988, 1995; Kang *et al.* 2004, 2006).



$$E^0 = +1.50 \text{ V}$$



$$E^0 = +1.29 \text{ V}$$

The oxidation by Mn oxide is selective to phenolic and aniline compounds, and, as a result, these are well known abiotic mediators for oxidative coupling, which results in the formation of humic substances in the natural environment (Bollag *et al.* 1995; Sparks 1995). Shindo & Huang (1982) tested 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.

In this study, we investigated the oxidative coupling reaction of 1-naphthol using birnessite ($\delta\text{-MnO}_2$), one of the common Mn oxides found in natural soil. To investigate kinetic characteristics of the reaction by birnessite, transformation efficiencies with respect to time were evaluated. The effects on the birnessite loadings and pH were also examined. The polymerised reaction products were analysed using mass spectrometry and UV-visible spectrometry to confirm that the removal was caused by oxidative polymerisation. The results of this study may contribute to a better understanding on the reaction by Mn oxide, especially as a noble method of PAHs removal, and provide basic information for further development to actual application.

METHOD AND MATERIALS

Materials

1-naphthol (1-NP) was obtained in high purity (>99%) from Sigma-Aldrich (St Louis, MO) and was used as received without further purification. Birnessite was prepared by boiling potassium permanganate in hydrochloric acid, as described by McKenzie (1971). The resulting oxide particles were filtered and repeatedly washed with deionised water to ensure the removal of excess reagents, then freeze-dried. FT/IR spectrum of the birnessite showed characteristic peaks at 930, 1,630, and 3,450 cm^{-1} , which matched those reported in the literature (McBride 1989a). As determined using a Micromeritics surface area analyser (Model ASAP 2010, Norcross, GA), the BET surface area of the prepared birnessite was 44.37 m^2/g .

Batch experiments

Individual transformation experiments were performed in sealed batch systems prepared in 20-ml serum bottles.

The serum bottles were filled with 20 ml of 1-NP standard solutions (40 mg/l), to which was added a certain amount of birnessite (12.5–50 mg), and then crimp-sealed using teflon-lined rubber septa. Each bottle prepared was wrapped with aluminium foil to prevent exposure to light, and loaded on an end-over-end rotary shaker at 30 rpm in $20 \pm 3^\circ\text{C}$. Reduction of 1-NP concentration was determined by periodic sampling of 500- μl reaction solution for immediate analysis by HPLC.

In order to evaluate the effect of solution pH on the transformation, the same experimental setup using 20-mL serum bottle with 20 ml 1-NP standard solutions (30 mg/l) and 25 mg of birnessite was employed as described above. Initial pH was adjusted to 4, 7, and 10 with 0.1 N HCl or NaOH. Samples were taken from the bottles and remaining 1-NP concentrations were analysed with HPLC with respect to time.

All the experiments were performed in triplicate, and the data represented in this manuscript are average values.

Analyses

The concentrations of remaining 1-NP were determined by a Shimadzu HPLC system (Tokyo, Japan) with UV absorbance detector operated at 254 nm, using a Waters C18 4.6×150 mm (5- μm particle size) reverse-phase column (Milford, MA). The mobile phase 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 which confirmed in preliminary tests that the loss by adsorption to membrane was minimal (<0.02%). Twenty microlitres of filtered sample was injected to HPLC for quantification.

In order to confirm the reduction of 1-NP concentrations caused by oxidative coupling by birnessite, UV-visible spectrometric and LC/MS analyses were performed for the reaction solutions with time. UV-visible absorption spectra were recorded on a Shimadzu UV-1601 system using 10 mm quartz cell for the wavelength range between 200 and 800 nm. Mass spectrometric analysis was carried out on an LCQ DECA XP mass spectrometer (Thermo-Electron Inc., Woburn, MA) with an electrospray interface used in the negative ion mode. The samples were run on a Shiseido HPLC system (Nanospace SI-2, Japan) using

a Luna[®] C18 1.0×250 mm (5- μm particle size) column (Phenomenex Inc., Torrance, CA). The mobile phase was 5% (A) and 95% (B) acetonitrile with gradient mode (A: B = 100: 0 (5') ~ 0: 100 (40')).

RESULTS AND DISCUSSION

Oxidative-coupling reaction of 1-naphthol by Mn oxide

In order to investigate the transformation of 1-NP by birnessite, samples from the reaction solutions (containing 25 mg of birnessite in 20 ml of 1-NP standard with pH 5.0) were taken for HPLC analysis, and Figure 1 shows the chromatograms with respect to time. As indicated in the chromatograms, the peak intensity of 1-NP shown at retention time of about 4.98 min was decreased with time and finally almost disappeared after 40 min of reaction. On the other hand, at the retention time of 1.02 min, peaks by reaction products were increased as 1-NP peaks reduced. In addition, at retention time of 2.92 and 4.08 min new peaks were observed, which may have been generated from reaction products of 1-NP transformation. However, a certain trend of the increase or reduction of these peaks was not found, since these peaks were probably generated from intermediates of the transformation or from reaction products that also were involved in further transformation by birnessite.

In order to confirm that the reaction products identified from HPLC analysis were oligomeric products of 1-NP formed by oxidative coupling reaction, reaction solutions

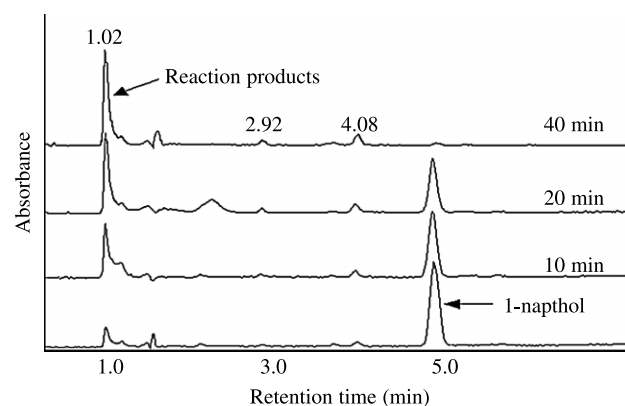


Figure 1 | HPLC chromatograms of 1-naphthol and its reaction products by birnessite with time.

were scanned with UV-visible spectrometer with respect to time, and the results are shown in Figure 2. For comparison, UV-visible absorption spectrum of 1-NP standard solution (40 mg/L, pH 5.0) is also shown. In the spectrum of 1-NP standard, the absorbance maximum (λ_{\max}) at 295 nm was found which was caused by the primary absorption band (E_2 -band) of benzene ring of 1-NP molecule (Silverstein & Webster 1997; Karthikeyan & Chorover 2000). This absorbance maximum, as shown in the figure, was reduced as 1-NP transformed, while the absorbance around the wavelength region of 450–600 nm was increased. This increase in absorption maximum in the wavelength region indicates the production of reaction products possessing absorption characteristics of the visible wavelength region. Although reduced Mn(II) may cause the increase in absorption maximum in the wavelength region, it was confirmed by experimental evaluation that Mn(II) present in the reaction solution (<0.02 mg/L) has a negligible effect on the absorption characteristics. This increase in absorption in the visible wavelength region is a phenomenon representing the red shift of absorption band caused by benzene rings connected via conjugated bonding (Silverstein & Webster 1997), which provides the evidence of oligomers formation by birnessite-mediated oxidative coupling reaction.

This transformation of 1-NP to oligomers may be quantitatively explained, as shown in Figure 3. In the figure, absorbance ratios at 295 nm and 525 nm (A_{525}/A_{295}), absorbance maxima of 1-NP and reaction products, respectively, are correlated with the reaction time. As shown in

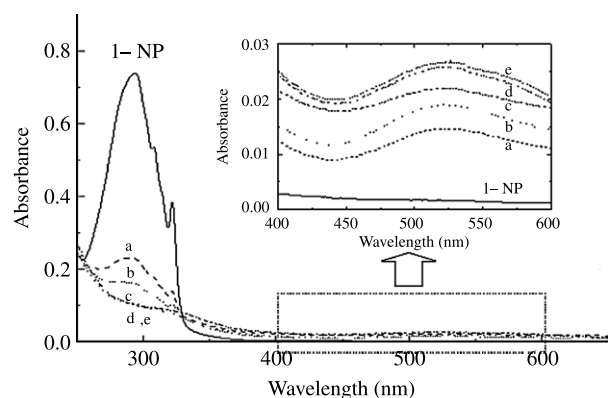


Figure 2 | UV-visible absorption spectra of 1-naphthol and its reaction products by birnessite with time elapsed (a) 5 min, (b) 10 min, (c) 20 min, (d) 40 min, (e) 50 min.

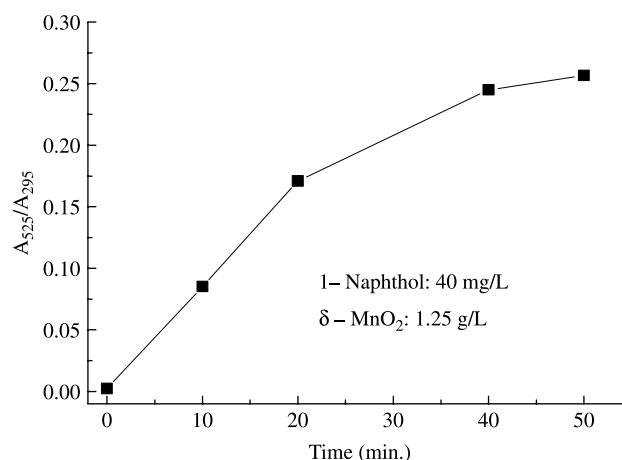


Figure 3 | UV-visible absorption ratios (A_{525}/A_{295}) for 1-naphthol and its reaction products by birnessite with respect to reaction times.

Figure 3, the absorption ratio of 1-NP standard is 0.002, and, upon reaction, it increased to about 0.25 after 50 min, which corresponds to about two orders of increase. In addition, the increase in the ratio was linear during the initial phase of the reaction, while the rate decreased afterwards, which represents typical monodic surface reaction characteristics. Shindo & Haung (1982), in their experiments of polyphenols transformation using Mn oxide, also observed this “browning effect” of the reaction solution, and suggested it was one of the major processes generating humic substances in the natural environment.

Based on the results obtained from UV-visible spectroscopic analysis, LC/MS analysis of the reaction products were performed in order to evaluate the degree of coupling (polymerisation). After 50 min of reaction, hydrophilic fraction of the reaction products was extracted using CH_2Cl_2 and separation funnel and this was used for the mass spectro-metric analysis. For the hydrophilic fraction, HPLC analysis was also performed, which confirmed that it corresponded to the peak of 1.02 min retention time shown in Figure 1. As shown in Figure 4, the molecular weight of the hydrophilic oligomers were distributed from 100 to 1,000 m/z with several prominent peaks at 497.2, 565.1, and 723.3 m/z, which may correspond to oligomers of more than three molecules of 1-NP. In their experiments using horseradish peroxidase (HRP), Xu *et al.* (2005) also reported that the average molecular weight of soluble oligomers of 1-NP was 400–600 m/z, which corresponds to naphthol trimer and tetramer, while those of oligomeric

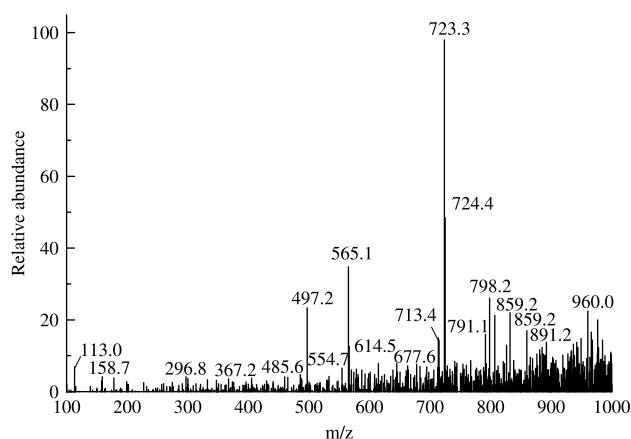


Figure 4 | LC/MS spectrum of reaction products formed.

precipitates was 853 Da, which corresponds to naphthol hexamer. However, soluble reaction products with higher molecular weight were produced in the reaction with birnessite, and the discrepancy with HRP may have been caused by several side reactions occurring by birnessite such as partial ring cleavage (Majcher *et al.* 2000) and removal of substituents (Dec *et al.* 2003).

Generally, oligomeric products produced from oxidative coupling form precipitates as molecular weight increases (McBride 1989b; Majcher *et al.* 2000). In the oxidative transformation of 1-NP by birnessite, the TOC concentration of the reaction solution decreased to approximately 50% after 24 h of reaction, which again indicates that approximately 50% of oligomers were precipitated out of the solution.

Reaction kinetics with respect to Mn oxide loadings

In order to investigate the reaction kinetics of oxidative transformation of 1-NP by birnessite, the transformation

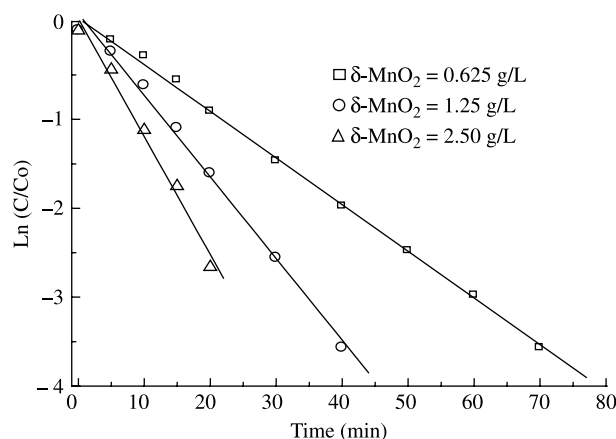


Figure 5 | Pseudo-first order disappearance of 1-NP at different birnessite loadings (conditions: 40 mg/l 1-naphthol, 20°C and pH 5.0).

rate with time was determined at various birnessite loadings. As shown in Figure 5, the transformation rate was increased with increased birnessite loading. With 0.625 g/L of birnessite loading, approximately 90 min of reaction time was required for 99% of transformation, while with increased birnessite loading to 2.5 g/L, 30 min was required for the same degree of transformation. Figure 5 also shows that the transformation follows pseudo-first order kinetics with an r^2 value of 0.993–0.999. In Table 2, the rate constants, k , are summarised with half-life times with respect to birnessite loading. As birnessite loading was increased four times from 0.625 to 2.5 g/L, the rate constants increased approximately 2.5 times from 0.0525 to 0.133 min^{-1} , and the half-life was decreased from 13.2 min to 5.3 min.

Since the transformation occurs on the surface of birnessite, the quantity of available birnessite surface area may be a more important variable on the reaction kinetics

Table 2 | Summary of kinetic constants and half-lives for the oxidative transformation of 1-NP by birnessite

| Birnessite | 1-naphthol (40 mg/L) | | | 1-naphthol (30 mg/L) ^a | | |
|--|----------------------|----------------------|---------|-----------------------------------|--------|---------|
| | 0.625 g/L | 1.25 g/L | 2.5 g/L | pH = 4 | pH = 7 | pH = 10 |
| k (min^{-1}) | 0.0525 | 0.0917 | 0.133 | 0.182 | 0.157 | 0.129 |
| r^2 | 0.999 | 0.996 | 0.993 | 0.999 | 0.999 | 0.998 |
| $t_{1/2}$ (min) | 13.20 | 7.35 | 5.30 | 9.81 | 4.41 | 5.37 |
| $k_{\text{surf}}^{\dagger}$ ($\text{L}/\text{m}^2\cdot\text{min}$) | | 9.3×10^{-4} | | | – | |

^aAmounts of Birnessite added is 1.25 g/L.

[†]Normalized to birnessite surface area of 44.37 m^2/g .

than birnessite mass is, and, therefore, more meaningful interpretation of the kinetic data can be performed by normalising the observed rate constants to birnessite surface area (Agrawal & Tratnyek 1996). As shown in Figure 6, linear correlation of observed rate constants versus birnessite surface area was obtained ($r^2 = 0.984$), assuming a constant specific surface area of $44.37 \text{ m}^2/\text{g}$, and the slope of the correlation is the specific rate constant, k_{surf} ($\text{L}/\text{m}^2\cdot\text{min}$), where rate constants obtained for each substrate are normalised to $1 \text{ m}^2/\text{L}$ birnessite (Table 2). This surface area-normalised rate constant is a variable independent on birnessite loadings, and, therefore, provides more generalised information for the quantitative evaluation of the reactivity of a certain substrate.

Reaction kinetics with respect to pH

pH is an important reaction variable determining the surface charge of birnessite as well as the degree of protonation of 1-NP. According to the reaction model of oxidative coupling, it is assumed that the reaction is initiated by the surface complexation of hydroxyl group of a reactant to manganese atom on the oxide surface (Stone & Morgan 1984; McBride 1987), which is affected by $\text{p}K_{\text{a}}$ value of the reactant, surface charge of Mn oxide, and solution pH (McBride 1989b). To evaluate the effect of solution pH, a series of batch experiments were performed at different solution pH of 4, 7 and 10, and the results are presented in Figure 7. The pseudo-first order rate constants obtained are also

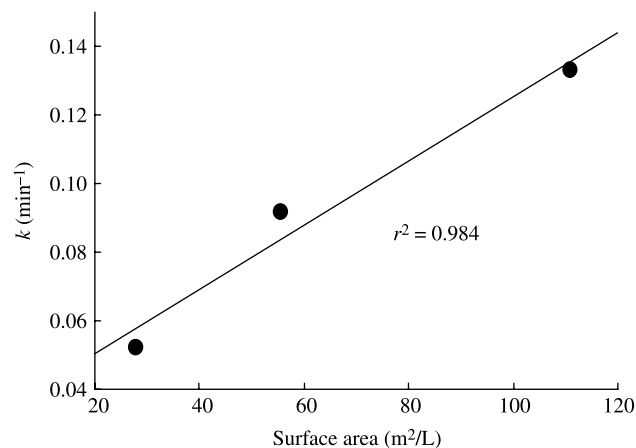


Figure 6 | Effect of birnessite surface area concentration on the pseudo-first order rate constants for the oxidative transformation of 1-naphthol.

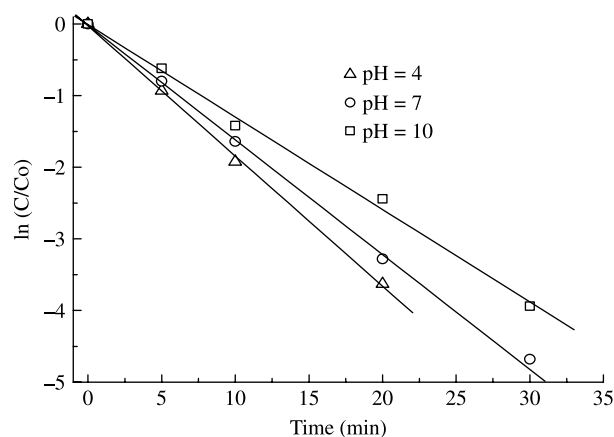


Figure 7 | Pseudo-first order disappearance of 1-naphthol at different pH (experimental conditions: 30 mg/l 1-naphthol, 1.25 g/l birnessite loading at 20°C).

summarised in Table 2 with corresponding half-lives. The rate constant was decreased as pH increased from 0.182 min^{-1} at pH 4 to 0.129 min^{-1} at pH 10, which shows that lower solution pH is more favourable for the transformation. By considering that the $\text{p}K_{\text{a}}$ value of 1-NP is 9.34 and point of zero charge (PZC) of birnessite is known to be 2.4–2.7 (Shindo & Huang 1984), this effect of pH can be anticipated. At pH conditions employed in the experiments (4–10), the surface of birnessite is negatively charged while the amount of negatively charged ions of 1-NP is increased as pH is increased. Therefore, the physical contact between the reactants is inhibited by electrostatic repulsion as pH increases, which, in turn, results in a reduced reaction rate. This result is typical in the reaction of metal oxide possessing

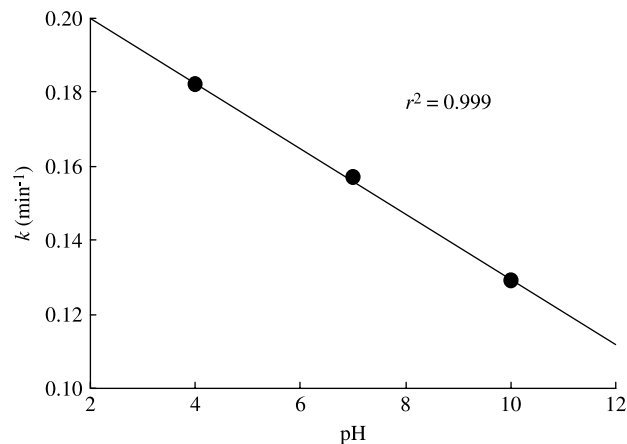


Figure 8 | Effect of pH on the pseudo-first order rate constants for the oxidative transformation of 1-naphthol by birnessite.

a low PZC value with weak acidic organic compounds (Odziemkowski & Gillham 1997).

For quantitative interpretation of the effect of solution pH on the reaction rate, the rate constants were correlated with pH as shown in Figure 8. As shown in the figure, a high linear relationship between rate constant and pH was observed ($r^2 = 0.999$), and this may provide basic information on the design of reaction condition for proper reaction time.

CONCLUSIONS

Manganese oxides are known to play an important role in the formation of humic substances in the natural environment through oxidative coupling reaction of phenolic compounds. In this study, we evaluated the potential of Mn oxide for the transformation (and eventually removal) of 1-naphthol, a typical PAHs degradation derivative, and provide basic information for a novel solution for PAHs treatment from wastewater.

Most removal processes for organic contaminants mainly depend on degradation methodology, while there are two contrary transformation pathways in natural carbon cycle: degradation, a fractionation process of large natural macromolecules into smaller and more labile molecules, and humification, a chemical aggregation process of small molecules to form macromolecules, mainly via oxidative coupling reaction. Especially for aromatic compounds, removal by degradation may be very inefficient mainly due to their high structural stability and, therefore, a high resistance to degradation. As a promising alternative for those contaminants, humification through oxidative coupling can be more effective and cost-competitive. In many cases, the transformation products form precipitates due to increased molecular weight, which significantly eases the separation from the aqueous phase. In addition, toxicity of the polymerised products is drastically reduced, as confirmed by various studies (Bollag *et al.* 1988; Xu *et al.* 2005; Jung *et al.* 2007), since humification itself is a natural detoxification and stabilisation process.

Of the mediators catalysing the oxidative coupling reaction, Mn oxide is the more economic and environmentally friendly candidate, since it can be obtained easily from Mn oxide-rich ores. We are currently working on the

hydroxylation of PAHs through partial degradation as a pre-treatment method. In addition, studies to enhance the applicability of Mn oxide in actual processes are also underway using natural Mn oxide.

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