Journal of Environmental Science and Health, Part A
Toxic/Hazardous Substances and Environmental Engineering

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Online Publication Date: 01 January 2008
To link to this article: DOI: 10.1080/10934520701792746
URL: http://dx.doi.org/10.1080/10934520701792746

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Detoxification of phenol through bound residue formation by birnessite in soil: Transformation kinetics and toxicity

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Oxidative coupling reaction of phenol mediated by birnessite was studied in aqueous phase and soil. Phenol was readily transformed by birnessite and almost all phenol disappeared in both samples after 24 hours of reaction. Phenol transformation kinetics was investigated by plotting reaction time against logarithm concentrations of residual phenol, revealing that exponential decrease of phenol was evident both in aqueous phase and soil, and maximum removal rates were 2.31–2.54 times higher in the presence of soil. Reaction products of phenol were identified by LC-MS and capillary electrophoresis. In aqueous phase, polyphenols were formed by self-coupling reaction of phenoxy radicals whereas phenol was found to be present as bound residues in soil, probably due to the cross-coupling reaction between the radicals and soil organic matter. Microtox System was employed to determine the toxicity after birnessite treatment, and the toxicity of phenol-spiked solution and soil samples decreased remarkably compared to that of phenol solution before treatment.

Keywords: Oxidative coupling, birnessite, phenol, bound residues, toxicity.

Introduction

Organic pollutants released into the soil environment can be either degraded, whether biologically or chemically, or incorporated into soil organic matter to form bound residues.[1] The formation of bound residues is a process of humification through an exothermic reaction named chemisorption. Since bound residues have different chemical structures from their parent molecules and are considered as a part of organic matter their biological and chemical availabilities decrease and thus their toxicity is also altered to a significant extent.[2–13] For this reason, studies have been conducted to make bound residues from soil pollutants as a remediation technology.[4,14]

Bound residues are formed by oxidative coupling reaction, and the reaction is catalyzed by oxidoreductive enzymes, and so far, most studies have concentrated on using enzymes such as peroxidase and laccase as catalysts.[2,3,6,8,10,11,15,16] Metal oxides are also known to have such catalytic activity. Unlike enzymes, they are stable and abundant in the nature, and reactions mediated by oxides do not require oxygen and/or peroxides as electron acceptors because metal oxides themselves act as electron acceptors as well as oxidation catalysts.[17–19] Birnessite (δ-MnO2), a special form of manganese oxide, has large a redox potential and is known to be involved in the formation of humic substances in soil.[20,21]

In this study, phenol was treated with birnessite in the absence and presence of soil, and transformation kinetic constants were derived. Moreover, the formation of phenolic polymers in aqueous phase from self-coupling reaction and phenolic bound residues in soil as a result of cross-coupling were identified. The toxicity expressed by the reaction products was also determined. Kang et al.[22] conducted a similar study with a fungicide cyprodinil, but the experiments were performed in aqueous phase containing humic acids.

Other reports[3,7,9,11,16] are also available with phenol in soil, but they used enzymes for initiating the oxidative coupling reaction. Selig et al.[13] studied the reaction between hydroxylated aromatics and birnessite, but they concentrated on sorption/desorption behavior and extractability. This work clearly shows the formation of phenol bound residues by birnessite and consequent decrease in toxicity in soil.
Materials and methods

Soil sample and birnessite preparation

A soil sample was collected from a pristine area in Seoul National University (Seoul, Korea), and air-dried, passed through a 2-mm sieve and stored for further use. The texture of the soil is clay, consisting of 26.1% sand, 27.4% silt, and 46.5% clay. It has 43.3 cmol/kg of cation exchange capacity and 13.2% of organic carbon. The pH of the soil-water suspension (1:1) is 6.1.

Birnessite was prepared by boiling potassium permananganate in hydrochloric acid as described by McKenzie [23]. The resulting oxide particles were filtered and repeatedly washed with deionized water, and freeze-dried until used. X-ray diffraction (XRD; DIP 2030, MAC Science, Japan) analysis showed that layer spacing was about 7.1 Å, which was well-matched with previously reported values [24,25]. The surface area was also determined to be 40.0 m²/g by BET analysis (ASAP 2010, Micromeritics, USA).

Birnessite treatment of phenol

To investigate the transformation of phenol by birnessite in aqueous phase, 50-mL Teflon centrifuge tubes were filled with 20 mL of phenol solution containing 1, 2, 3, or 4 mg phenol/mL dH₂O (deionized water) and 1 g birnessite (i.e., 50 mg/mL). The tubes were well-mixed on a horizontal shaker (i.e., 200 rpm) for 24 hr at an ambient temperature, and centrifuged at 15,000 g for 20 min.

The supernatant of each tube was transferred to a 2-mL vial for phenol determination and the remaining solution was saved for further analyses. The same experiment was performed in the presence of soil. Ten-gram portions of soil sample were added to 50-mL Teflon centrifuge tubes, and the tubes were provided 20 mL of phenol solution containing 1, 2, 3, or 4 mg phenol/mL dH₂O (i.e., 2, 4, 6, 8 mg phenol/g soil) and 1 g birnessite (i.e., 100 mg/g soil). The tubes were well-mixed on a horizontal shaker (i.e., 200 rpm) for 24 hr at an ambient temperature, and centrifuged at 15,000 g for 20 min. The supernatant of each tube was transferred to a 2-mL vial for HPLC determination and the resulting solid was saved for further extraction.

Extraction of phenol

After 24-hr birnessite reaction in the presence of soil, solvent extraction was performed to determine the concentration of phenol remaining in soil. Twenty milliliters of methanol was added to supernatant-removed soil solid in a 50-mL Teflon tube, and the methanol-soil mixture was shaken vigorously on a horizontal shaker for 24 hr at an ambient temperature. The tube was then centrifuged at 15,000 g for 20 min, and the supernatant was transferred to a 2-mL vial for phenol determination. The remaining solid was further extracted by One PSE (Applied Separations, USA) compliant with EPA Method 3545 (i.e., Pressurized Fluid Extraction), but additional phenol was not detected.

Analytical methods

The concentration of phenol dissolved in extracting solution (i.e., methanol) was determined by HPLC equipped with an auto sampler (Waters Alliance System, 2690 Separation Module, USA). Reverse-phase C-18 column (Waters PAH Column, 5 µm, 4.6 × 250 mm) and Waters 996 Photodiode Array Detector were employed. Injection volume was 20 L, column temperature was 27°C, and detection wavelength was 254 nm. Mobile phase was water/acetonitrile (50/50) with a flow rate of 0.5 mL/min. All samples were filtered through 0.45 m GHP filter before analyses.

Fig. 1. Disappearance of phenol by birnessite treatment (a) in aqueous phase and (b) in soil (Reaction mixture: 20 mL of phenol solution +10 g of soil +1 g of birnessite).
Phenol detoxification by birnessite in soil

The resulting products of oxidative coupling reaction such as phenol polymers and phenolic bound residues were determined by LC-MS (QUATTRO LC Triple Quadrupole Tandem Mass Spectrometer, Micromass, UK) and capillary electrophoresis (HP-3D Capillary Electrophoresis, Hewlett Packard, USA). The analysis conditions for capillary electrophoresis were adapted from Huang and Weber. [9]

Toxicity test
As a measure of bioavailability of birnessite-treated products, the toxicities of phenolic polymers in solution phase and phenolic residues bound to humic substances were determined by using Microtox System (Azur Environmental, USA). Acute toxicity was evaluated according to ASTM Extended (9 dilution) Basic Test Method as suggested by the manufacturer. Each aqueous sample was diluted to nine steps, and the dilution ratio for each step was 50%.

Results and discussion

Transformation kinetics of phenol

Phenol transformation was very fast in aqueous phase by birnessite treatment (Fig. 1a). After 2 hours of reaction, almost all phenol disappeared in solutions containing 1, 2, and 3 g phenol/L and about 80% of initial phenol was removed in the solution with 4 g phenol/L. The same trend was also found in soil (Fig. 1b). The relative

Fig. 2. Phenol transformation kinetics by birnessite (a) exponential fit in aqueous phase, (b) double exponential fit in aqueous phase, (c) exponential fit in soil, and (d) double exponential fit in soil.
Table 1. Analysis of phenol transformation kinetics in the absence and presence of soil

<table>
<thead>
<tr>
<th>Initial amount of phenol (mg)*</th>
<th>Aqueous phase</th>
<th></th>
<th>Soil suspension</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exponential fit</td>
<td>Double exponential fit</td>
<td>Exponential fit</td>
<td>Double exponential fit</td>
</tr>
<tr>
<td></td>
<td>Maximum removal rate</td>
<td>$R^2$</td>
<td>Maximum removal rate</td>
<td>$R^2$</td>
</tr>
<tr>
<td>200</td>
<td>0.027</td>
<td>0.81</td>
<td>0.067</td>
<td>0.96</td>
</tr>
<tr>
<td>400</td>
<td>0.029</td>
<td>0.92</td>
<td>0.053</td>
<td>0.99</td>
</tr>
<tr>
<td>600</td>
<td>0.024</td>
<td>0.89</td>
<td>0.044</td>
<td>0.99</td>
</tr>
<tr>
<td>800</td>
<td>0.020</td>
<td>0.81</td>
<td>0.040</td>
<td>0.99</td>
</tr>
</tbody>
</table>

*Phenol concentration: aqueous phase 1, 2, 3, 4 g/L dH$_2$O; soil suspension 20, 40, 60, 80 mg/g soil.

values of residual phenol to initial phenol concentrations were transformed into logarithm scale (i.e., ln(C/C$_0$)) and plotted against reaction time, and the relationships were regressed using exponential and double exponential functions (Fig. 2).

Exponential regression did not adequately describe the time-dependent trend of phenol transformation, but double exponential fit did. In addition, double exponential decrease of phenol was more evident in the presence of soil rather than in the absence of soil (Table 1). The transformation rates decreased with an increase in phenol concentration for the aqueous phase as well as the soil systems.

Phenol transformation by birnessite is surface-catalyzed reaction and the active sites on birnessite surface can be saturated, which might have resulted in the declined reactivity

Fig. 3. LC-MS chromatograms of the supernatants of (a) phenol-containing aqueous phase and (b) in phenol-spiked soil after birnessite treatment.
in response to the increase in phenol concentration. A similar relationship between rate constant and reactant’s concentration was also reported when pentachlorophenol was oxidized with manganese dioxide.\[^{26}\] Interestingly, phenol was more rapidly removed when soil was present.

Within the phenol concentrations tested, 2.25- to 2.54-folds increase of maximum rate was observed. The reason can be attributed to the presence of soil organic matter. In the absence of soil, only self-coupling reaction between phenoxy radicals occurred, but when soil was present, cross-coupling reaction between phenoxy radicals and soil organic matter was also possible,\[^{9}\] which generated phenolic bound residues.

**Identification of bound residue formation**

Reaction products of phenol by birnessite were analyzed by LC-MS. When soil was not present self-coupling reaction predominated and thus phenol molecules were polymerized into dimers (m/z value 184.78) and tetramers (m/z value 370.62) as shown in Figure 3 a. In the presence of soil, phenol polymers were not evident (Fig. 3b), indicating that self-coupling was not the major reaction. Although various reaction products from different peroxidase enzyme systems for a given phenolic pollutant are identified the reason is not yet clear.

For example, chloroperoxidase and lignin peroxidase tend to generate more reaction products than does horseradish peroxidase for some phenolics.\[^{27}\] Moreover, few or no study exists identifying the reaction products from birnessite. Our data show that the number and intensity of peaks decreased remarkably in the presence of soil, which suggests that reaction products were removed from aqueous phase and probably bound to soil organic matter through cross-coupling reaction.

In an attempt to identify the formation of bound residues of phenol, the dissolved organic matter was analyzed before and after birnessite treatments by capillary electrophoresis. Capillary electrophoresis separates dissolved electrolytes, and their migration patterns through the capillary column depend on their respective charge-to-mass ratio.\[^{8}\]

All electrolytes present as neutral forms move together along the electrophoresis column at the rate of electroosmotic flow (EOF), and anionic components move...
Table 2. Acute toxicities of phenol-spiked soil and aqueous samples after birnessite treatment

<table>
<thead>
<tr>
<th>Descriptions</th>
<th>Aqueous sample</th>
<th>Soil sample</th>
<th>Phenol solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference EC$_{20}$ value experimentally determined (mg/L)</td>
<td>NA$^*$</td>
<td>NA$^*$</td>
<td>8.43</td>
</tr>
<tr>
<td>Dilution factor to achieve reference EC$_{20}$ value</td>
<td>10.11</td>
<td>3.64</td>
<td>NA$^*$</td>
</tr>
<tr>
<td>Hypothetical phenol concentration calculated from dilution factor and reference EC$_{20}$ value (mg/L)</td>
<td>85.25</td>
<td>30.67</td>
<td>NA$^*$</td>
</tr>
<tr>
<td>Actual phenol concentration experimentally determined (mg/L)</td>
<td>ND$^{**}$</td>
<td>ND$^{**}$</td>
<td>1,714$^{***}$</td>
</tr>
</tbody>
</table>

$^*$Not applicable. $^{**}$Not detected. $^{***}$Initial concentration of phenol.

more slowly than the neutral forms due to retardation. As shown in Figure 4, the electropherogram after reaction was very similar to the graph before reaction but magnified in scale, which reflects the binding of ionized phenolic compounds (i.e., phenoxy radicals) to organic matter.

**Toxicity of phenolic bound residues**

To investigate the toxicity of phenolic bound residues, EC$_{20}$ values of birnessite-treated aqueous and soil samples which had been spiked with phenol were determined by Microtox System, and the results were compared (Table 2). To obtain the reference EC$_{20}$ of 8.43 mg/L, the solution with an initial phenol concentration of 1,714 mg/L had to be diluted 10.11-fold. Moreover, the soil sample after birnessite treatment was less toxic than the aqueous sample, requiring only a 3.64-fold dilution. This demonstrates that birnessite treatment is responsible for toxicity reduction and moreover, the treatment is more efficient in the presence of soil.

Assuming that only phenol molecules resulted in toxicity in the samples after birnessite treatment, residual phenol concentration can be calculated from dilution factor and reference EC$_{20}$ value as described by Huang and Weber.[8] As shown in Table 2, calculated phenol concentrations were 85.25 and 30.67 mg/L in aqueous phase and in soil, respectively. However, phenol was not detected by HPLC analysis in the 2 samples. This discrepancy may indicate that reaction products other than phenol were responsible for the toxicity.

Indeed, in aqueous phase not containing organic matter, phenoxy radicals generated by the birnessite treatment formed polyphenols as well as other unidentified intermediates as demonstrated by LC-MS chromatograms (Fig. 3). Polyphenols may be a plausible candidate responsible for the toxicity, but other unidentified products shown in chromatograms may also be possible. It is also worthwhile to note that catalytic reaction products sometimes are more toxic than the parent compound.[28,29] However, the production of more toxic intermediates was not evident in our system using birnessite.

**Conclusion**

Phenol was more rapidly removed by birnessite in the presence of soil rather than in aqueous phase, probably due to cross-coupling reaction between phenoxy radicals and soil organic matter. The formation of bound residues of the reaction products was determined by capillary electrophoresis analysis. After birnessite treatment, phenol was detected in neither aqueous phase nor soil and in addition, the toxicities of phenol-spiked solution and soil also decreased remarkably. Based on this study, a means to remove polycyclic aromatic hydrocarbons by birnessite through the formation of bound residues is under development as a potential remediation technology.

**Acknowledgments**

This research was mainly sponsored by Seoul R&BD Program (No. 10676). Additional financial supports were provided by the KOSEF through the AEBRC at POSTECH and by the Basic Research Program of the Korea Science & Engineering Foundation (Grant No. R01-2006-000-10136-0). The authors thank the Research Institute of Engineering Science at Seoul National University for technical assistance and the SNU SIR BK21 research Program funded by Ministry of Education & Human Resources Development.
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