



Dioxygen in combination with hydrazine: A practical system for degradation of a broad spectrum of toxic organics in water

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ABSTRACT

Green and cost-effective eradication of pollutants from water is an important and long-standing goal in environmental chemistry. A broad spectrum of toxic organics in water was efficiently destroyed in the presence of dioxygen in combination with hydrazine hydrate at 150 °C. Under this operating condition, two typical classes of toxic organic chemicals, phenols and nitrobenzene derivatives were totally destroyed. The mineralization rate of these organics was 35–86%. Furthermore, when this degradation system was applied to degradation of actual waste water of wood pulp bleaching with chlorine (COD: 1830 mg/L), 77% COD decrease and 52% TOC mineralization of the wastewater were observed. In each case, the major degradation products are small molecular compounds, such as methanol, formic acid and acetic acid except CO/CO₂. In the case of chlorophenols degradation, no dioxins and any other toxic compounds are detected by ¹H NMR. After degradation reaction, the hydrazine was also decomposed into N₂ and H₂O, and no remaining hydrazine is found.

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1. Introduction

Nowadays, enormous numbers of chemicals are used in industry, farming, and home, and a lot of them are finally released into water systems deliberately or inadvertently. Consequently, a variety of toxic organics in water constitutes an important environmental hazard [1,2]. Eradication of these pollutants from water is of worldwide concern. However, progress in this field is hindered by the inadequacy of available approaches for degradation and/or detoxification of them in water, especially when the organics are present in water at low concentration and as components of complex mixtures [1,3].

Biological methods have been commonly employed for the treatment of organics in water [4,5]. However, many toxic organics are xenobiotic toward enzymes, especially for the enzymes with low specificities [3,6,7]. Several chemical methods for degradation of the organics in water have been studied extensively [8–12]. Fenton oxidations have been widely used for their advantages of broad substrate applicability [13,14]. However, these oxidation processes usually utilize a large excess of iron salts under strong acidic conditions resulting in generate a large amount

of the iron-containing sludge, which lead to the proliferation of algae [15]. Up to now, wet air oxidation (WAO) is considered as one of the cleanest and efficient techniques for treatment of the pollutants in water, but its severe operating conditions, such as high temperature (200–320 °C) and pressure (2–20 MPa) lead to the high capital costs and safety implications [16,17]. To reduce the harsh process conditions, catalytic wet oxidation (CWO) is emerging as a versatile strategy to degrade the pollutants [18–22]. However, CWO has its own inherent disadvantages. Under homogeneous conditions, CWO usually requires a separation step to remove the toxic metals from the final effluent. For heterogeneous catalytic system, deactivation of the catalysts is a recurring problem due to sintering, poisoning or fouling. Moreover, metal catalysts may be dissolved into the liquid phase under hot acidic conditions, which is potentially toxic to the environment. TiO₂-catalyzed photo-oxidation has been actively explored recently, but this technique has met with a limited degree of success with regard to efficiency, economy, and industrial viability [23–26]. Very recently, metal complexes of macrocyclic ligands in conjunction with H₂O₂ have been employed to destroy toxic organics in waters. These degradation systems have many impressive advantages such as high catalytic efficiency and mild reaction conditions [27–31], but its catalysts preparation is difficult, and the probable necessity of a buffered solution in the degradation system (containing inorganic salts) also required. Sen et al. have reported the combination of O₂ and Pd for deep oxidation degradation of a

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broad range of functional organics in aquatic medium in the presence of molecular hydrogen or carbon monoxide, but the system required expensive metal Pd as the catalyst [32]. On the other hand, nitro-containing organics remained recalcitrant substrates toward most oxidative degradation systems. For example, nitrobenzene compounds were generally accepted believed to be persistent pollutants because of the strong electro-withdrawing properties of nitro group leading to the strong chemical stability of aromatic ring. Thus decades efforts aimed at the treatment of nitro aromatic compounds have met with a limited degree of success. Protocols to efficiently degrade nitro aromatic compounds are still scarce. Only recently have a few examples involving degradation of nitrobenzene compounds with ozone and Fenton reaction been reported [33–36]. None of the degradation systems mentioned here have been shown to degrade nitrobenzene compounds in water with O_2 .

To the best of our knowledge, an ideal degradation procedure should meet the following criteria: first, the process should be economical, namely, only using inexpensive and readily available oxidants and catalysts. Second, the degradation system should be competent for destroying a broad spectrum of toxic organics with a variety of functional groups, as well as these organics present at low concentration, and as components of complex mixtures. As such, one key criterion to the process is the operation should not introduce any substances into the water, i.e., total non-use of metals, organic solvents and buffering solvents as well as any others that may cause harmful components to the environment. Thereby, the process dispenses with the need for second treatment for them. Herein we reported our preliminary results toward achieving these goals.

Recently we have reported a highly efficient system for degradation of trichlorophenol in water using sodium nitrite/dioxygen [37]. The degradation system met with success in high removal efficiency of trichlorophenol and its simple economical degradation process. Knowing that trichlorophenol is one of important by-products of wood pulp bleaching with chlorine, we attempted to apply the same degradation system to treat the wastewater of wood pulp bleaching. Unfortunately, the attempts were frustrated because of the formation of nitration products during the wastewater treatment. Definitely, it is necessary to develop another innovative degradation system that could remove a wide range of organics from water including the pollutants in the wastewater of wood pulp bleaching. Such a degradation system may be achieved while we realized that hydrazine in combination with dioxygen could produce hydrogen peroxide under a certain conditions [38–40]. We reasoned that the active oxidative species for substrate destruction might be produced *in situ* while hydrazine reacted with dioxygen. In this paper, we describe the discovery and development of a highly efficient process for degradation of a wide range of organics in water using dioxygen in combination with hydrazine hydrate without any other additives.

2. Experimental

2.1. Chemicals and reagents

All organic compounds, hydrazine hydrate were domestic reagent and used without further purification.

2.2. Apparatus and spectrum conditions

General HPLC analysis was performed on Kromasil C18 column using Agilent 1200 series diode array detector for screening oxidative degradation conditions and Agilent G1312B Bin pump

SL with G1315C detector for analyzing substrate degradation. The GC–MS analysis was performed on an Agilent 6890/5973 GC–MS (EI, 70 eV). The carrier was helium, and a HF-5 capillary column (30 m × 0.25 mm) was used. Electron impact ionization was at 70 eV. For ion-chromatography analysis, a Dionex 1000 IC system with an ED-40 electrochemical detector operating in conductivity mode and an AS 9-HC anion separator column was used. Total Organic Carbon (TOC) analysis for TCP was performed using a liquid TOC analyzer.

2.3. Ion chromatography analysis methods for the substrates degradation

Analysis conditions: for analysis of inorganic chloride, ion-chromatography was used. Inorganic chloride was determined on ion chromatography (Dionex ICS-1000), equipped with an AS 9-HC anion separator column (250 mm × 4 mm) and an DS-6 electrochemical detector. The suppressor current was 45 mA. The eluent was 9 mM aqueous NaOH solution and the flow rate was 1.0 mL/min. The samples used for Ion Chromatography analysis were diluted 2 or 3 times.

2.4. GC–MS analysis for 4-chlorophenol degradation

2.4.1. General degradation procedure and the sample preparation for GC–MS analysis (A)

The degradation of 4-chlorophenol was carried out in a 100 mL Teflon-lined autoclave equipped with a magnetic stirrer. 4-chlorophenol solution (20 mL, 1 mmol/L) and hydrazine (40 μ L, 1 mol/L) were added to the autoclave. The autoclave was then closed and charged with dioxygen to 0.6 MPa and then heated to the desired 150 °C (the heating-up time from room temperature to 150 °C requires about 15 min). The stirring speed was set at 300 R/min. After 4 h reaction at 150 °C, the autoclave was cooled to room temperature with cool water bath and carefully depressurized. A small part of the reaction mixture was directly used as the sample for HPLC analysis, and the remaining part of the reaction mixture was concentrated. The organic residue was methylated by adding MeS^+OH^- (1.5 mL, 0.2 M methanol solution). The methylated products were directly used for GC–MS analysis.

2.4.2. Sample preparation for GC–MS analysis (B)

The degradation reaction was repeated for five times. These degradation mixtures were combined and the water was removed by vacuum evaporation to leave a residue (pH < 3), which was methylated by adding MeS^+OH^- (1.5 mL, 0.2 M methanol solution). The resulting mixture was analyzed by GC–MS. The temperature program of the column was set as follows: at 45 °C, hold time, 3 min; from 45 °C to 280 °C at 8 °C/min. The carrier was helium, and a HF-5 capillary column (30 m × 0.25 mm) was used.

2.5. 1H NMR analysis for degradation products of phenols

Sample preparation: 4-chlorophenol in D_2O (20 mL, 1 mmol/L) was degraded according to the degradation method described above. The D_2O degradation mixture was directly used for 1H NMR analysis to identification of the reaction products. The preparation procedure of other four substrates for 1H NMR analysis was the same.

Quantification of degradation products: pentaerythritol was used as the external standard to determine the quantification of the reaction products. The pentaerythritol was recrystallized twice before use.

2.6. The detection of remaining hydrazine in reaction mixtures

Before degradation: the mixture of 4-chlorophenol (1 μmol) and hydrazine hydrate (4 μmol) in 1 mL water was added 1 mL solution of 4-methoxybenzaldehyde (1 mg/mL in methanol), and it was heated at 50 °C for half hour. After the mixture cooled down to room temperature, a white crystalline compound was precipitated. The white crystalline compound was isolated by filtering, and the crystalline compound was then solved in 1 mL methanol, which was used for HPLC analysis.

After degradation: after degradation reaction, the reaction mixture of 4-chlorophenol 1 mL was treated with 4-methoxybenzaldehyde (1 mg in 1 mL methanol) under 50 °C for half hour. There was no white crystalline compound appeared. The mixed solution was directly used for HPLC analysis.

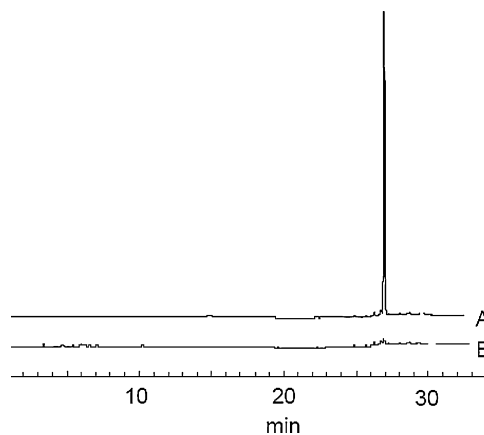


Fig. 1. The HPLC comparison of 4-chlorophenol between before and after degradation. (A) Before degradation. (B) After degradation.

3. Results and discussion

Our initial experiment was carried out using 4-chlorophenol as a test substrate and dioxygen in combination with hydrazine hydrate as the oxidizing agent. In a typical degradation process, a mixture of 4-chlorophenol (1 mmol/L, 20 mL) and 0.02 mmol hydrazine was stirred under 0.6 MPa of dioxygen at 150 °C for 4 h (the heating-up time was not included). High-performance liquid chromatography (HPLC) analysis of the resulting solution showed that 100% of the 4-chlorophenol had been degraded, but some products were generated and the reaction mixture turned into primrose yellow. Prolonging the reaction time to 6 h led to 100% degradation of the 4-chlorophenol and no obvious products was detectable, but the reaction mixture remained primrose yellow. Increasing the amount of hydrazine to 0.04 mmol, and the reaction was carried out under 150 °C, 0.6 MPa for 4 h, we found that the 4-chlorophenol was totally destroyed while no obvious products generated (Fig. 1). Furthermore, the reaction mixture became colorless and transparent. The total organic carbon (TOC) of the colorless reaction solution was measured and the results indicated that 40% of the organic carbon was mineralized. Chloride ion was measured by ion chromatography and the results showed 77% of the chlorine atoms of the 4-chlorophenol were released as innocuous inorganic chloride (Table 1, entry 2). Upon closer detection of the reaction products by HPLC compared with authority nitro compounds, we observed that

no nitration compounds were detectable in the reaction mixture. These results clearly demonstrated that the 4-chlorophenol was totally destroyed and a substantial amount of the starting substrate was mineralized. Control experiments without hydrazine indicated no degradation of 4-chlorophenol under the above experimental conditions. As such, the control experiments were implemented with argon in place of O_2 . The results indicated that the COD of reaction mixture remained hardly unchanged before and after reaction using argon.

Having reached a highly efficient process for degradation of 4-chlorophenol, we next examined the range of pollutants to which this degradation system could be applied. Toward this end, two broad classes of organics, phenols and nitrobenzene derivatives, were selected as model pollutants. Phenols model those organic pollutants found with significant quantities in waters, and nitrobenzene derivatives model those persistent organic pollutants. The tested scope of the pollutants in this degradation system is summarized in Table 1. As can be seen in Table 1, the degradation system displayed highly efficient degradation for a wide range of model pollutants. All the phenols, even those considered to be very persistent ones were quantitatively destroyed and a considerable amount was mineralized (entries, 1–7). Similarly, 3-chloroaniline

Table 1
Degradation of organics in water with dioxygen and hydrazine.^a

Entry	Substrate	Hydrazine hydrate ^b	Removal of substrates (%)	Removal of TOC (%)	Mineralization of Cl (%)	Degradation products ^c
1	1-Naphthol	10	100	55	–	Formic acid (2%), acetic acid (4%), methanol (3%), malonic acid (9%) and aromatic compounds (trace)
2	4-Chlorophenol	2	100	40	77	Formic acid (7%), acetic acid (10%), methanol (22%)
3	2,4-Dichlorophenol	3	99	37	70	Formic acid (6%), acetic acid (10%), methanol (14%)
4	2,4,6-Trichlorophenol	3	97	35	69	Formic acid (15%), acetic acid (10%), methanol (12%)
5	4-Nitrophenol	5	100	64	–	Formic acid (20%), acetic acid (4%), methanol (6%), succinic acid (8%)
6	Benzoquinone	3	100	67	–	–
7	Phenol	5	100	86	–	–
8	Nitrobenzene	10	89	29	–	–
9	2-Nitrotoluene	10	90	23	–	–
10	2,4-Dinitrotoluene	10	64	12	–	–
11	4-Chloronitrobenzene	10	71	10	72	–
12	3-Chloroaniline	5	100	43	51	–
13 ^d	4-Chlorophenol	2	100	43	–	–
14 ^e	Wastewater	–	–	52	–	–

^a Reaction conditions: 0.6 MPa O_2 , 4 h, 150 °C.

^b The mole ratio of hydrazine to substrate.

^c The percentage of degradation products determined by ^1H NMR analysis in total carbon.

^d The hydrazine hydrate was added with two times.

^e Reaction conditions: actual wastewater of wood pulp bleaching with chlorine (10 mL, COD = 1830 mg/L), 75 mg hydrazine hydrate (80%), 0.9 MPa O_2 , 4 h, and 150 °C. The COD of treated wastewater decreased 77%.

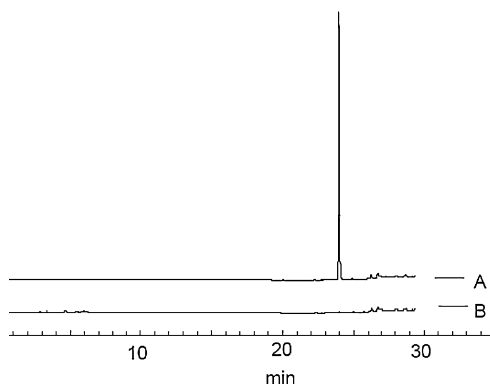


Fig. 2. The HPLC comparison of 2,4,6-trichlorophenol between before and after degradation. (A) Before degradation. (B) After degradation.

was degraded with 100% removal (entry, 12). The degradation system also showed powerful competence for destroying the persistent pollutants. For example, trichlorophenol, a typical persistent pollutant which has been usually selected as a model pollutant for examining new degradation systems for their degradation abilities, was near quantitative degradation with 35% TOC mineralization and 69% dechlorination (Table 1, entry 4). The HPLC comparison of 2,4,6-trichlorophenol between before and after degradation was clearly showed in Fig. 2. We were pleased to find that the present degradation system was able to degrade a wide range of nitrobenzene derivatives. The 4-nitrophenol was completely destroyed with 64% TOC mineralization (Fig. 3). Surprisingly, the dinitrotoluene, the benzene ring with two strong electro-withdrawing nitro groups, was also considerably removed (Table 1, entry 10). In addition to a wide range of substrate applicability, several features of this simple and cheap degradation system are worth noting. First, the degradation system displays fairly green. The system did not add any metals, organic agents, organic ligands as well as inorganic salts (e.g., buffering solvents). Naturally, the system is intrinsically devoid of the future trouble caused by these auxiliary substances, and the system is also free of the risk of secondary pollution by metal catalysts during treatment. In order to confirm whether the hydrazine remained in the degradation mixtures, we utilized 4-methoxybenzaldehyde to trap the hydrazine and detected the resulting 4-methoxybenzaldehyde hydrazone by HPLC. A clear peak corresponding to 4-methoxybenzaldehyde hydrazone was observed before degradation. However, the peak corresponding to

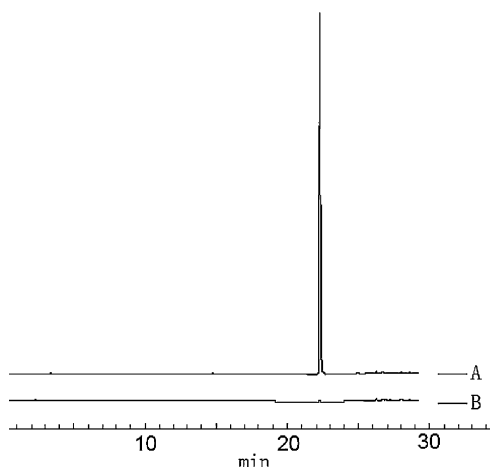


Fig. 3. The HPLC comparison of 4-nitrophenol between before and after degradation. (A) Before degradation. (B) After degradation.

4-methoxybenzaldehyde hydrazone did not appear after degradation, and only 4-methoxybenzaldehyde peak was observed (see supplementary material). These results clearly showed that although more than stoichiometric amount of hydrazine to the substrate was used in the degradation system, the hydrazine was completely consumed away in the reaction mixtures. Several reports on oxidation of the hydrazine in water into hydrogen peroxide with dioxygen have showed that the nitrogen atoms of hydrazine were converted into molecular nitrogen in the reaction [38–40]. Indeed, we did not detect any nitrate and nitrite in all the final reaction mixtures by ion chromatography (see supplementary material). The results also showed that no NO_2 and NO generated during the reaction because NO_2 could react with water to generate nitric acid. Among the degradation products, no nitrated products were detected (Table 1). Secondary, the degradation system also displays considerable promise for its practical application in industrial equipment. In current system, only inexpensive hydrazine hydrate and dioxygen were used as the reagents. This renders the degradation method interesting from an economic point of view. In addition, we have investigated the degradation system at various pH values, and the results showed that the pH value ranging from 2 to 11 had no significant influence on the degradation efficiency of the current degradation system. The broad pH applicability of the degradation method makes the degradation operation feasible at an alkaline condition, which would minimize the corrosiveness to the industrial equipments and decrease the costs of equipment. In order to verify the feasibility of industrialization of the degradation process, we applied the degradation system to actual wastewater of wood pulp bleaching with chlorine (COD = 1830 mg/L, TOC = 738 mg/L, BOD = 494 mg/L). At the similar conditions, 77% of COD was decreased and 52% of TOC of the wastewater was mineralized (Table 1, entry 14). The final BOD of the treated wastewater was reduced to 108 mg/L. The color of the treated wastewater became colorless. Although a slightly high reaction temperature (150 °C) was required to perform the reaction, the operation could run on a relatively low level of energy consumption at an industrial scale by energy exchange. Overall, when all the facets of this new oxidation system are considered, the use of inexpensive hydrazine hydrate and dioxygen as the reagents as well as its broad range substrate applicability rendered it very attractive for potential application at an industrial scale for the treatment of environmental pollutants.

The identification and quantification of reaction products would enable us to comprehensively evaluate the new oxidative degradation system. Gas chromatography–mass spectrometry (GC–MS) was used to identify the oxidation products in the reaction mixture. Samples for GC–MS were prepared according to the methods reported by Collins and Lenoir [27]. The result showed that no products were detected in the degradation of trichlorophenol. Considering the low concentrations of degradation products in the reaction mixture, we further determined the sample that was prepared from the combination of the repeated trichlorophenol degradation mixture of five times with GC–MS. The results showed that no products were detected either. Similarly, no products were detectable for the degradation of 4-chlorophenol with GC–MS. However, when the five time degradation mixtures of 4-chlorophenol were combined and treated with the same method mentioned above, we observed the major products via GC–MS analysis were succinic acid and 2-hydroxysuccinic acid, as well as some less amount of detectable products including 2-hydroxyacetic acid, oxalic acid, 2-hydroxypropanoic acid, adipic acid, etc. Of particular interest is the observation that most detectable degradation products do not contain chlorine atoms and nitro group. Proton nuclear magnetic resonance (^1H NMR) (400 MHz) was also used to identify and determine the degradation products in reaction mixture. Sample preparation for ^1H NMR can be found in Section 2.

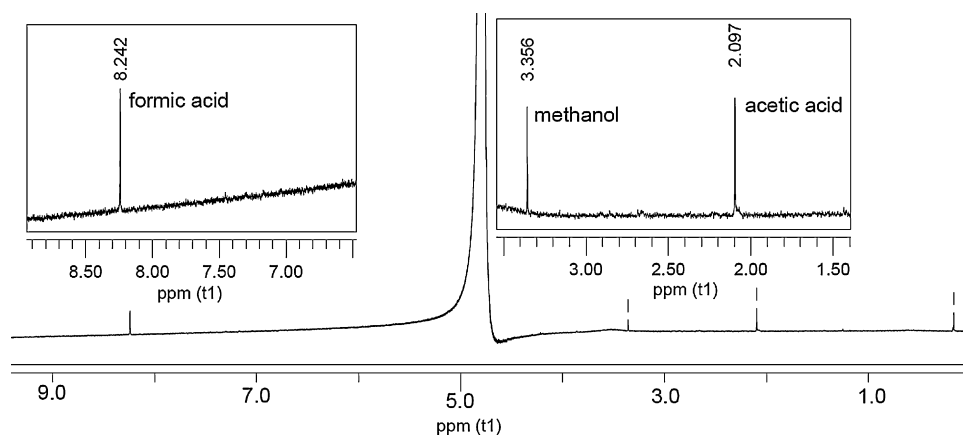


Fig. 4. ^1H NMR spectra and partial enlargement of 2,4,6-trichloro-phenol after degradation.

The results showed that only methanol, formic acid and/or acetic acid were detected with ^1H NMR for each degradation mixture. The amount of methanol, formic acid and/or acetic acid was determined in the degradation mixture with pentaerythritol as external standard (Table 1). Considering the extent of mineralization, the fates of a majority of the carbon for phenols have been accounted for. Of particular importance is the observation that oxidative degradation of chlorophenols using current degradation system did not lead to detectable aromatic products in the reaction mixture by ^1H NMR (supporting information). For example, in the ^1H NMR spectra for degradation mixture of trichlorophenol, we did not observe any peaks at 6.5–8.2 ppm (Fig. 4) suggesting no detectable aromatic proton. This clearly implicated that neither dioxins nor other toxic compounds are detectable.

4. Conclusions

We have shown that the only use of simple and inexpensive dioxygen in combination with hydrazine hydrate can efficiently remove recalcitrant pollutants in water. Under relatively mild conditions, a broad spectrum of toxic organics, including persistent nitrobenzene compounds and the organic components in actual wastewater of wood pulp bleaching, were oxidized into CO_2 and/or CO and a small fraction of biodegradable organic products. To the best of our knowledge, few degradation procedures are able to destroy such a wide range of pollutants in waters with dioxygen without resorting to the extreme measure of high temperature combustion. Moreover, the degradation system is applicable to both base and acidic reaction conditions. This renders the degradation process favorable in its industrial application. In addition, this system is intrinsically devoid of auxiliary substances including solvents, metal salts, and buffering solvents, which is free of the risk of secondary pollution during treatment. Except the O_2 , the only substance introduced deliberately to the system, hydrazine hydrate was oxidized to N_2 and H_2O during the treatment. Therefore, this practical, inexpensive and efficient degradation system displays considerable promise for disposal of a variety of recalcitrant organic pollutants in waters.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.06.025.

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