



Effects of reducing agents on the degradation of 2,4,6-tribromophenol in a heterogeneous Fenton-like system with an iron-loaded natural zeolite

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ABSTRACT

The effects of reducing agents on the degradation of 2,4,6-tribromophenol (TrBP) were investigated in a heterogeneous Fenton-like system using an iron-loaded natural zeolite (Fe-Z). The catalytic activity for TrBP oxidation in the presence of the Fe-Z and H₂O₂ was not appreciable. The addition of a reducing agent, such as ascorbic acid (ASC) or hydroxylamine (NH₂OH), resulted in an enhancement in the degradation and debromination of TrBP. TrBP was completely degraded and debrominated at pH 3 and 5 in the presence of NH₂OH, while the degradation was significantly suppressed at pH 7 and 9. Although the rates of TrBP degradation were relatively constant at pH 3, 5, 7 and 9 in the presence of ASC, the percent degradation reached a plateau at 70%. These results show that ASC functions as a strong HO• scavenger, as opposed to NH₂OH, at pH 3 and 5. Thus, adding NH₂OH is preferable for the degradation of TrBP via a Fenton-like system using Fe-Z as the catalyst. It is noteworthy that the complete mineralization of TrBP was achieved at pH 5, when NH₂OH and H₂O₂ were sequentially added to the reaction mixture. Analysis of the surface of Fe-Z by X-ray photoelectron spectrometry indicated that the Fe(III) on the surface of the catalyst was reduced to Fe(II) after treatment with ASC. Thus, the role of RAs can be of assistance in Fe(III)/Fe(II) redox cycles on the Fe-Z surface and enhance the generation of HO• via the decomposition of H₂O₂.

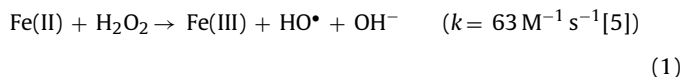
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1. Introduction

2,4,6-Tribromophenol (TrBP) is used in the manufacturing of TVs, computers and other household electric appliances as a flame retardant intermediate. As a result of extensive use, TrBP can be found in soils, landfill leachates and sewage sludge [1]. TrBP could have an endocrine disrupting activity *in vivo*, because it has been shown to interfere with the thyroid hormone system by competitive binding to transport proteins [2]. In terms of reducing the potential for pollution and related health issues, it is important to develop the techniques for the oxidative degradation of TrBP in contaminated environments. However, bromophenols are more difficult to oxidize than other halogenated phenols, such as fluoro-phenols and chlorophenols [3].

Fenton and Fenton-like processes have been the focus of studies dealing with the oxidative degradation of organic pollutants. In such systems, H₂O₂ is catalytically decomposed by Fe(II) to generate a powerful oxidant, the hydroxyl radical (HO•). The overall

process is referred to the Haber–Weiss reaction as below [4]:



Numerous studies related to the degradation of chlorophenols by homogeneous Fenton and Fenton-like systems have appeared [6–8], but much less information is available concerning the degradation of bromophenols. The homogeneous Fenton processes is limited to the pH range from 2.5 to 3.5, because Fe(III)-hydroxides are converted into sludge, leading to the deactivation of catalytic activity for oxidation [9]. To overcome such problems, heterogeneous Fenton-like systems in which Fe(II) or Fe(III) are supported to a solid support have been examined: e.g., minerals [10–13] and cation exchange resins [14,15].

In particular, Fe-loaded zeolites have been demonstrated to function as active catalysts in the degradation of organic pollutants in the presence of H₂O₂ [16–21]. In these studies, synthesized zeolites such as Y-, ZSM-5 and Beta zeolites were mainly employed and Fe²⁺ or Fe³⁺ were loaded via cation-exchange reactions. Although natural zeolites are cheap and widely distributed, they have not been used extensively as catalysts, but are mainly utilized as

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Table 1
Inorganic element content, cation exchange capacity (CEC), specific surface area (SSA), total pore volume and average pore diameter for original zeolite and Fe-Z.

Sample	Inorganic elements (%)				CEC (cmol kg ⁻¹)	SSA (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)	Average pore diameter (nm)
	Al	Si	Ca	Fe				
Original zeolite	2.5 ± 0.46	40.8 ± 5.7	21.4 ± 1.4	0.49 ± 0.05	150 ± 22	33.3	0.108	13
Fe-Z	2.38 ± 0.22	38.9 ± 0.02	14.9 ± 0.2	1.54 ± 0.06	71.7 ± 6.1	26.2	0.131	20

adsorbents [22] and soil amendments [23–25]. The surface areas of natural zeolites (16–38 m² g⁻¹) [22–25] are much smaller than those the synthesized materials (300–800 m² g⁻¹) [17–21], because of the presence of impurities such as quartz and feldspar. Such smaller surface areas of natural zeolites may be a disadvantage in terms of achieving a higher catalytic activity.

In homogeneous system, Fenton and Fenton-like systems combined with light irradiation [7,8,26] and electrochemical processes [27] have been examined to accelerate the redox cycle of Fe(III)/Fe(II) and the generated HO[•]. Although the addition of reducing agents (RAs) seems to be simple and effective in accelerating the reduction of Fe(III) to Fe(II), they may also serve as inhibitors of oxidative Fenton processes because of their oxidation by HO[•]. It has, however, been reported that the addition of RAs, such as ascorbic acid (ASC) and hydroxylamine (NH₂OH), to homogeneous Fenton-like systems can be effective in enhancing the generation of HO[•], ultimately leading to the degradation of organic substrates [28–30]. In the present study, the addition of RAs, such as ASC, NH₂OH, *p*-hydroquinone, oxalic, gallic and humic acids, to a heterogeneous Fenton-like system with an iron-loaded natural zeolite (Fe-Z) was examined. The reactivity of the heterogeneous Fenton-like system was evaluated using the oxidative degradation of TrBP as a model system.

2. Materials and methods

2.1. Materials

ASC, NH₂OH, *p*-hydroquinone, oxalic and gallic acids, employed as RAs, were purchased from Nacalai Tesque (Kyoto, Japan). The humic acid, a natural RA, was extracted from a Shinshinotsu peat soil sample (Hokkaido, Japan), as described in a previous report [31]. TrBP (98% purity) was purchased from Tokyo Chemical Industry (Tokyo, Japan), and a stock solution (0.01 M) was prepared by dissolving it in 0.02 M NaOH. The standard sample of 2,6-dibromo-*p*-benzoquinone (2,6DBQ) was synthesized according to a previous report [32]. A natural zeolite sample was obtained from the town of Niki (Hokkaido, Japan). All other reagents were purchased from Wako Pure Chemicals (Osaka, Japan) and were used without further purification. The ultra-pure water, prepared by a Millipore ultra-pure system from distilled water, was used in all experiments.

2.2. Synthesis of Fe-Z

The cation-exchange capacities (CECs) for each sample were determined, as described in a previous report [23], and the CEC of the natural zeolite was determined to be 170 ± 7 cmol kg⁻¹, as shown in Table 1. The zeolite powder was stirred in aqueous FeSO₄(NH₄)₂SO₄·6H₂O under a N₂ atmosphere at room temperature for 72 h, in which the amount of iron was adjusted to the equivalent mole of CEC for the zeolite. After filtration of the slurry, the resulting solid was washed with distilled water and then freeze-dried. The powder was calcined at 500 °C for 8 h to obtain the Fe-loaded catalyst (Fe-Z). The inorganic element compositions (Al, Si, Ca and Fe) and specific surface areas (SSAs) for the original zeolite and Fe-Z were determined, as described in a previous report

[24]. As shown in Table 1, the iron content (wt%) in the Fe-Z was 1.54 ± 0.06%, corresponding to be 276 ± 11 μmol-Fe g⁻¹. In the present study, this was considered to be moles of catalytic sites in the Fe-Z. The specific surface areas (SSAs), total pore volume and pore size were determined by a N₂-BET method using a BECKMAN COULTER SA3100-type instrument.

2.3. Assay for the reaction mixture

Test solutions, which contained TrBP (100 μM) and the RAs (0.25–10 mM) at pH 3, 5, 7 or 9, were prepared, and 30 mL aliquots of these solutions were then placed in a 100-mL Erlenmeyer flask that contained powdered Fe-Z (2.7–54.2 mg). After adding an aqueous solution of H₂O₂ (0.25–100 mM), the reaction mixture was subjected to shaking at 25 °C. During the reaction period, an 800 μL aliquot of the test solution was withdrawn and then mixed with a 400 μL of 2-propanol, followed by vigorous mixing. After centrifugation, a 20 μL aliquot of the supernatant was injected into a PU-980 type HPLC system (Japan Spectroscopic Co. Ltd.) to determine the concentration of the residual TrBP in the reaction mixture. The detailed conditions for the HPLC analysis are described in Supplementary data (Text S1). When 2-propanol was added to a mixture of TrBP and Fe-Z without H₂O₂, nearly 100% of the TrBP was recovered. However, in the absence of 2-propanol, only 2–3% of the TrBP was adsorbed to Fe-Z. Thus, the adsorption of TrBP to the Fe-Z is negligible. The concentration of Br⁻ in the reaction mixture was analyzed by a DX-120 type ion chromatography (Dionex).

The oxidation products, such as 2,6DBQ, that were produced in the reaction were acetylated, and these resulting acetyl derivatives were analyzed using a GC/MS system after extraction with *n*-hexane. The detailed procedures are described in Supplementary data (Text S2). The mass spectra of the detected peaks were assigned based on peaks for fragmentation ions.

In the test for TrBP mineralization, aqueous mixtures containing 5 mM NH₂OH and 100 μM TrBP at pH 3, 5, 7 or 9 were prepared, and 30 mL aliquots of these solutions were placed to the 100-mL Erlenmeyer flask that contained 13.1 mg of Fe-Z. After adding a 150 μL aliquot of 1 M aqueous H₂O₂, the flask was allowed to shake for 180 min. After the reaction, a 20 mL aliquot of the reaction mixture was mixed with 1 M aqueous Na₂SO₃ (1 mL), and the TOC of the solution was analyzed using a TOC-V CSH-type analyzer (Shimadzu).

The consumption of H₂O₂ during the reaction was monitored using a 30-mL aliquot of the reaction mixture, which contained H₂O₂ (5 mM) and Fe-Z (436 mg L⁻¹ for NH₂OH and 216 mg L⁻¹ for ASC) in the absence and presence of RAs (5 mM for NH₂OH and 7 mM for ASC) at pH 3 and 9. A 200-μL aliquot of the reaction mixture was withdrawn and transferred to a 1.5-mL centrifuge tube. After centrifugation, a 10 μL aliquot of the supernatant was diluted to 5 mL with pure water. The H₂O₂ in this solution was quantitatively determined by an *N,N*-diethyl-*p*-phenylenediamine colorimetry [33].

The iron in the reaction mixture, eluted from the Fe-Z after a 180 min period, was analyzed by ICP-AES after filtering the reaction mixture through a membrane filter (0.45 μm).

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