



Sulfurized limonite as material for fast decomposition of organic compounds by heterogeneous Fenton reaction



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HIGHLIGHTS

- Used limonite degrades organic compounds by heterogeneous Fenton reaction.
- Sulfurized limonite removes methylene blue color in seconds.
- Recycled limonite can be used for biogas purification and wastewater treatment.

GRAPHICAL ABSTRACT



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ABSTRACT

Rapid decomposition of wastewater contaminants using sulfurized limonite (S-limonite) was investigated. Limonite is used for desulfurization of biogases, and S-limonite is obtained from desulfurization plants as solid waste. In this work, the profitable use of S-limonite in water treatment was examined. The divalent Fe in S-limonite was expected to produce OH radicals, as Fe²⁺ ions and limonite thermally treated with H₂ do. Methylene blue was used for batch-wise monitoring of the decomposition performance. The decomposition rate was fast and the methylene blue solution color disappeared in only 10 s when a small amount of H₂O₂ was added (1 mM in the sample solution) in the presence of S-limonite. The OH radicals were formed by a heterogeneous reaction on the S-limonite surface and Fenton reaction with dissolved Fe²⁺. The decomposition of pentachlorophenol was also examined; it was successfully decomposed in batch-wise tests. The surfaces of limonite before sulfurization, S-limonite, and S-limonite after use for water treatment were performed using scanning electron microscopy and X-ray photoelectron spectroscopy. The results show that S-limonite reverted to limonite after being used for water treatment.

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1. Introduction

Wastewater treatment is an important issue for all industrial workers, inhabitants in the vicinity of factories, and local governments. In biological wastewater treatment plants, most organic

compounds are decomposed by biological activities, helped by air circulation in the wastewater pool. However, some compounds do not degrade well in this process, for example, colored matter in excreta from stockyard waste and chlorinated organic matter. Various treatments have therefore been investigated for the effective degradation of contaminants, such as ozone-assisted degradation [1], photocatalytic decomposition on titanium oxide, and coagulation using polyferric materials [2]. The Fenton reaction is also attractive because it is based on the formation of OH radicals, which

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have high oxidation potentials [3,4]. Photo-Fenton reactions [5] and Fenton-like reactions using Fe^{3+} [6] have also been reported as advanced techniques. These Fenton reactions are based on the production of OH radicals from H_2O_2 , catalyzed by Fe^{2+} ions. In addition to homogeneous catalyses, heterogeneous Fenton systems have been investigated recently, to maintain the oxidation effect for long time. Lu et al. [7] and Gordon and Marsh [8] used goethite ($\alpha\text{-FeOOH}$) as a solid catalyst in the decomposition of 2-chlorophenol in the presence of H_2O_2 . The reaction with goethite starts with the dissolution of Fe ions from the goethite. The deposited ferric oxide can be removed by crystallization in a fluidized bed [9]. New materials for the heterogeneous Fenton reaction have been investigated recently, such as schwertmannite [10], acid-activated fly-ash [11], Fe_3O_4 magnetic nanoparticles [12–14] and core-shell-structured $\gamma\text{-Fe}_2\text{O}_3$ -based nanocomposites [15]. Also natural materials, such as clay [16–18] and pyrite [19], act as the catalyst for the heterogeneous Fenton-like reaction.

In this work, we investigated the decomposition of organic matter by a heterogeneous Fenton reaction using limonite after its use for desulfurization (S-limonite). Limonite [$\alpha(\gamma)\text{-FeOOH}$], as well as goethite, was expected to be a heterogeneous catalyst for the reaction. In our prefecture, Kumamoto, limonite is produced over a large area near the Mt. Aso volcano. Ferrous-ion-rich groundwater moves to the ground surface and deposits limonite. Limonite is therefore an abundant material in the Aso area. This natural material is mainly used for desulfurization of waste gases produced from biological sewage treatment towers [20,21]. The limonite characteristics can be improved by physical and chemical treatments. Tsubouchi et al. treated limonite with H_2 in a furnace and used the material for high-temperature decomposition of ammonia [22]. The decomposition of coal tar can also be conducted using limonite [23]. Limonite has high potential for gas/water purification, and several kinds of surface improvements such as sintering, macropore production, and treatment with H_2S have been attempted to obtain more effective water treatment abilities. Limonite treated with H_2S is easily obtained from biogas treatment towers. Brown limonite becomes black (S-limonite) by adsorption of H_2S after its use for desulfurization. Water treatment using S-limonite is described in this paper.

2. Experimental

2.1. Material

Limonite balls (≈ 5 mm in diameter) were obtained from Japan Limonite (Aso, Japan); they were prepared from limonite powder. Four types of limonite material were used: as-received, sintered, macroporous, and sulfurized (S-limonite). The sintered limonite was prepared in a furnace (KDF S70G, Denken, Oita, Japan) at 130°C for 30 min, 400°C for 30 min, and 900°C for 2 h in an air atmosphere. After treatment, the furnace temperature was gradually decreased by natural cooling. The macroporous material was prepared from ground limonite powder (2 g) mixed with sodium bicarbonate (2 g) to prepare into paste with 2 mL of water. The paste applied on a $25\text{ mm} \times 25\text{ mm}$ stainless-steel square plate was treated at 900°C for 2 h in the furnace. S-limonite was obtained from the round limonite after being used as a desulfurizer for 1 month in a waste sludge treatment plant. The limonite surface became black as a result of ferric sulfide formation. The S-limonite was stored in a sealed can after purging with nitrogen gas.

For OH radical formation, H_2O_2 (30% solution, Wako Pure Chemical, Osaka, Japan) was used after appropriate dilution. The organic compounds tested in the decomposition experiments were methylene blue ($\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}\cdot\text{Cl}\cdot 3\text{H}_2\text{O}$), obtained from Wako, and pentachlorophenol (PCP) from Tokyo Kasei (Tokyo, Japan). Formation of OH radicals was monitored using 1,2-diaminobenzene

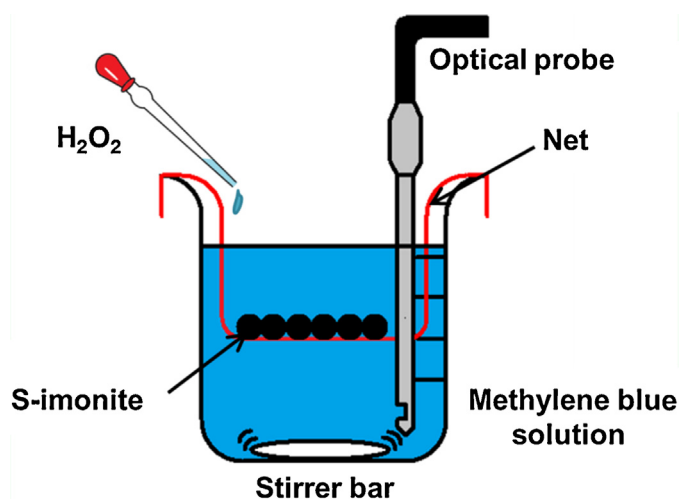


Fig. 1. Experimental setup for decomposition of methylene blue solution with S-limonite.

dihydrochloride (*o*-phenylenediamine dihydrochloride: ODPA) obtained from Tokyo Kasei.

2.2. Decoloration of methylene blue

The four types of limonite (2.0 g) were each put in a kitchen net hanging in a beaker containing 100 mL of $16\ \mu\text{M}$ methylene blue solution, as shown in Fig. 1. The solution was stirred with a 25-mm Teflon bar at 250 rpm. Into the methylene blue solution, $100\ \mu\text{L}$ of 1.0 M H_2O_2 was added to start the decomposition; the initial H_2O_2 concentration corresponded to 1.0 mM. Long-term reaction monitoring was performed by taking the methylene blue solution (2 mL) at intervals, placing them in a cubic glass cell, and measuring the absorbance at 660 nm using a double-beam spectrophotometer (U-2800; Hitachi High-Tech, Tokyo, Japan). Short-term changes in the spectrum of the methylene blue solution were monitored by inserting an optical probe (PD300LM-1.5 M) connected to a fiber optic spectrophotometer (SEC2000-UV/VIS, both from BAS, Tokyo, Japan).

The formation of OH radicals was monitored in situ in the same way as methylene blue decomposition, using the fiber optic probe. In this case, 3.0 mM ODPA was used instead of methylene blue solution [24,25].

2.3. Decomposition of PCP

PCP ($100\ \mu\text{M}$) decomposition was performed in the same way as that of methylene blue with 2.0 g of S-limonite and 5 mM H_2O_2 , and the remaining PCP was analyzed batch wise. Water samples (1 mL) taken from the beaker were filtered using a $0.45\text{-}\mu\text{m}$ syringe filter, and a portion of sample ($20\ \mu\text{L}$) was injected in a carrier stream of high-performance liquid chromatography (HPLC; LC-10A Dvp, Shimadzu, Kyoto). The PCP was analyzed with a separation column (Symmetry C18 ODS $5\ \mu\text{m}$, ϕ 4.6 mm \times 150 mm, Waters, Milford, MA, USA), 50/50 aqueous acetic acid (3.0%)/acetonitrile as the eluent, and the absorbance monitoring at 300 nm.

2.4. Surface analysis of limonite and S-limonite

The surfaces of the limonite materials were observed using scanning electron microscopy (SEM; JSM-6390LV; JOEL, Tokyo, Japan). Sulfur speciation in the limonites was examined using X-ray photoelectron spectroscopy (XPS; SigmaProbe, Thermo Electron, Yokohama, Japan) as follows. Limonite samples were ground

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