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Decomposition mechanism of methylene blue caused by metallic iron-maghemite mixture

Shiro Kubuki · Koya Shibano · Kazuhiko Akiyama ·
Zoltán Homonnay · Ernő Kuzmann ·
Mira Ristić · Tetsuaki Nishida

Abstract Decomposition mechanism of methylene blue (MB) caused by a mixture of metallic iron-maghemite (Fe^0-γFe_2O_3) was investigated by means of ^{57}Fe-Mössbauer spectroscopy, X-ray diffractometry (XRD), Ultraviolet-Visible Absorption Spectroscopy (UV-vis) and electrospray-ionization mass spectroscopy (ESI-MS). Ten day-leaching test of 10 μmol L^{-1} MB aqueous solution and Fe^0-γFe_2O_3 mixture (mass ratio 3:7) showed a decrease in the concentration from 10.5 to 4.45 μmol L^{-1} with first-order rate constant (k) of $1.57 \times 10 - 1$ day -1. An ESI-MS study of Fe^0-γFe_2O_3 mixture (3:7) after the leaching test revealed new peaks at m/z of 100, 110 and 137 due to fragmentation of MB, in addition to those observed at m/z of 284, 270 and 256 which were ascribed to MB, Azure B and Azure A, respectively. ^{57}Fe-Mössbauer spectra of Fe^0-γFe_2O_3 mixture (3:7) resulted in a decrease in absorption area (A) for Fe^0 ($\delta = 0.00_{\pm 0.01}$ mm s^{-1}, $H_{\text{int}} = 33.0_{\pm 0.1}$ T) from 37.5 to 21.3, 9.7, 7.9, 7.0 and $4.5_{\pm 0.5}$ %, together with an increase in A from 0.0 to 5.0, 13.8, 17.2, 21.0 and $22.4_{\pm 0.5}$ % for octahedral (O_h) iron ($Fe^{II} + Fe^{III}$) of Fe_3O_4. XRD study of these samples indicated that the peak intensity at 2Θ of 44.7°

S. Kubuki (✉) · K. Shibano · K. Akiyama
Department of Chemistry, Graduate School of Science and Engineering,
Tokyo Metropolitan University, Minami-Osawa 1-1, Hachi-Oji, Tokyo 192-0397, Japan
e-mail: kubuki@tmu.ac.jp

Z. Homonnay · E. Kuzmann
Laboratory of Nuclear Chemistry, Institute of Chemistry, Eötvös Loránd University,
Pázmany P. s., 1/A, Budapest 1117, Hungary

M. Ristić
Division of Materials Chemistry, Ruđer Bošković Institute,
P. O. Box 180, Zagreb 10008, Croatia

T. Nishida
Department of Biological and Environmental Chemistry,
Faculty of Humanity-Oriented Science and Engineering, Kinki University,
Kayanomori 11-6, Iizuka, Fukuoka 820-8555, Japan

being ascribed to Fe^0 was decreased, while that of 35.6° due to Fe_3O_4 was almost constant; relative peak ratio of Fe^0/Fe_3O_4 was decreased from 26.3 to 2.76 after the leaching, indicating that Fe^0 in the Fe^0-γFe_2O_3 mixture was oxidized to Fe_3O_4. These experimental results suggest that Fe^0-γFe_2O_3 mixture could be utilized for the cleaning or decomposition of toxic organic compounds like trichloroethylene.

Keywords Metallic iron · Maghemite · Methylene blue (MB) decomposition · Ultraviolet-Visible Absorption Spectroscopy (UV-vis) · Electrospray ionization mass spectrometry (ESI-MS) · ^{57}Fe-Mössbauer spectroscopy

1 Introduction

Chlorinated volatile organic compounds (CVOC) like trichloroethylene (TCE) had been widely used until 1980s as solvent and degreaser in cleaning facilities and semiconductor industry. TCE is now prohibited to use because it has a risk to cause cancer. Several TCE detoxification methods have been developed using metallic alloy catalyst [1] or activated charcoal filter, but TCE decomposition rate is slow. Kubuki et al. have recently reported that a mixture of industrial by-product of metallic iron (Fe^0) and iron oxide with the mass ratio of between 2:8 and 5:5 rapidly decomposed TCE from the concentration of 10 to 0.5 ppm after 7 days [2]. In the present study, methylene blue (MB) was used as a simulating material of TCE, and decomposing process with Fe^0-γFe_2O_3 mixture with the mass ratio of 3:7 was investigated by means of ^{57}Fe-Mössbaur spectroscopy, X-ray diffractometry (XRD), Ultraviolet-Visible Absorption Spectroscopy (UV-vis) and electrospray ionization mass spectroscopy (ESI-MS).

2 Experimental

Mixture of Fe^0-γFe_2O_3 was prepared with Fe^0 (Wako 097–04791, 99.9 %, $\phi <$ 45 μm) and γFe_2O_3 (High Purity Chemicals No. 282965, 99 %, $\phi <$ 1 μm). Each mixture of 500 mg with a mass ratio of 3:7 was soaked in 20 mL of 10 μmol L^{-1} aqueous solution of methylene blue (MB). Leaching test was conducted at 30 °C for 10 days using a glass vial wrapped by aluminum foil. Reaction between Fe-γFe_2O_3 mixture and MB aqueous solution was carried out in a dark room in order to exclude photocatalytic effects. MB concentration before and after leaching test was determined by UV-vis spectrometry in the wavelength range of 200 and 800 nm, using a source of tungsten-deuterium lamp under an output power of 20 W. Mass of decomposition products originating from MB was measured by a positive ion mode ESI-MS in the m/z range of 50 and 350. For the structural characterization of Fe^0-γFe_2O_3 mixture, Mössbauer spectra were measured at room temperature in a conventional constant acceleration mode using a 925 MBq ^{57}Co(Rh) source. Velocity scale and isomer shift (δ) were calculated with respect to α-Fe. Mössbauer spectra were analyzed by Mosswinn 3.0i XP assuming Lorenzian curves. XRD pattern was recorded from 2Θ of 10 to 80° at 0.02° intervals at a scanning rate of 5° min^{-1}, using Cu-K_α X-rays ($\lambda = 0.1541$ nm) generated under tube voltage and current of 50 kV and 300 mA, respectively.

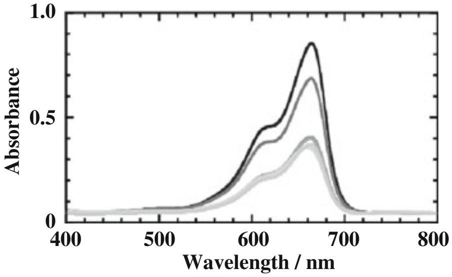

Fig. 1 UV-vis spectra of 10 μmol L^{-1} methylene blue (MB) before (*top*) and after 1, 3, 5, 7 and 10 day leaching with Fe^0-γFe_2O_3 mixture (3:7)

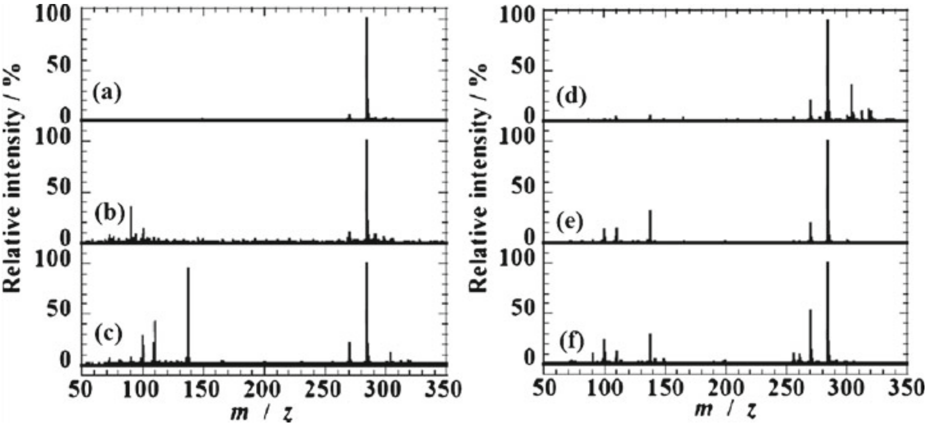

Fig. 2 ESI-MS profiles of 10 μmol L^{-1} MB measured after leaching test with Fe^0-γFe_2O_3 mixture (3:7) for (**a**) 0, (**b**) 1, (**c**) 3, (**d**) 5, (**e**) 7 and (**f**) 10 days

3 Results and discussion

UV-vis spectra of 10 μmol L^{-1} methylene blue (MB) aqueous solution before and after leaching with Fe^0-γFe_2O_3 mixture (3:7) are shown in Fig. 1. MB concentration can be determined by Lambert-Beer equation, *i.e.*,

$$Abs. = \varepsilon C_t\, l, \tag{1}$$

where *Abs.*, ε, C_t and l are absorbance, molar absorption coefficient ($= 7.9 \times 10^5$ L mol^{-1} cm^{-1} at 660 nm for MB [3]), concentration of MB solution after t-day leaching and optical path length (1 cm), respectively. By using (1), decrease of MB concentration was observed from 10.5 to 8.66, 5.15, 5.05, 4.70 and 4.45 μmol L^{-1} after leaching of 0, 1, 3, 5, 7 and 10 days, respectively. MB decomposition did not occur when only Fe^0 or γ-Fe_2O_3 was leached with MB aqueous solution. This result indicates that MB was decomposed by leaching with Fe^0-γFe_2O_3 mixture (3:7). A rate constant of first order reaction (k) can be estimated by following equation, *i.e.*,

$$C_t = C_0 \exp(-kt)\,. \tag{2}$$

A rate constant of first-order reaction for MB decomposition (k_{MB}) was determined to be $1.5_7 \times 10^{-1}$ day^{-1}. Figure 2 shows ESI-MS profiles of 10 μmol L^{-1} methylene

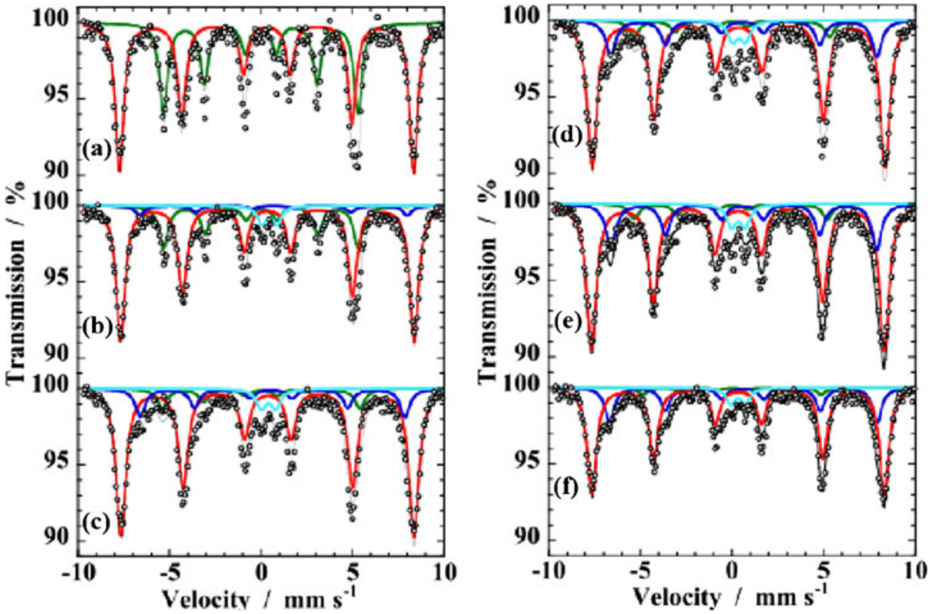

Fig. 3 Mössbauer spectra of Fe^0-γFe_2O_3 mixture (3:7) measured after leaching test with 10 μmol L^{-1} MB for **(a)** 0, **(b)** 1, **(c)** 3, **(d)** 5, **(e)** 7 and **(f)** 10 days

blue (MB) measured before and after the leaching test. Before the leaching, an intense peak was observed at m/z of 284, which was attributed to original MB (Fig. 2a). Peak intensity ratio of Azure B ($m/z = 270$)/MB ($m/z = 284$) was increased from 5.1 to 52.6 after the leaching. This result suggests that MB was oxidatively decomposed by substituting $-$H at the terminal position of MB for $-CH_3$. New peaks appeared at m/z of 100, 110 and 137 after leaching (Fig. 2b–f) indicate that MB was decomposed when mixed with Fe^0-γFe_2O_3 mixture.

As shown in Fig. 3, Mössbauer spectra of Fe^0-γFe_2O_3 mixture (3:7) before leaching (Fig. 3a) consist of two hyperfine sextets (*hfs*); one due to α-Fe with δ of $0.00_{\pm 0.01}$ mm s^{-1} and internal magnetic field (H_{int}) of $33.0_{\pm 0.1}$ T, and the other to γFe_2O_3 with δ of $0.32_{\pm 0.01}$ mm s^{-1} and H_{int} of $49.5_{\pm 0.1}$ T. A decrease in absorption area (A) for Fe^0 was calculated to be 37.5 to 21.3, 9.7, 7.9, 7.0 and $4.5_{\pm 0.5}$ % after leaching of 0, 1, 3, 5, 7 and 10 days, respectively. In these spectra, new absorption peaks (*hfs*) appeared which could be assigned to octahedral (O_h) species due to $Fe^{II} + Fe^{III}$ with apparent δ of $0.63_{\pm 0.01}$ mm s^{-1} and H_{int} of $45.3_{\pm 0.1}$ T, of which A was increased from 0.0 to 5.0, 13.8, 17.2, 21.0 and $22.4_{\pm 0.5}$ % (Fig. 3b–f). At the same time, paramagnetic Fe^{III} (O_h) species with δ and Δ of 0.38 and 0.79 mm s^{-1}, respectively was observed with an increasing A from 0.0 to 4.5, 4.6, 4.7, 4.9 and $5.0_{\pm 0.5}$ %. These results indicate that magnetite (Fe_3O_4) and lepidocrocite (γ-FeOOH) were precipitated when Fe^0-γFe_2O_3 mixture was reacted with MB. A rate constant of first order reaction of Fe^0 oxidation (k_{Feox}) and Fe $^{II+III}(O_h)$ production ($k_{Fe^{2.5+}(Oh)}$) were calculated by applying (2) substituting each A_t for C_t. As a result, k_{Feox} and $k_{Fe^{2.5+}(Oh)}$ of $1.5_4 \times 10^{-1}$ and $1.5_0 \times 10^{-1}$ day^{-1} were respectively obtained from the decrease in A for Fe^0 and from the increase in A for $Fe^{II} +^{III}$ (O_h), which

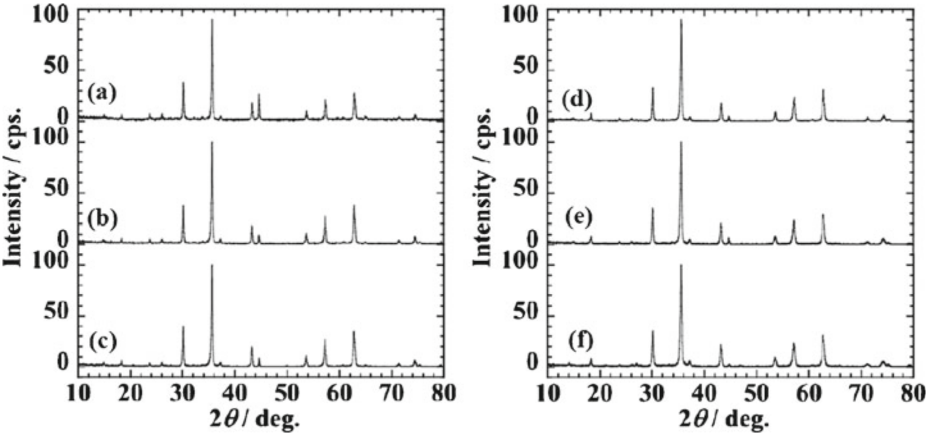

Fig. 4 XRD patterns of Fe^0-γFe_2O_3 mixture (3:7) measured after leaching test with 10 µmol L^{-1} MB for (**a**) 0, (**b**) 1, (**c**) 3, (**d**) 5, (**e**) 7 and (**f**) 10 days

suggests that decomposition of MB and precipitation of Fe_3O_4 proceeded by the same kinetics. Therefore, it is reasonable to consider that leaching test of Fe^0-γFe_2O_3 and MB aqueous solution resulted in the production of Fe_3O_4 by oxidized Fe^0 occupies vacant O_h sites of γ-Fe_2O_3.

Oxidation of Fe^0 and production of Fe_3O_4 was also reflected by XRD patterns for Fe^0-γFe_2O_3 mixture (3:7) measured after leaching test, as shown in Fig. 4; relative intensity (in %) observed at 2Θ of 44.7° being attributed to Fe^0 gradually decreased from 26.3 to 9.76, 9.04, 5.16, 6.88 and 2.76 with the leaching time. In a recent leaching test with 10 mg L^{-1} trichloroethylene (TCE) and Fe^0-γFe_2O_3 mixture (3:7) with smaller particle size resulted in larger TCE decomposition rates (3.0×10^{-1} day^{-1}) and Fe_3O_4 production without precipitation of γ-FeOOH [2]. These results indicate that decomposition rate of organic compounds are closely related to the particle size of Fe^0 and γFe_2O_3. In the studied system, oxidation of metallic Fe^0 was occurred by γFe_2O_3 which provides vacant O_h sites for production of Fe_3O_4 and takes a role of oxidizing agent like H_2O_2 in Fenton reaction. It is concluded that decomposition of MB proceeds under the oxidation from Fe^0 to Fe^{II} or Fe^{III} and that Fe^0-γFe_2O_3 mixture is effective in decomposing CVOCs.

4 Summary

Decomposition of 10 µM methylene blue (MB) aqueous solution could be confirmed after leaching with Fe^0-γFe_2O_3 (3:7) mixture for 10 days. MB was decomposed into Azure B, Azure A and fractured compounds by Fe^0-γFe_2O_3 mixture, which was finally converted to Fe_3O_4 since Fe^0 was oxidized to Fe^{II} or Fe^{III} by occupying vacant octahedral sites of γFe_2O_3. It is expected that Fe^0-γFe_2O_3 mixture might be utilized for cleaning toxic organic compounds like trichloroethylene.

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