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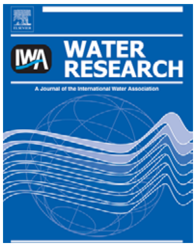

Various factors affecting photodecomposition of methylene blue by iron-oxides in an oxalate solution

Fahmida Gulshan [a], *Sayaka Yanagida* [a,1], *Yoshikazu Kameshima* [a,2], *Toshihiro Isobe* [a], *Akira Nakajima* [a], *Kiyoshi Okada* [a,b,*]

[a] *Department of Metallurgy and Ceramics Science, Tokyo Institute of Technology, O-okayama, Meguro, Tokyo 152-8552, Japan*
[b] *Materials and Structures Laboratory, Tokyo Institute of Technology, Nagatsuta, Midori, Yokohama, Kanagawa 226-8502, Japan*

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ABSTRACT

The effect of various factors on the photodecomposition of methylene blue (MB) by iron oxides calcined at various temperatures in various concentrations of oxalate solutions was investigated by illuminating with UV, visible and solar radiation. Iron oxides were prepared by a gel evaporation method and calcined at 200–700 °C. XRD showed that the as-synthesized iron oxides were amorphous, but formed maghemite (γ-Fe_2O_3) at 200–400 °C and hematite (α-Fe_2O_3) at $\geq$500 °C. The effect of the various iron oxides, their contents, the oxalate concentration and wavelength of the light source (UV, visible and solar) were all found to strongly influence MB photodecomposition. The optimal contents of the iron oxides increased greatly from 25 to 2000 mg/L at higher calcining temperatures. The MB photodecomposition rate at each optimal iron oxide content was related to the calcining temperature in the order 700 °C $<$ uncalcined $<$ 500 °C $<$ 400 °C $<$ 300 °C. The MB degradation was confirmed to occur by visible light illumination. Excellent photodecomposition was found at pH 2–5, but the photodegradation decreased greatly at pH $>$ 6, consistent with the presence of iron–oxalate complexes. A much higher concentration of hydroxyl radicals was generated in the present system compared with those from a commercial TiO_2 (ST-01), as determined by the coumarin method. Since this process does not require the addition of hydrogen peroxide and shows good efficiency even under solar light, it is an economically viable method for pre-treating and/or decolorizing wastewaters containing dyes.

1. Introduction

During the production of textile dye, more than 15% is lost in the wastewater stream, causing environmental problems (Park and Choi, 2003). These organic pollutants can be degraded on the surface of some minerals such as iron oxides by solar radiation in the natural environment. Most iron oxides and hydroxides, including hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), magnetite (Fe_3O_4), goethite (α-FeOOH), lepidocrocite (γ-FeOOH), etc, show semiconductor properties with narrow band gaps (2.0–2.3 eV) and should therefore be photoactive under solar radiation (Leland and Bard, 1987). Recently, advanced oxidation processes (AOP) such as the Fenton reaction have been found to be very effective for removing organic pollutants

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[*] *Corresponding author*. Materials and Structures Laboratory, Tokyo Institute of Technology, Nagatsuta, Midori, Yokohama, Kanagawa 226-8502, Japan. Tel.: +81 45924 5323, fax: +81 45924 5338.
E-mail address: okada.k.ab@m.titech.ac.jp (K. Okada).

[1] Present address: Sumitomo 3M Ltd, Minami-Hashimoto, Sagamihara, Kanagawa 229-1185, Japan.

[2] Present address: Department of Environmental Chemistry and Materials, Okayama University, Tsushimanaka, Kita, Okayama 700-8530, Japan.

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from wastewater (Sedlak and Andren, 1991; Kusvuran et al., 2005). The Fenton system involves the generation of hydroxyl radicals (•OH) which can degrade most organic compounds to carbon dioxide and water due to their high oxidation potential ($E^0 = +2.80$ V) (Buxton et al., 1988). More recently, ozone, electricity and light have been incorporated in the Fenton AOP system to increase the efficiency of •OH generation. Thus, photo-Fenton and photo-Fenton-like reactions have been extensively utilized to degrade azo dyes (Moraes et al., 2004; Tang and Chen, 1996; Bandara and Kiwi, 1999; Kiwi et al., 2002; Tao et al., 2005). In these reactions, H_2O_2 is added as the direct source of •OH (Pera-Titus et al., 2004; Kremer, 1999). However, H_2O_2 is an extremely reactive compound and does not survive in nature for long, limiting the usefulness of Fenton and Fenton-like systems for the degradation of organic matter in a natural environment.

It is known that a combination of iron oxides and polycarboxylic acids can form a photochemical system to give a photo-Fenton-like reaction without the addition of H_2O_2, and with much higher quantum efficiency than with $Fe(OH)^{2+}$ or iron oxides alone (Siffert and Sulzberger, 1991; Faust and Zepp, 1993). Since the polycarboxylic acids are also abundant in the natural environment, this photochemical oxidation process can directly utilize natural materials (iron oxides and polycarboxylic acids) in combination with solar energy, to decompose organic pollutants economically. It is therefore meaningful to investigate the photodecomposition of organic pollutants in the iron oxide–polycarboxylate complex system to better understand the transformation of organic pollutants. Oxalic acid is one of the most active polycarboxylic acids, and has been reported by Li et al. (2006) to degrade bisphenol A faster than other carboxylic acids such as citric, tartaric, malonic, malic and succinic acid. The photochemistry of Fe(III)–oxalate complexes has been studied by many workers (Parker, 1954) and Fe–oxalate complexes are known to exhibit strong ligand-to-metal charge absorption bands in the near-UV and visible region.

Photochemical processes in the co-presence of iron oxide and oxalate have previously been described in detail (Zuo and Deng, 1997; Balmer and Sulzberger, 1999). During the photochemical reaction of Fe(III)–oxalate complexes under illumination by UV and/or visible light, superoxides and hydroperoxyl radicals ($^\bullet O_2^-/^\bullet O_2H$) (Eqs. (2)–(6)) are formed as the key intermediates. H_2O_2, thought to be formed from $^\bullet O_2^-/^\bullet O_2H$, (Eqs. (7) and (8)) participates in a classical Fenton reaction with Fe(II), formed by photo-reduction of Fe(III), producing •OH (Eq. (9)):

$$\text{Iron oxide} + nH_2C_2O_4 \rightarrow [Fe(III)(C_2O_4)_n]^{(2n-3)-} \tag{1}$$

$$[Fe(III)(C_2O_4)_n]^{(2n-3)-} + h\nu \rightarrow [Fe(III)(C_2O_4)_2]^{2-} + {}^\bullet(C_2O_4)^{-} \tag{2}$$

$$[Fe(III)(C_2O_4)_n]^{(3-2n)-} + h\nu \rightarrow [Fe(II)(C_2O_4)_{(n-1)}]^{(4-2n)} + {}^\bullet(C_2O_4)^{-} \tag{3}$$

$${}^\bullet(C_2O_4)^{-} \rightarrow CO_2 + {}^\bullet(CO_2)^{-} \tag{4}$$

$${}^\bullet(CO_2)^{-} + O_2 \rightarrow CO_2 + {}^\bullet O_2^{-} \tag{5}$$

$${}^\bullet O_2^{-} + H^+ \rightarrow {}^\bullet O_2H \tag{6}$$

$${}^\bullet O_2^{-} + Fe^{3+} \rightarrow Fe^{2+} + O_2 \tag{7}$$

$${}^\bullet O_2^{-}/{}^\bullet O_2H + nH^+ + Fe^{2+} \rightarrow Fe^{3+} + H_2O_2 \tag{8}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^\cdot OH \tag{9}$$

Oxalic acid is first adsorbed on the surface of the iron oxide in suspension, forming $[Fe(III)(C_2O_4)_n]^{(2n-3)-}$. This complex can be excited under illumination to form $[Fe(II)(C_2O_4)_{(n-1)}]^{(4-2n)-}$ and the oxalate radical ${}^\bullet(C_2O_4)^-$ (Eq. (3)). The oxalate radicals are readily transformed to the carbon-centered radical ${}^\bullet(CO_2)^-$ (Eq. (4)) (Chen et al., 2007), from which the excited electrons are transferred to the adsorbed oxygen molecules, forming superoxide ions ${}^\bullet(O_2^-)$ (Eq. (5)). Fe(III) can react with ${}^\bullet O_2^-$ to form O_2 and Fe(II), and Fe(II) reacts with ${}^\bullet O_2^-$ and ${}^\bullet O_2H$ to form H_2O_2 in acidic solution with Fe(III) (Eqs. (7) and (8)). Fe(II) is reoxidized to Fe(III) in the presence of O_2. After H_2O_2 is formed, hydroxyl radicals (•OH) can be generated by the reaction of Fe(II) with H_2O_2 as described by Eq. (9). The formation of •OH in the Fe(II)–oxalate system (Ma et al., 2006) and in H_2O_2 (Li et al., 2007a) have been confirmed by photochemistry.

In this study, methylene blue(MB) was selected as a model organic pollutant and its degradation was studied in the presence of various iron oxides in oxalate solution under UV, visible and solar illumination. Several key factors such as the iron oxide phases, oxalate concentrations, light sources and iron oxide contents were investigated to provide a better knowledge of this photochemical AOP reactions. Since formation of Fe-oxalate and generation of OH radicals are thought to be important in this AOP reactions, they were examined by changing pH of the solution and a coumarin method (Louit et al., 2005). Photodecomposition ability of the present system was compared with commercial TiO_2 powders.

2. Experimental

2.1. *Sample*

Iron oxide samples were prepared by the Pechini process (Vivekanandhan et al., 2006) using ferric nitrate ($Fe(NO_3)_3{\bullet}9H_2O$) and ethylene glycol. Ferric nitrate was dissolved in ethylene glycol at a molar ratio of $Fe(NO_3)_3{\bullet}9H_2O$: ethylene glycol = 1:3 with the addition of a minimum volume of water. The resulting solution was evaporated on a hotplate stirrer at 90 °C, during which the nitrate-glycol solution auto-ignited, producing a voluminous foam and eventually yielding a loose powder. The samples were dry-ground in a planetary ball mill (LAPO-1, Ito Seisakusho, Japan) using a Si_3N_4 pot with 30 Si_3N_4 balls (5 mm∅) at 300 rpm for 3 h with a ball/sample mass ratio of 30/1. After grinding, the samples were calcined at 200 °C, 300 °C, 400 °C, 500 °C and 700 °C in air for 5 h at a heating rate of 10 °C/min.

Since titania is well known to show photocatalytic property, two commercial titania powders of P25 (Degussa,