Decolorization of methyl orange by green rusts with hydrogen peroxide at neutral pH

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ABSTRACT

Heterogeneous Fenton-like processes using green rusts (GRs) with hydrogen peroxide ($H_2O_2$) were studied to decolorize methyl orange (MO) in aqueous solution at an initial pH of 7.0. In this study, two types of crystal structure for GRs, the hydroxycarbonate GR(CO$_3^{2-}$) (GR1) and the hydroxsulphate GR(SO$_4^{2-}$) (GR2), were synthesized by partial oxidation of Fe(OH)$_3$ suspension under light irradiation and distinguished by X-ray diffraction (XRD) due to different characteristic peaks. In oxidation reactions, decolorization rate of MO, bubbling air through the solution, was about 65% (experiment B), whereas, it was up to 95% in the presence of $H_2O_2$ (experiment C) within 60 min. The comparative tests of GR1 and GR2 show that the reduction capability of GR2 is stronger than GR1, which may be due to Fe(II) content and interlayer anions. XRD analysis and Fourier transform infrared spectroscopy revealed that the oxidation end products of GR2 were mainly a poorly crystallized mixture of magnetite (Fe$_3$O$_4$) and hydroxy ferric oxide (FeOOH). However, when GR was immediately oxidized, the weakly crystallized goethite ($\alpha$-FeOOH) and lepidocrocite ($\gamma$-FeOOH) were formed for O$_2$ and $H_2O_2$, respectively. Based on the intermediates obtained, a probable decolorization mechanism has been proposed.

Key words | decolorization, Fenton-like oxidation, green rust, methyl orange

INTRODUCTION

Green rusts (GRs) are mixed ferrous–ferric hydroxides belonging to the general class of layered double hydroxides. They can be synthesized in the laboratory by partial oxidation of Fe(II) or by coprecipitation of Fe(II) and Fe(III) salts in aqueous solutions. Their general formula can be written as [Fe$_{\text{i-x}}$Fe$_{\text{x}}$] ($OH$)$_2$ $\times$ [x/nAn$^{n-}$·nH$_2$O]$^{x-}$ where An$^{n-}$ is the intercalated anions (containing the major anions Cl$^-$, SO$_4^{2-}$, CO$_3^{2-}$, but also F$^-$, I$^-$, Br$^-$, SO$_3^{2-}$, S$_2$O$_3^{2-}$, C$_2$O$_4^{2-}$, SeO$_3^{2-}$) and x is the Fe(III) molar fraction (0.25 < x < 0.67) (Drissi et al. 1995; Génin et al. 1996; Burdorfeau et al. 2012). Green rust compounds are divided into two types based on the interlayer anion. GR1 contains monotonetic and planar ions (e.g., Cl$^-$ and CO$_3^{2-}$) with rhombic structure. GR2 contains three-dimensional ions (e.g., SO$_4^{2-}$) with hexagonal structure (Génin et al. 1998).

Because of the presence of Fe(II), GRs are very reactive compounds. They have been extensively used for the reduction of inorganic contaminants such as nitrates/nitrite, Cr$^{VI}$, Se$^{IV}$, U$^{VI}$, Ag$^{I}$, Au$^{III}$, Cu$^{II}$ and Hg$^{II}$ (O’Loughlin et al. 2003; Katsuya et al. 2010). The synthetic GRs have also been reported mainly for the reduction or dechlorination of chlorinated compounds (CHCl$_3$, CCl$_4$, trichloroethylene, perchloroethylene, polychlorinated biphenyls, DDT (dichlorodiphenyltrichloroethane), DDE (dichlorodiphenyl-dichloroethylene), cis-dichloroethylene and vinyl chloride), nitroaromatic compounds RDX (Research Department Explosive: cyclotrimethylene trinitramine), and phenol (O’Loughlin & Burris 2004; Matta et al. 2008; Hanna et al. 2010; Han et al. 2012). However, the use of GR as an Fe(II) source to promote the oxidation reaction and to decolorize azo organic pollutants has been scarcely investigated (Kone et al. 2009).

The traditional Fenton’s reagent (dissolved Fe(II) + $H_2O_2$) works at pH values below 4, which is harmful for the environment. The reaction of Fe-bearing minerals such as iron oxides and hydroxides with hydrogen peroxide can effectively oxidize the organic molecules at circum-neutral pH, and the GR’s performance is superior to other species (Matta et al. 2007; Hanna et al. 2008). The aim of this study was to evaluate the abilities of synthetic...
hydroxycarbonate GR(CO$_3$$^2$$^–$) (GR1) and hydroxysulphate GR(SO$_4$$^2$$^–$) (GR2) to reduce Methyl Orange (MO), an azo dye, at neutral pH. In this work, the rate of decolorizing is initially investigated under different experimental conditions; the decolorizing mechanism of MO in the Fenton-like system (GR$_s$ + H$_2$O$_2$) is also investigated. Simultaneously, the oxidation end products of GRs under various experimental conditions were analysed.

**METHODS**

**Preparation of green rusts**

GR1 and GR2 were synthesized using the modified procedure reported by Drissi et al. (1995) and Génin et al. (1996). After addition of NaHCO$_3$ solution, an appropriate amount of NaOH solution (6 M) was added into the well-stirred aqueous solution of FeSO$_4$ (1.0 M, 50 mL) in a 250 mL beaker. The pH of the mixture was adjusted by adding NaOH to reach certain pH values (8.0). The volume of the solution was adjusted to 100 mL with distilled water. Air was then passed at a rate of 0.272 m$^3$/h through the suspension under irradiation with a 100 W incandescent lamp (Foshan, China) at 25°C. The precipitate was washed with O$_2$-free deionized water as well as ethanol, purging with 99.99% nitrogen, to remove excess ions in the aqueous solution and on its surface, then vacuum-dried at 40–50°C for 24 h. The obtained GRs were characterized by X-ray diffraction (XRD) patterns (Bruke D8).

**Oxidation experiments**

Ten millilitres of MO stock solution (0.45 mM) was mixed with the desired amount of GRs under continuous stirring in 100 mL of solution. The pH was maintained at a value around 7.0. The difference between experiment A and experiment B is the gas environment. In experiment A, N$_2$ gas was continuously bubbled into the solution, but O$_2$ gas was continuously bubbled in experiment B. In experiment C, oxidation was initiated by addition of 1 mL 30% (w/v) H$_2$O$_2$. The oxidation of MO by H$_2$O$_2$ operated in the same conditions without GRs is called experiment D. Each experiment lasted about 60 min.

At selected time intervals, 5 mL aliquots were collected and filtered. MO decolorization in all experiments was measured through UV–visible (UV–vis) spectra analyses (U-3010, Hitachi). The concentrations of MO samples were quantified by measuring the absorption intensity at 464 nm, and decolorization rate (D%) of MO was calculated based on the mass balance according to equation:

$$D\% = \frac{(A_0 - A)}{A_0} \times 100\% \quad (1)$$

where $A_0$ and $A$ are the absorption intensity of MO solution at initial and selected time, respectively.

Each series of experiments were repeated three times and the results were collected as the mean of all the values.

The oxidation end products of GRs were identified by XRD and Fourier transform infrared (FTIR) spectra (FTIR-8900, Shimadzu).

**RESULTS AND DISCUSSION**

**XRD analysis**

The XRD patterns of GR2 and GR1 are shown in Figure 1. The diffractogram (Figure 1(a)) exhibits the diffraction lines of GR2 synthesized by partial oxidization of Fe(OH)$_2$ suspension solution, in agreement with previous data (Ona-Nguema et al. 2004). A series of $d_{hkl}$ spacings, (001), (002), (003), (102) and (103), are characteristic peaks of GR2. A similar procedure was used to form GR1 where NaHCO$_3$ is added after the precipitation of Fe(OH)$_2$ from ferrous sulphate and NaOH. The XRD pattern of GR1 is shown in Figure 1(b). All main lines found in the XRD pattern are
typical of GR1. Angular positions of the diffraction peaks lead to a series of $d_{hkl}$ spacings close to that proposed by Benali et al. (2001). So, GR2 and GR1 were confirmed.

Decolorization reaction of MO

Figure 2(a) shows the time evolutions of the UV–vis spectra of MO during the decolorization process in the presence of GR2 and H$_2$O$_2$. The peak at 464 nm, the strong absorbance band at the visible region, is attributed to a conjugated structure formed by the azo bond, which is affected by the electron-donating dimethylamino group. The other peak at 273 nm is associated with the aromatic ring, which is ascribed to the $\pi \rightarrow \pi^*$ transition (Galindo et al. 2000).

At the first step (10 min) of the decolorization process, the absorbance value at 464 nm sharply decreased. After 20 min reaction, both bands at 464 and 273 nm became very much weaker, while absorbance at a lower UV region (<250 nm) increased, due to the formation of intermediate benzene-like organic compounds during the process of degradation (Devi et al. 2009). After 55 min, the corresponding absorbance at 464 nm almost completely disappeared. However, the UV absorbance region (<250 nm) did not decrease, which indicates that the intermediates of degradation in the solution were not degraded along with the decolorization of the residual MO.

Figure 2(b) shows the decolorization activities of MO under different reaction conditions in GR2 system. When H$_2$O$_2$ was used as an oxidant in the absence of GR2, very low decolorization of MO solution was observed (experiment D). Similarly, decolorization rate of MO was smaller when GR2 was used as a reactant in the absence of H$_2$O$_2$ (experiment A). Decolorization effects significantly increased when oxidants were added to the system. Decolorization rate, bubbling air through the solution, was up to about 65% (experiment B). However, it was observed that degradation was about 95% with the application of H$_2$O$_2$ (experiment C).

To compare the efficiency of the GR2 to a well-known iron oxide used in Fenton-like reactions, the oxidation experiments were carried out in the presence of GR1, and showed a slight difference from the GR2 system (Figure 3). Figure 3(a) illustrates the typical UV–vis spectra of MO during the decolorization process in the GR1 and H$_2$O$_2$ solution. In the first 5 min, the absorbance at 464 nm decreased rapidly, but the reduction was less than that of the GR2 system. Then, as the oxidation reaction proceeded, absorbance values decreased slowly, and the solution was almost transparent after 60 min. Decolorization rates of MO under different conditions in the GR1 system are shown in Figure 3(b). The results of experiment A for GR1 were similar to those of GR2. When oxidant was added into the reaction solution, decolorization rate of MO decreased from 65% for GR2 to 50% for GR1 in experiment B, and from 95% for GR2 to 90% for GR1 in experiment C. The reduction capability of GR2 is stronger than GR1, consistent with the results reported in the literature (Hanna et al. 2010). This difference may be probably due to the fact that the surface reactivity of the mixed oxides depended on surface properties such as structural Fe(II) content. The Fe(II) content obtained by chemical titration is higher for GR2 (2:1) than for GR1 (from 2:1 to 1:2). This observation is consistent with the findings of Bond & Fendorf (2003) for chromate reduction by different GRs. Another reason is the effect of interlayer anions. The oxidation of GR may lead to the ejection of the interlayer anion (CO$_3^{2-}$) from the GR structure to aqueous solution, which can affect the oxidation yield.

Figure 2 | (a) UV–vis spectra of MO solution in GR2/H$_2$O$_2$ system and (b) decolorization rates of MO versus time in GR2 system.
Decolorization mechanism of MO

From the above results, it can be found that Fe(II) content plays a central role in redox reactions. Fe(II) was also found to be more effective than Fe(III) for the generation of hydroxyl radicals (Matta et al. 2008). To explain the interactions between H₂O₂ and the iron surface, a Fenton-like mechanism of heterogeneous reactions, analogous to the solution phase reactions according to the classical Haber-Weiss cycle, is proposed (Kwan & Voelker 2005).

\[ \text{Fe(II)} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(III)} + \text{HO}^- + \text{HO} \cdot \quad (2) \]

\[ \text{Fe(III)} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(III)}(\text{H}_2\text{O}_2) \quad (3) \]

\[ \text{Fe(III)}(\text{H}_2\text{O}_2) \rightarrow (\equiv \text{Fe(II)}\cdot \text{O}_2\text{H}) + \text{H}^+ \quad (4) \]

\[ (\equiv \text{Fe(II)}\cdot \text{O}_2\text{H}) \rightarrow \equiv \text{Fe(II)} + \text{HO}^- \cdot \cdot \text{O}_2^- \quad (5) \]

Because the pKₐ of HOO⁻·O₂⁻ is 4.8, the superoxide radical (O₂⁻) may be the main active substance at neutral pH (Hanna et al. 2010). The superoxide radical O₂⁻ reacts as follows:

\[ \equiv \text{Fe(III)} + \text{O}_2^- \rightarrow \equiv \text{Fe(II)} + \text{O}_2 \quad (6) \]

If only Fe(III) is originally present, Fe(II) is slowly generated by reactions (3)–(5) initiating oxidation reaction (2). In the case of mixed Fe(II)-bearing mineral, reactions involving both Fe(II) and Fe(III) may occur. Therefore, the presence of Fe(II) in the Fe-bearing minerals can enhance the production rate of HO· in the dominant step (Equation (2)) (Matta et al. 2008).

As soon as Fe(II) is formed, the reaction of Equation (2) may take place leading to HO· radical generation and mineralization of organic compound (MO):

\[ \text{MO} + \text{HO} \cdot \rightarrow \text{products} \quad (7) \]

In order to investigate the role of hydroxyl radicals in the Fenton-like reactions, the decolorization process with the two GRs was carried out in the presence of excess 2-propanol as an HO· scavenger (Hanna et al. 2010). When 2-propanol (3% v/v) was added in the GR/H₂O₂ system, the oxidation of MO was inhibited, which confirms the predominant role of hydroxyl radical in this Fenton-like reaction system. Since hydroxyl radicals (HO·) directly attack the azo double bond of MO molecules, chromophoric characteristic of the dye is lost by producing other intermediates which do not absorb in the visible region (Figure 4). Because the reaction constant of hydroxyl radical with MO molecule may be low, involving a very slow mineralization process of MO under our experimental conditions, intermediates were not completely mineralized. These facts are consistent with the observation of Matta et al. (2007). They observed that cleavage of the azo group yielded two nitroso or nitro aromatic compounds, which undergo further decomposition. The end products may include acetic acid, succinic acid, benzoquinone, nitrobenzene, dinitrobenzene and sulfanilic acid-like compounds (Hou et al. 2007). The toxicity of products should be taken into account, which is our next research focus.
Identification of the oxidation end products of GRs

In order to identify the mineralogy of the oxidation products of GRs, the solid structure was analyzed by XRD and FTIR at the end of the oxidation reaction. Figure 5(a) shows the diffractograms of the remaining precipitates in the GR2 system. The results show that a poorly crystallized mixture of magnetite (Fe₃O₄) and hydroxy ferric oxide (FeOOH) are obtained in experiment A. Because the oxidation rapidity influences strongly the crystallinity and the nature of the final products, the formations of very weakly crystallized goethite (α-FeOOH) and lepidocrocite (γ-FeOOH) are expected for experiments B and C, respectively. The results are in agreement with the findings of Kone et al. (2009).

The IR spectra of remaining precipitates are shown in Figure 5(b). The characteristic absorption peak of Fe₃O₄ is at 580.3 cm⁻¹. For α-FeOOH, the bands appear at 887.8–891.6 and 797.4 cm⁻¹ for the in-plane and out-of-plane Fe–O–H bending vibrations, whereas, for γ-FeOOH, the bands at 1020.1 and 750.3 cm⁻¹ are assigned to in-plane and out-of-plane Fe–O–H-bending vibrations, respectively. The results show that a single phase of α-FeOOH is obtained in experiment B, whereas γ-FeOOH single phase is found in experiments C. A mixture of FeOOH and Fe₃O₄ is formed with only GR2. IR results are consistent with the XRD results.
CONCLUSIONS

The GR1 and GR2 were synthesized by partial oxidation of Fe(OH)$_2$ suspension solution and characterized by XRD. An active heterogeneous reaction system using GRs at neutral pH was tested for the decolorization of MO. When oxidant was added into reaction solution, the decolorization rate of MO increased from 50% for GR1 to 65% for GR2 in the presence of O$_2$, and from 90% for GR1 to 95% for GR2 in the presence of H$_2$O$_2$. A heterogeneous Fenton-like reaction mechanism was proposed. The hydroxyl radical (HO·) was the main active substance to attack the MO molecular. The oxidation of GRs with H$_2$O$_2$ may lead to the formation of poorly crystallized iron oxide. These results could be used to understand the transformation of organic pollutants in iron-rich soils in the presence of H$_2$O$_2$. In summary, this report has demonstrated that the GRs could be used to eliminate organic pollutants in aqueous solution and to develop the wastewater treatment process.

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