



# Quantitative characterization of hydroxyl radical generation in a goethite-catalyzed Fenton-like reaction



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## HIGHLIGHTS

- ·OH was quantified under various conditions in a heterogeneous Fenton-like reaction.
- ·OH could be generated at neutral pH in a goethite-catalyzed Fenton-like reaction.
- Higher H<sub>2</sub>O<sub>2</sub> concentration could result in more useless quench of ·OH.
- The inhibition effect for ·OH generation followed: H<sub>2</sub>PO<sub>4</sub><sup>-</sup> > SO<sub>4</sub><sup>2-</sup> > Cl<sup>-</sup> > NO<sub>3</sub><sup>-</sup>.

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## ABSTRACT

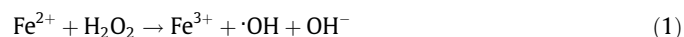
In order to find out the truth of influence of solution chemistry on the oxidation efficiency of a goethite-catalyzed Fenton-like reaction, the amount of hydroxyl radicals (·OH) was quantified by using coumarin as its trapping agent to produce the only fluorescent derivative 7-hydroxycoumarin (7-HC), because ·OH was the reactive species responsible for the oxidation activity of Fenton reactions. The concentration of ·OH achieved maximum at solution pH of 3 and decreased with an increase of solution pH value. However, considerable amount of ·OH can also generate at near neutral pH (i.e. pH 6 and 7). The concentration of ·OH was increased both with increasing of goethite and H<sub>2</sub>O<sub>2</sub> dosages, but H<sub>2</sub>O<sub>2</sub> could compete with coumarin to scavenge ·OH to reduce the formation of 7-HC when the concentration of H<sub>2</sub>O<sub>2</sub> was too high. Anions inhibited ·OH generation followed an order of H<sub>2</sub>PO<sub>4</sub><sup>-</sup> > SO<sub>4</sub><sup>2-</sup> > Cl<sup>-</sup> > NO<sub>3</sub><sup>-</sup> > ClO<sub>4</sub><sup>-</sup>. Higher concentrations of Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> resulted in greater inhibition of ·OH generation. Results of this study demonstrated that the influence of solution chemistry on the oxidation efficiency of the goethite-catalyzed Fenton-like reaction was greatly attributed to the effect of solution chemistry on the amount of ·OH formed in the process of reaction.

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## 1. Introduction

Advanced oxidation processes (AOPs) have shown great potential in the degradation of refractory organics in soil and water treatment. The homogenous Fenton process is a well-known example of AOPs, where the powerful hydroxyl radical (·OH) generated through the decomposition of hydrogen peroxide catalyzed by ferrous ion, as shown in Eq. (1). The ·OH is a strong oxidant, and it can degrade most organic contaminants rapidly and non-selectively through H abstraction or addition to C–C unsaturated bonds (Benitez et al., 2005). However, the homogenous Fenton process

suffers from narrow operation pH (optimum pH ~2.8) and iron sludge formation. To overcome these disadvantages, solid iron-contained catalyst were used instead of free iron ions, which were named heterogeneous Fenton-like process. In these processes, ·OH was generated through the decomposition of H<sub>2</sub>O<sub>2</sub> catalyzed by the iron bonded on the surface of solid catalyst (Lin and Gurol, 1998), and this offers some advantages over the classical homogeneous reaction, such as the absence of sludge formation, operation at near-neutral pH, and the possibility of recycling iron solids (Garrido-Ramirez et al., 2010). Many kinds of biorefractory compounds such as phenol, nitrophenol, dyestuff and berbisides could be effectively degraded in heterogeneous Fenton-like systems under various reaction conditions (Barreiro et al., 2007; Soltani and Entezari, 2014; Singh et al., 2014; Shi et al., 2014).



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Since  $\cdot\text{OH}$  was the reactive species responsible for the degradation of organic pollutants in AOPs, it is critical to quantitative determination of  $\cdot\text{OH}$  generation. The quantitative results can be used to evaluate the extent in which  $\cdot\text{OH}$  is involving in the degradation of pollutants, and to better understand the activity of different processes. However, the short lifetime (usually  $10^{-9}$  s) and high reactivity of  $\cdot\text{OH}$  interfered its direct quantitative determination.

Several methods have been developed to measure  $\cdot\text{OH}$  concentrations in liquid. Electron paramagnetic resonance technique (EPR/ESR) was one of the most frequently used methods. This method transferred  $\cdot\text{OH}$  to compounds contained unpaired electrons, which can be measured in a magnetic field (Kim and Metcalfe, 2007; Luo et al., 2009). Although it is sensitivity and selectivity in the detection of  $\cdot\text{OH}$ , the ESR method requires an expensive instrument system and a skillful technique, and the formed adduct is still short-lived (less than 10 min) (Tresp et al., 2013). Radical scavenging or trapping methods, in which scavengers were used to trap  $\cdot\text{OH}$ , could also be used to quantify the concentration of  $\cdot\text{OH}$ . Coumarin (COU) is one of the trapping reagents, which can react directly with  $\cdot\text{OH}$  to produce highly fluorescent compound, 7-hydroxycoumarin (7-HC) (Scheme 1) (Lout et al., 2005). The amount of 7-HC generated reflects the amount of generated  $\cdot\text{OH}$  in the system. This method is sensitive and stable, and has been used in several AOPs systems to quantify  $\cdot\text{OH}$ . For example, COU was used to quantify the  $\cdot\text{OH}$  generated in a photocatalytic system based on  $\text{TiO}_2$  (Zhang and Nosaka, 2013), in an ozone/zeolite/ $\gamma$ -alumina system (Ikhlaq et al., 2012), and in polymer electrolyte fuel cells (Ohguri et al., 2010).

According to our previous study (Lin et al., 2014), the degradation kinetics of PCB28 could be significantly influenced by solution chemistry in a goethite-catalyzed Fenton-like reaction, but the mechanism of solution chemistry affecting the oxidation activity of the goethite-catalyzed Fenton-like reaction is still unknown. Considering that the concentration of powerful  $\cdot\text{OH}$  is an important factor to control the oxidation activity of the heterogeneous Fenton-like reaction, thus the purpose of this study was to investigate the influence of various operating parameters on the concentration of  $\cdot\text{OH}$  in a goethite catalyzed Fenton-like reaction. Goethite chosen as the catalyst in this study for its ubiquity in the environment and high catalytic activity in the Fenton-like reaction (Lin et al., 2014, 2015). Effects of operating parameters such as initial coumarin concentration, goethite dosage,  $\text{H}_2\text{O}_2$  dosage, solution pH on the amounts of  $\cdot\text{OH}$  generation have been quantitatively discussed. Considering that inorganic anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , etc.) are always present in wastewater or soils, we also examined the effect of anions on  $\cdot\text{OH}$  formation in this system.

## 2. Experimental

### 2.1. Materials

Goethite ( $41.6 \text{ m}^2 \text{ g}^{-1}$  surface area) was synthesized according to the method described by Schwertmann and Cornell (2000). HPLC-grade methanol was obtained from Merck (Darmstadt, Germany). COU ( $\geq 99\%$ ) and 7-HC (99%) were purchased from Sigma-Aldrich and were used without further purification. All other reagents such as  $\text{HClO}_4$ ,  $\text{NaOH}$ ,  $\text{NaClO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaH}_2\text{PO}_4$ ,

$\text{NaCl}$ ,  $\text{NaNO}_3$ , and  $\text{H}_2\text{O}_2$  (30 wt%) were obtained from Shanghai Chemical Factory (Shanghai, China). All solutions were prepared by using ultrapure water obtained from a Milli-Q Advantage A10 water purification system (Millipore, Bedford, MA).

### 2.2. Experiments and adsorption measurements using the heterogeneous Fenton-like system

In the present study, the  $\cdot\text{OH}$  concentration was determined via analyzing the generation amount of 7-HC, as described by Czili and Horváth (2008) and Maezono et al (2011). Specifically, a proportion of the  $\cdot\text{OH}$  that were continuously generated during the Fenton-like process could be trapped by the COU to form the only fluorescent product 7-HC whose concentration can be taken as a cumulative measurement of the  $\cdot\text{OH}$  produced throughout the reaction time.

All experiments were carried out in the 500 mL brown, sealed borosilicate flasks at  $25^\circ\text{C}$  under constant stirring (150 rpm). First, 200 mL of COU solution was added to the reaction vials. A specified amount of goethite was added to the flask, and the pH was adjusted to 3–7 by using  $0.1 \text{ mol L}^{-1} \text{ HClO}_4$  or  $0.1 \text{ mol L}^{-1} \text{ NaOH}$  solutions.  $\text{H}_2\text{O}_2$  (30 wt%) was introduced into the flasks to initiate the reaction. At a designated time, 4 mL of the solution were immediately collected by syringe and subsequently filtered through a  $0.45 \mu\text{m}$  polytetrafluoroethylene membrane, and 1 mL of methanol was added to the filtrates to quench the reaction. The concentrations of COU and 7-HC in the filtrates were measured by HPLC.

Adsorption experiments were performed at pH 3 and goethite concentration of  $1 \text{ g L}^{-1}$ . The COU concentration ranged from  $1 \times 10^{-5}$  to  $4 \times 10^{-3} \text{ mol L}^{-1}$ . The mixtures were stirred, and sample aliquots were collected and filtered at a designated time, as described above. The observed equilibrium time for COU sorption was 45 min. The percent removal of COU by adsorption decreased with increased in COU concentration; about 4% of the initial concentration ( $1 \times 10^{-5} \text{ COU mol L}^{-1}$ ) was adsorbed on goethite. These results indicate that COU adsorption had a negligible effect on the quantification of  $\cdot\text{OH}$  generated by the system. Each experiment was performed in triplicate, and standard deviation is shown.

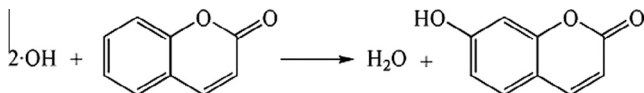
### 2.3. Analysis

The 7-HC concentration was analyzed on a Waters 2695 Alliance system (Milford, MA, USA) equipped with a 2475 multi-wavelength fluorescence detector. The excitation and emission wavelengths were set at 332 and 456 nm, respectively. The COU concentration was analyzed on the same system equipped with a Waters 2996 photodiode array detector set at a wavelength of 275 nm and a Phenomenex Gemini C18 column ( $150 \text{ mm} \times 4.6 \text{ mm I.D.}$ ,  $5 \mu\text{m}$ ) coupled with a Phenomenex Gemini C18 guard cartridge ( $4.0 \text{ mm} \times 3.0 \text{ mm I.D.}$ ). The column temperature was set at  $30^\circ\text{C}$ . All analyses were performed by isocratic elution using a mobile phase of HPLC-grade methanol and 0.5% acetic acid solution (30:70, v/v) at a flow rate of  $0.8 \text{ mL min}^{-1}$ . The injection volumes for COU and 7-HC were 10 and 1  $\mu\text{L}$ , respectively. External standard method was used for both qualitative and quantitative analyses. The retention times of COU and 7-HC were about 5.5 and 10.7 min, respectively.

## 3. Results and discussion

### 3.1. Preliminary observations

Since the concentration of trapping agent will affect the  $\cdot\text{OH}$  capture rate and efficiency as reported in previous studies (Tai



**Scheme 1.** Formation of 7-hydroxycoumarin in the reaction of coumarin with hydroxyl radical.

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