



Research article

EDTA-Fe(III) Fenton-like oxidation for the degradation of malachite green

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ABSTRACT

Industrial waste, urban sewage and aquaculture have led to severely increased grades of environment pollutants such as dyes, pesticides and fertilizer. The use of technologies for purifying contaminated waters can be difficult and toxic due to the anti-photolysis, anti-oxidation and anti-bio-oxidation characteristics of organic pollutants, and there is therefore a significant need for new approaches. Here, we report methods of Fenton oxidation and EDTA-Fe(III) Fenton-like oxidation which can be used to degrade malachite green (MG: a dye and antibiotic-like substance) from contaminated water. Compared with the degradation rate (59.34%) of the Fe(III)/H₂O₂ Fenton process, the EDTA-Fe(III) Fenton-like oxidation got a better degradation rate (92.7%) at neutral pH conditions. By conducting a series of parallel controlled experiments (changing parameters such as the reactant concentration, temperature, and pH), we report the relationships between the degradation effect and different parameters, and we fitted their pseudo first order kinetic curves. Furthermore, we repeated to adjustment of the concentrations of MG in solutions to test the cycle performance and catalytic activities of EDTA-Fe(III)/H₂O₂ system and it showed good repeatability in the first five rounds and all of them keep the degradation efficiencies greater than 80%. By conducting comparative spin-trapping electron paramagnetic resonance (EPR) experiments, we showed indirectly that the ·OH contributes to the degradation of MG. Additionally, the results of the EPR experiments showed that EDTA contributes to the generation of ·OH in the EDTA-Fe(III)/H₂O₂ Fenton-like system. By conducting total organic carbon (TOC) analysis experiments, we found that EDTA was also oxidized to some extent during the degradation of MG. In all, the findings of this work widen the range of the optimal pH values up to neutral condition for degradation of MG by use of EDTA-Fe(III) Fenton-like system. And this system could be used as one approach for the degradation of organic pollutants at neutral conditions and provide some initial information regarding EDTA-Fe(III) Fenton-like oxidations. It's significant for the expansion of the homogenous Fenton-like family and its application in the field of water treatment.

1. Introduction

Water pollution affects millions of people worldwide and has become a major global risk results in breeding diseases, death and natural catastrophes (Shlomo et al., 2009; Johnston et al., 2011; Shannon et al., 2008; Bolisetty and Mezzenga, 2016; Zhao et al., 2018; Jinisha et al., 2018; Gozzi et al., 2018). It also affects plants and organisms living in lakes, rivers and oceans, and it may harm human beings. The major sources of water pollution are unregulated industries such as aquaculture, farm production and the paper industry, from which increasing amounts of toxic pollutants (including organic and inorganic pollutants) are put into water resources without treatment (Mearns et al., 2015; La Riviere, 1989; Banks et al., 1997; Rabbani et al., 2015; Bisschops and Spanjers, 2003; Rozzi et al., 1999; Fernandez et al., 2018;

Fei et al., 2018; Dai et al., 2018). Among these pollutants, high concentrations of organic pollutants may have a long-term negative impact on water. As a polycyclic aromatic hydrocarbon refractory organic compound, malachite green (MG) is usually used as a dyestuff or controversially applied as an antibiotic in aquaculture (Gessner and Mayer, 2000; Srivastava et al., 2004). It is traditionally used as a dye for materials such as paper, leather and cloth, and millions of kilograms of MG are produced annually for these purposes (Gessner and Mayer, 2000). As an antibiotic, it is widely used against Saprolegnia and Ichthyophthirius multifiliis, which infects fish eggs in commercial aquacultures (Srivastava et al., 2004).

However, MG is highly toxic to living organisms, can eventually reduce their growth, fertility rate and food intake, and possesses carcinogenic properties (Culp et al., 1999). Therefore, the use of MG has

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been forbidden in the United States and in many other countries (Cha et al., 2001). Several methods exist to remove MG from contaminated water, and all are associated with specific advantages and disadvantages. Physical methods (such as adsorption, filtration and coagulation) require simple equipment, simple operation and established technology (Andreoli and Sabogal-Paz, 2017; Gottfried et al., 2008). However, these methods transfer organic matter from the liquid phase to the solid or gaseous phase and may produce secondary pollutants in the form of high quantities of sludge (Kurniawan et al., 2006; Loh, 2013; Hasheminasab et al., 2014). Biological methods (such as aerobic and anaerobic methods) are associated with the biochemical oxygen demand (BOD) in wastewater and show dissatisfactory performance in coping with the degradation of toxic refractory organics (Onodera et al., 2015; Guo et al., 2012). Furthermore, the microbial systems in biological methods face several problems associated with objective change factors and nutrition system maintenance (West, 2013).

To overcome the above problems, several groups have attempted to develop a variety of new technologies. Of these technologies, the Fenton method has widely been used due to its wide treatment range and high efficiency (Aplin and Waite, 2000; Huang et al., 1993; Coria et al., 2018; Caram et al., 2018; Brindha et al., 2018). Fenton's reagent is a solution of hydrogen peroxide with Fe(II) as a catalyst that is used to oxidize contaminants or waste water (Walling, 1975; Kuo, 1992; Lefebvre and Legube, 1990; Kim et al., 2004; Aboudalle et al., 2018). Fe(II) is oxidized by hydrogen peroxide to Fe(III), forming a hydroxyl radical ($\cdot\text{OH}$) and a hydroxide ion in the process. Fe(III) is then reduced back to Fe(II) by another molecule of hydrogen peroxide, forming a hydroperoxyl radical ($\text{HOO}\cdot$) and a proton. The net effect is a disproportionation of hydrogen peroxide to create two different oxygen-radical species, with water ($\text{H}^+ + \text{OH}^-$) as a byproduct, and then the oxygen-radical groups are involved in the organic decomposition reaction (Walling, 1975).

In comparison with other oxidants, the hydroxyl radical produced by Fenton's reagent has a higher oxidation electrode potential (Table S1) (Walling, 1975; Liu et al., 2014). However, in the traditional water treatment process, the optimum pH value range of Fenton oxidation is narrow (near 3) (Kuo, 1992; Lefebvre and Legube, 1990; Kang and Chang, 1997; Kavitha and Palanivelu, 2005; Rivas et al., 2004; Yun and Hwang, 2000; Mousset et al., 2018; Li et al., 2018), which greatly interferes with the development of Fenton technology.

Herein, we used malachite green (MG) as a target pollutant to investigate the degradation performance of a facile process of Fenton oxidation ($\text{Fe(III)/H}_2\text{O}_2$) and Fenton-like oxidation ($\text{EDTA-Fe(III)/H}_2\text{O}_2$) under neutral conditions (near 7) and different variable levels of reactants. Ethylenediamine tetraacetic acid (EDTA) is a good chelate and shows a desirable performance in forming chelates with almost all metal ions. Research have reported in many papers that EDTA can stabilize Fe(III) in Fenton-like solutions, which can even widen the range of the optimal pH values up to neutral condition (Xia et al., 2018). However, few reported the stability of EDTA and its own degradation in Fenton reaction processes. Considering the organic properties of EDTA, we believe that this question needs to be addressed. In this study, we investigated the effects of EDTA as a complexing agent on the degradation of MG and its inferred mechanism. The experiments confirmed that the $\text{EDTA-Fe(III)/H}_2\text{O}_2$ system contributes to the generation of $\cdot\text{OH}$ during Fenton oxidation, and at the same time, EDTA may also self-degrade under the actions of $\cdot\text{OH}$. This assessment was further supported by using a UV–Vis spectrophotometer, total organic carbon analyser and electron paramagnetic resonance (EPR). The findings of this study could be used as one approach for degradation of organic pollutants at neutral condition. It's significant for the expansion of the homogenous Fenton-like family and its application in the field of water treatment.

2. Experimental methods

2.1. Chemicals and materials

Analytical grade malachite green (MG) with 95% purity and iron chloride hexahydrate ($\text{FeCl}_3\cdot 6\text{H}_2\text{O}$) were obtained from Aladdin. A 30% aqueous solution of hydrogen peroxide was purchased from Sinopharm Chemical Reagent (SCR). The other chemicals used in the study were also analytical-grade and purchased from Aladdin. Milli-Q water with a resistivity higher than $18.25 \text{ M}\Omega \text{ cm}$ at RT was used in all experiments. Ferric chloride (FeCl_3) and ethylenediaminetetraacetic acid disodium (EDTA) stock solutions were prepared with a specific concentration of $1000 \mu\text{M}$ by dissolving specific quantities ($0.1352 \text{ g Fe(III) chloride hexahydrate}$ and 0.1861 g EDTA) into 500 mL deionized water, and the pH value was adjusted to 7 by using 0.1 mol/L NaOH solution. Malachite green (MG) stock solution with a given concentration of $100 \mu\text{M}$ was prepared by dissolving 0.0116 g of malachite green (MG) into 250 mL of deionized water. Both of them were stored under dark conditions at 4°C for further use.

2.2. Comparison of the degradation effect of MG by $\text{Fe(III)/H}_2\text{O}_2$ and $\text{EDTA-Fe(III)/H}_2\text{O}_2$

In this study, we tested the effect of EDTA in the $\text{Fe(III)/H}_2\text{O}_2$ system on the degradation of MG. In detail, we divided the experiments into two groups; the concentration of FeCl_3 in the first group was $500 \mu\text{M}$, while the concentration of EDTA-Fe(III) was $500 \mu\text{M}$ ($\text{EDTA: FeCl}_3 = 1:1$) in the second group. Furthermore, the initial concentrations of MG and H_2O_2 were 10 and 20 mM , respectively. Two groups were put in a shaker at 180 rpm under room temperature for further study.

2.3. Degradation of malachite green by $\text{EDTA-Fe(III)/H}_2\text{O}_2$

The EDTA-Fe(III) and H_2O_2 concentrations in the kinetic study of MG degradation were $500 \mu\text{M}$ and 20 mM , respectively, with a $10 \mu\text{M}$ initial MG concentration. In detail, kinetics experiments were conducted at 20°C and $\text{pH} = 7.0$ in a shaker, the solution was shaken at 180 rpm , and water samples were withdrawn intermittently and passed through a $0.22 \mu\text{m}$ cellulose membrane. Then, they were analysed using a UV–Vis spectrophotometer (UV-2550, Shimadzu, Japan) in order to calculate their time-dependant degradation capacities.

A UV–Vis spectrophotometer was also used in the follow-up study to test the degradation effect of MG and the degradation kinetics under other factors such as pH, temperature and reactant concentration. The degradation of MG was followed photometrically at $\lambda = 617 \text{ nm}$ using a UV–Vis spectrophotometer.

The degradation isotherms were conducted with an EDTA-Fe(III) concentration of $500 \mu\text{M}$, H_2O_2 concentration of 20 mM and MG concentration of $10 \mu\text{M}$. Then, the solutions were put in a shaker at 180 rpm , and the specific temperatures were $20, 30, 40$ and 50°C . Water samples were withdrawn intermittently and filtered to test the degradation effect.

The effect of the pH value was investigated to test the degradation performance under different acidity conditions (Kuo, 1992; Kim et al., 2004; Kishimoto and Nakatsubo, 1998; Bigda, 1995). In detail, with an EDTA-Fe(III) concentration of $500 \mu\text{M}$, H_2O_2 concentration of 20 mM and MG concentration of $10 \mu\text{M}$, the pH values of the water samples were adjusted at 3 to 7 and were then placed in a shaker at 180 rpm at room temperature (RT).

The effect of reactant concentration was investigated to test degradation influence under different reactant doses. In this study, we changed the concentration of several reactants (MG, FeCl_3 , H_2O_2). In detail, the FeCl_3 concentrations were $100, 250, 500$ and $750 \mu\text{M}$; the H_2O_2 concentrations were $10, 20, 30$ and 40 mM ; and the MG concentrations were $5, 10, 20$ and $30 \mu\text{M}$. All batches were univariate

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