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Enhancement of Fenton oxidation for removing organic matter from hypersaline solution by accelerating ferric system with hydroxylamine hydrochloride and benzoquinone

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ABSTRACT

Fenton oxidation is generally inhibited in the presence of a high concentration of chloride ions. This study investigated the feasibility of using benzoquinone (BQ) and hydroxylamine hydrochloride (HA) as Fenton enhancers for the removal of glycerin from saline water under ambient temperature by accelerating the ferric system. It was found that organics removal was not obviously affected by chloride ions of low concentration (less than 0.1 mol/L), while the mineralization rate was strongly inhibited in the presence of a large amount of chloride ions. In addition, ferric hydrolysis–precipitation was significantly alleviated in the presence of HA and BQ, and HA was more effective in reducing ferric ions into ferrous ions than BQ, while the H₂O₂ decomposition rate was higher in the BQ-Fenton system. Electron spin resonance analysis revealed that OH[•] production was reduced in high salinity conditions, while it was enhanced after the addition of HA and BQ (especially HA). This study provided a possible solution to control and alleviate the inhibitory effect of chloride ions on the Fenton process for organics removal.

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Introduction

The Fenton process is one of the most promising advanced oxidation technologies due to its advantages of high performance, process simplicity, low cost and low reagent toxicity (Zhang et al., 2013). The process depends on the in situ production of hydroxyl radicals, which can effectively destroy and mineralize many organic contaminants in water (Kwon et al., 1999;

Tang and Huang, 1996). Generally, the efficiency of an advanced process is related to the amount of hydroxyl radicals (OH[•]) produced during the treatment (Pignatello et al., 2006). OH[•] production is mainly dependent on ferric system reactions (Reactions (2) and (3)), which constitute the rate-limiting step in the whole Fenton process (Neyens and Baeyens, 2003; Pignatello et al., 2006). The Fenton (Reaction (1)) and Fenton-like reactions for OH[•] generation are strongly dependent on water pH. Oxidative degradation of organic contaminants by Fenton reactions usually gives optimal results at a pH of approximately 3 (Lu et al., 2005; Pignatello et al., 2006). The Fe³⁺ catalyst begins to precipitate above pH 3 in the form of relatively inactive hydrous oxyhydroxides, while ferric system

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reactions are inhibited at a pH level of less than 3 (Grebel et al., 2010; Zhang et al., 2014).



A high content of inorganic salts, especially sodium chloride, is contained in many wastewaters, such as the water from the manufacture of pesticides, resins, herbicides, pharmaceuticals and dyes. Industrial processes, such as oil and gas recovery or crystallization, also generate wastewater of high salinity. Saline wastewater with hydrocarbons can also be found in petroleum-based industry sites, as a result of petroleum spills in the sea or over coastal areas or as a result of accidents during transportation (Bacardit et al., 2007). The presence of inorganic anions (chloride ions and sulfate ions) may weaken the efficiency of oxidation processes based on hydroxyl radicals for the oxidative degradation of organic contaminants (Ratanatamskul et al., 2010). The influence of chloride ions on the Fenton mechanism is attributable to the complexation of $\text{Fe}^{2+}/\text{Fe}^{3+}$ with Cl^- and the scavenging of hydroxyl radicals, which may generate less-reactive chloride radicals rather than hydroxyl radicals (Machulek et al., 2007; Zhang et al., 2013).

Currently, many technologies have been developed to improve Fenton oxidation for removing organic contaminants from aqueous solutions, such as photo-assisted (Al Momani et al., 2006; Kusic et al., 2006; Lau et al., 2002), microwave-enhanced (Liu et al., 2013; Yang et al., 2009), heating (Pliego et al., 2012; Zazo et al., 2011), and quinone (Chen and Pignatello, 1997; Gomez-Toribio et al., 2009) and hydroxylamine hydrochloride (HA) (Chen et al., 2011) redox cycling. As mentioned above, a major drawback of the Fenton system has been the accumulation and hydrolysis-precipitation of ferric ions, which could further slow down the whole Fenton process. Some studies attempted to improve the conversion rate from Fe(III) to Fe(II) with addition of reductants to enhance the organic removal efficiency of Fenton process. Chen et al. (2011) found that the presence of hydroxylamine hydrochloride (NH_2OH , HA) in Fenton's reagent accelerated the Fe(III)/Fe(II) redox cycles, leading to relatively steady Fe(II) recovery, and thus, increased reaction rates. In addition, Chen and Pignatello (1997) demonstrated that the hydroquinones could also reduce Fe(III) to Fe(II), and quinones acted as electron-transfer catalysts between dihydroxycyclohexadienyl radicals – the $\cdot\text{OH}$ adducts of phenols – and Fe(III) through a semiquinone radical.

In our previous study, the thermal Fenton process was used to remove organic contaminants (mainly composed of glycerin) from wastewater from epoxy resin manufacturing (Zhang et al., 2013). Because the process was still very complicated and heating was required to improve the organic removal efficiency, we attempted to use HA and benzoquinone (BQ) as Fenton enhancers to remove glycerin from saline water at ambient temperature. The aims of this study are to (1) investigate the organic removal efficiency enhancement by the addition of HA and BQ; (2) understand the effect of HA and BQ addition on the

kinetic variation in H_2O_2 and iron speciation during the Fenton process; and (3) examine the effects of HA and BQ addition on the production of hydroxyl radicals to unravel the underlying mechanism.

1. Materials and methods

1.1. Materials

All of the chemical reagents used in this study were of analytical grade. Hydrogen peroxide (H_2O_2), iron sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), potassium titanium oxalate, ammonium acetate, ammonium ferrous sulfate, ammonium fluoride, phenanthroline, potassium persulfate, sodium chloride, sulfamic acid, sodium nitrate, and sodium acetate were purchased from Sinopharm Pharmaceutical Co., Ltd. BQ and HA were supplied by Aladdin Industrial Inc. (Shanghai, China). 5-Tert-butoxycarbonyl-5-methyl-1-pyrroline-N-oxide (DMPO) was purchased from J&K Scientific Ltd.

1.2. Experimental procedure

1.2.1. Fenton oxidation procedure

All of the experiments were carried out at $20 \pm 0.5^\circ\text{C}$ in 500-mL triangular flasks under constant stirring with a PTFE-coated magnetic stirrer in ultrapure water. Glycerin solution (100 mg/L as total organic carbon (TOC)) was prepared as a target organic substance. The chloride ions introduced into the reaction system were from sodium chloride. BQ or $\text{NH}_2\text{OH} \cdot \text{HCl}$ and Fe(II) at the desired concentrations were spiked into 500 mL of the reaction mixture. Each run was initiated by adding the desired dosage of H_2O_2 . The pH changed by less than 0.2 units during the process. Samples were withdrawn at set intervals and quenched by raising the solution pH to approximately 7–9 before the TOC and H_2O_2 analysis.

1.2.2. Analytical methods

The H_2O_2 concentrations were measured by a titanium potassium oxalate colorimetric method using a Hitachi U 2910 UV-vis spectrometer at a wavelength of 510 nm. A torch TOC analyzer (Tekmar, Torch, USA) was used for TOC determination. Ferrous ion was determined with the modified O-phenanthroline spectrophotometric method described by Chen and Pignatello (1997). Five millimolar NH_4F was mixed with an equal volume of reaction solution, and the absorbance at 510 nm was measured using 10-cm quartz sampling cells. The strong complexation of Fe^{3+} by F^- was used to stop any further conversion of Fe^{3+} after the reaction. BQ was analyzed by HPLC on a 5 μm , 25 cm \times 5 mm Spherisorb ODS-2 C-18 column and detected with a diode array UV/vis detector (Hewlett-Packard, Palo Alto, USA). The mobile phase was 30% acetonitrile/70% water with 0.08% trifluoroacetic acid.

A nitroxide spin-trapping agent DMPO was used in the electron spin resonance (ESR) process. The chemical solutions of H_2O_2 , NH_2OH , Fe(II) and DMPO ($C_{\text{DMPO}} = 25 \text{ mmol/L}$) were mixed. Ten seconds after mixing, the sample solution was transferred into a 100- μL capillary tube that was then fixed in the cavity of the EPR spectrometer. The EPR spectrum was measured with an EPR spectrometer (A200 ESP 300E

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