Chemical Engineering Journal 313 (2017) 938–945

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Comparison of Fenton, UV-Fenton and nano-Fe_3O_4 catalyzed UV-Fenton in degradation of phloroglucinol under neutral and alkaline conditions: Role of complexation of Fe^{3+} with hydroxyl group in phloroglucinol

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HIGHLIGHTS

- Phloroglucinol was able to be efficiently degraded under initial pH from 7.0 to 9.0 by Fenton-based processes.
- Fenton, UV-Fenton and nano-Fe_3O_4 catalyzed UV-Fenton were compared.
- Fe(III)-phloroglucinol complex and significant pH decrease of reaction solution were observed.

ARTICLE INFO

Article history:
Received 30 August 2016
Received in revised form 25 October 2016
Accepted 30 October 2016
Available online 1 November 2016

Keywords:
Fenton
UV-Fenton
Nano-Fe_3O_4 catalyzed UV-Fenton
Phloroglucinol degradation
Fe(III)-phloroglucinol complex

ABSTRACT

Phloroglucinol degradation at initial pH from 7.0 to 9.0 has been investigated in Fenton, UV-Fenton and nano-Fe_3O_4 catalyzed UV-Fenton (Hetero-Fenton). Within the reaction time given in this study (not more than 4 h), 150 $mg \cdot L^{-1}$ phloroglucinol was completely removed, while there was some difference in TOC removal efficiency: about 90% for UV-Fenton, nearly 60% for Fenton and Hetero-Fenton. Increasing initial pH from 7.0 to 9.0, there was an obvious decline in the degradation rate. The average values of H_2O_2 utilization efficiency were 0.65 ± 0.01 for Fenton, 0.66 ± 0.09 for UV-Fenton, and 1.35 ± 0.15 for Hetero-Fenton, suggesting Hetero-Fenton required less H_2O_2 consumption. Solution pH could decrease to strongly acidic conditions of $pH < 4.0$ and the generation of organic acids including formic, acetic, oxalic, and maleic acids depended on the type of oxidation process. The spectrophotometric study showed phloroglucinol would complex with Fe(III) at pH 7.0 to form homogeneous aqueous solution which exhibited strong light absorption in the wavelength range of 400 nm to 600 nm. Therefore, formation of Fe(III)-phloroglucinol complex and pH decrease to strongly acidic condition played important roles in Fenton degradation under neutral and alkaline pH. The result of effect of pollutant content showed phloroglucinol at lower concentrations of 20 and 50 $mg \cdot L^{-1}$ could still be completely removed by all Fenton-based systems at pH 7.0, however, in Fenton with 20 $mg \cdot L^{-1}$ phloroglucinol, a significantly decreased degradation rate was observed due to the slowdown of pH drop and inhibited formation of Fe(III)-phloroglucinol complex.

1. Introduction

Phenolic compounds are common organic contaminants of interest in various industrial wastes [1], most of which show low biodegradability, posing serious risk to environmental and human health once discharged into natural water. Due to the recalcitrant nature of some phenolic compounds, the degradation rate by conventional biological treatment is too slow [2]. Phloroglucinol, a phenol derivative that is used in the synthesis of pharmaceuticals and explosives, is relatively hard to biodegradation. The benzene nucleus of phloroglucinol furnishes some of this inertness because of its resonance structure stability and its meta substituted hydroxyl groups [3]. Phloroglucinol concentration can reach up to 5.0 $g \cdot L^{-1}$ in wastewater from a phloroglucinol manufacturing plant and phloroglucinol with average concentration of 0.174 $\mu g \cdot L^{-1}$ was also detected in China's Xiangjiang River [4,5].

The production of $^{\cdot}OH$ at ambient temperature and pressure in the presence of H_2O_2 and Fe^{2+}, a powerful reactant that is able to

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http://dx.doi.org/10.1016/j.cej.2016.10.133
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degrade a wide variety of xenobiotics at diffusion-limited reaction rates, accounts for the widespread use of the Fenton reaction among advanced oxidation processes (AOPs) for the abatement of recalcitrant compounds in water and wastewater [6,7]. Esplugas et al. [8] compared various AOPs for degradation of phenol in aqueous solution and found Fenton's reagent showed the fastest degradation rate, 40 times higher than UV process and photocatalysis with TiO_2 and 5 times higher than ozonation. The optimal pH for Fenton reaction usually lies in the range of 2–4 [9]. While ferrous salts are quite soluble in water even at neutral pH, ferrous ion will tend to coprecipitate with Fe(III) oxyhydroxides if the two ions are present together and the pH is brought up above 3 [6]. The requirement in most cases of Fenton application for mildly acidic is one of the major drawbacks that limit its widespread acceptance. Great efforts have been made to extend the pH range over which Fenton can perform well. Many chelating ligands like nitrilotriacetic acid, 1,2-dihydroxybenzoic acid, and picolinic acid are used to maintain soluble iron at near neutral pH [6], thus effectively catalyzing Fenton reaction over a wide range of pH. Polyhydroxy aromatic compounds as chelating agents may be more active by virtue of their ability to reduce Fe(III). On the other hand, addition of the chelating agent may scavenge $HO^{\cdot}$, resulting in a decreased proportion of $HO^{\cdot}$ used for target pollutant removal. A lot of studies have shown that Fe(III) would be chelated with some phenolic compounds [10,11]. Aggarwal and coworkers [12] found the formation of Fe (III) complexes with phenolic acids like l-hydroxy-2-naphthoic acid, sulpho-p-cresotic acid and acetyl-p-cresotic acid and the composition of violet colored complex in each system was 1:1. Tannins are plant-based polyphenolic compounds and strong transition metal chelating and reducing agents. Bolobajev and coworkers [13] reported presence of tannic acid would enhance Fenton degradation of 2,4,6-trichlorophenol by its chelating and reducing activity with ferric iron. However, there is scarce study to investigate Fenton degradation of phenolic contaminants under neutral and alkaline conditions by virtue of soluble phenol-Fe(III)-complexes.

Heterogeneous Fenton using solid iron compounds or solid materials rich in iron is an alternative way to expand the active pH range. Several studies have shown that iron contained catalyst, usually in the form of nano-particles, can effectively activate H_2O_2 at neutral pH to degrade organic compounds [14–17]. Although oxidation is generally much slower than the corresponding solution reaction at the same reagent concentrations, the heterogeneous reactions are sometimes more efficient; that is, they consume less H_2O_2 per mole contaminant degraded. Tian et al. [18] observed using $Fe_2(MoO_4)_3$ catalyzed Fenton-like for Acid Orange II removal, the reduction of 100 $mg \cdot L^{-1}$ Acid Orange II reached 94.1% within 60 min under initial pH 6.7, and the efficiency was slightly affected by pH ranging from 3 to 9. Heterogeneous Fenton can perform with or without UV irradiation. UV introduction can drastically reduce the H_2O_2 dosage required to achieve the same removal efficiency as without UV [14]. This is most likely due to the production of ferric complexes with intermediates of carboxylic acids on the surface of catalyst, then accelerating photoreductive dissolution of iron in the presence of UV [19], resulting in enhanced homogeneous photo-Fenton reaction in solution. It is widely accepted that UV enhancement in photo-Fenton is due to the enhanced Fe(Π) redox cycle along with an increased yield of hydroxyl radical. Fe(III) complexes like $Fe(OH)^{2+}$ and R-CO_2-Fe(III) undergo ligand-to-metal charge transfer (LMCT) excitation, dissociating to give Fe(Π) and an oxidized ligand [6]. Photo-Fenton would consume less reagent concentrations than conventional Fenton reaction. In order to reduce the electric cost for artificial UV illumination, until recently, high intensity UV-LED (light-emitting diode) has been evaluated as an energetically efficient light source instead of conventional low or medium-pressure mercury lamp [20], implying UV-LED excited photo-Fenton would become a very promising technology for UV-based AOPs.

This study examined Fenton, UV-Fenton and nano-Fe_3O_4 catalyzed UV-Fenton for phloroglucinol degradation in aqueous solution at initial neutral and slightly alkaline pH for comparative purpose. The influences of initial solution pH (7.0, 8.0, 9.0) and phloroglucinol concentration (20, 50 and 150 $mg \cdot L^{-1}$) on treatment efficiency were assessed with respect to TOC removal and phloroglucinol reduction. The change of solution pH during treatment processes was monitored and carboxylic acids as intermediates including formic, acetic, oxalic and maleic acids were analyzed. At last, light absorption spectra of phloroglucinol alone and mixture of phloroglucinol and Fe^{3+} salt under pH 7.0 at the wavelength ranging from 190 nm to 1100 nm were evaluated to reveal the complexation of Fe^{3+} with hydroxyl group in phloroglucinol. This study will provide insight into the mechanism of phenolic pollutant degradation by Fenton under neutral and alkaline pH.

2. Experimental

2.1. Chemicals and materials

All reagents used in this study were analytical grade and were used after received. Nano-Fe_3O_4 with particle size of 50–100 nm, sodium formate, sodium acetate, sodium oxalate, maleic acid, methanol, acetonitrile and KOH solution for HPLC analysis were purchased from Sigma-Aldrich. Phloroglucinol, hydrogen peroxide (35% w/w), ferrous sulphate heptahydrate, dichloromethane, potassium titanium oxalate, perchloric acid, sulfuric acid, sodium hydroxide, potassium dichromate and silver sulphate were supplied by Shanghai Chemical Reagent Company (China). All solutions were prepared using ultra-pure water with resistance of 18.2 MΩ·cm.

2.2. Experimental procedure

Batch experiments were carried out in 1250 mL glass reactors covered on the outer wall with aluminum foil to avoid the interference of room solar light. Magnetic stirrer was used at the stirring velocity of 700 rpm to homogenize the reaction solution. The reaction volume was 1000 mL, and temperature was maintained at 25 ± 2 °C via a cooling water circulation system. The starting concentrations were 150 $mg \cdot L^{-1}$ for phloroglucinol and 495 $mg \cdot L^{-1}$ for H_2O_2, which corresponds to the stoichiometric amount of H_2O_2 necessary to oxidize phloroglucinol to CO_2 and H_2O. For catalysts, 175 $mg \cdot L^{-1}$ $FeSO_4 \cdot 7H_2O$ was added in homogeneous Fenton including Fenton and UV-Fenton, whereas 500 $mg \cdot L^{-1}$ nano-Fe_3O_4 in heterogeneous Fenton. In UV-based Fenton, a 10 W UVC-lamp (L: 220 mm, D: 25 mm, Konche, Shenzhen) was inserted into solution to provide irradiation of 220 ~ 275 nm. The initial pH value was adjusted at 7.0, 8.0 and 9.0, respectively, by $HClO_4$ and NaOH solutions. Samples were taken at fixed time intervals and filtered through 0.22 μm PES membrane for analysis·H_2O_2 concentration was instantly measured before addition of Na_2SO_3; Na_2SO_3 was added to the samples to stop continuing oxidation reaction, then waiting for analysis of COD, TOC and phloroglucinol concentration. Due to residual Na_2SO_3 in samples interfering with COD measurement, the samples would undergo air oxidation for 30 min under strongly acidic condition prior to COD analysis [21]. Each experiment was conducted in duplicate and the averaged data were presented. The standard deviations were always less than 10% unless otherwise stated.