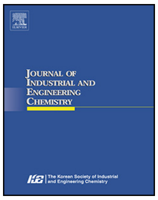
Journal of Industrial and Engineering Chemistry 21 (2015) 53–69

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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



Review

Review on the main advances in photo-Fenton oxidation system for recalcitrant wastewaters

Shima Rahim Pouran[1], A.R. Abdul Aziz*, Wan Mohd Ashri Wan Daud[2]

Chemical Engineering Department, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

ARTICLE INFO

Article history:
Received 10 February 2014
Received in revised form 5 May 2014
Accepted 5 May 2014
Available online 12 May 2014

Keywords:
Biodegradability enhancement
Chelating agents
Modified Fenton
Non-biodegradable wastewater

ABSTRACT

This paper reviews the main advances in photo-Fenton oxidation treatment for recalcitrant wastewaters. This oxidation method is able to produce biodegradable intermediates and mineralize such pollutants effectively when the main operational conditions are at optimum level. However, cost of the process is one of the main limitations. Several strategies have been put in practice to minimize cost and improve photo-Fenton efficiency primarily through application of heterogeneous catalysts and/or chelating agents. In addition, cost can be further reduced by applying solar energy and integrating biological treatment technologies in the treatment process.

Contents

1. Introduction

The rapid global economic growth has resulted in clean water crisis and environmental pollution since industrial revolution. Literature indicate an increasing trend in generation of wastewaters with recalcitrant characteristics from the many activities of

---

* Corresponding author. Tel.: +60 3 79675300; fax: +60 3 79675319.
E-mail addresses: rahimpooran@yahoo.com (S. Rahim Pouran), azizraman@um.edu.my, rshazrin@gmail.com (A.R. Abdul Aziz), ashri@um.edu.my (W.M.A. Wan Daud).
[1] Tel.: +60 3 796 75206; fax: + 60 3 796 75319.
[2] Tel.: +60 3 79675297; fax: + 60 3 79675319.

http://dx.doi.org/10.1016/j.jiec.2014.05.005
1226-086X/

industrial societies [1]. Recalcitrant compounds are chemicals that are to various degrees resistant to microbiological degradation in soil and water [2]. A large number of these pollutants are toxic in nature even at micro quantities [3]. Wastewaters containing these compounds are known to be high in chemical oxygen demand (COD) and low in biological oxygen demand (BOD). These non-biodegradable molecules enter the environment predominantly through industrial activities.

Currently, one of the fundamental concerns is water pollution abatement via effective treatment of wastewaters containing recalcitrant compounds. Biological methods can effectively treat wastewaters with high biodegradability ratio ($BOD_5/COD \geq 0.4$) [4]. However, in most industries, conventional treatment technologies cannot produce effluents that meet water quality criteria and effluent limitation guidelines for recalcitrant pollutants. Traditional treatment techniques only succeed in contaminants transfer from liquid phase to solid phase [5].

To effectively treat recalcitrant effluent, the scope should encompass degradation as well as mineralization of organic contaminants. That is conversion of probe molecule to its highest stable oxidation state: water, carbon dioxide, and the oxidized inorganic anions of any heteroatoms present, mainly to inorganic acids [6]; or to more easily degradable molecules, that can be removed biologically. Accordingly, advanced oxidation processes (AOPs) are considered as powerful methods for degradation of these pollutants due to their ability for removing almost any organic contaminant [5,7–11]. Glaze et al. [12] defined AOPs as water treatment processes at near ambient temperature and pressure that produce very active radicals for degradation of pollutants. In water/wastewater treatment, AOPs generally refer to a group of processes that cover O_3 and H_2O_2 as oxidants with assistance of light, catalyst (e.g. Fe^{2+}, Fe^{3+} and TiO_2), ultrasonic insertion and/or thermal input [13] and there are several combinations such as Fenton (H_2O_2/Fe^{+2}), photo-Fenton (H_2O_2/UV/Fe^{+2}), peroxidation combined with Ultraviolet light (H_2O_2/UV), Peroxone (O_3/H_2O_2), Peroxone combined with Ultraviolet light (O_3/H_2O_2/UV), O_3/UV system, $O_3/TiO_2/H_2O_2$ and O_3/TiO_2/Electron beam irradiation [8,14–16]. These oxidation processes are cost effective technologies and give rise to non-selective active species that oxidize a wide variety of non-biodegradable compounds. AOPs have been used at various scales for overall organic content (COD) reduction [17], specific pollutant destruction [11,16], sludge treatment [18–20], increase of bioavailability of recalcitrant organics [21], destruction of micropollutants [22,23] and color and odour removal [24].

Application of an AOP with potential for generating relatively higher amount of the radical is found to be more attractive in high-strength organic wastewaters. In this context, photo-Fenton (ph-F) process, an energetically improved Fenton process, has been established to treat this category of wastewaters. Several studies have been reported in literature on the successful application of ph-F for treatment of recalcitrant wastewaters exclusively or in conjugation with conventional biological technologies. The present study reviews the application of ph-F oxidation method for treatment of various recalcitrant wastewaters and evaluates its effectiveness in contaminant mineralization and biodegradability enhancement when coupled with biological or other conventional treatment methods. It also reviews the effects of different operational conditions on photo-Fenton oxidation efficiency of organic contaminant removal. Recent advances and developments for enhanced degradation of organic contaminants over broad pH values and cost minimization factors are also highlighted.

2. Fenton-based reactions

Fenton chemistry has been comprehensively explained in previously published reviews [6,25,26]. Accordingly, a brief introduction is presented in this review to clarify the following discussion. Fenton oxidation process is a catalytic reaction of H_2O_2 with iron ions [27] that predominantly produces $^{\bullet}OH$ radicals as the central oxidizing species [28], as shown in Eq. (1) [6]:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + \cdot OH \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2 \cdot + H^+ \quad (2)$$

The existence of $^{\bullet}OH$ radicals in Fenton reaction has been proven using spin-trapping experiments [29]. However, possibility of other mechanisms apart from free radical has also been proposed on account of captured complexes between iron and H_2O_2 in Fenton reaction medium using optical absorption measurements [30]. The Fenton process initiated by Fe^{3+} or other metals at low oxidation states such as Cu^{2+} and Co^{2+} is called Fenton-like reaction (Eq. (2)) [11]. Fenton-like reaction is of slower rate compared to Fenton reaction (42–79 L mol^{-1} S^{-1} vs. 0.002–0.01 L mol^{-1} S^{-1}). Similar conclusions have been obtained for C.I. Acid Orange 8 (AO8) and C.I. Acid Red 17 (AR17) degradation with both Fenton and Fenton-like processes [31]. In this study, decolorization efficiency for AO8 and AR17 was respectively 93% and 98% with Fenton oxidation, while the degradation efficiencies of 89% and 78% were obtained using Fenton-like process under the optimum conditions for both dyes.

Photo-Fenton (ph-F) process is combination of Fenton reagents (H_2O_2 and Fe^{2+}) and UV–vis radiation ($\lambda < 600$ nm) that gives rise to extra $^{\bullet}OH$ radicals by two additional reactions: (i) photo-reduction of Fe^{3+} to Fe^{2+} ions as shown in Eq. (3) [32] and (ii) peroxide photolysis via shorter wavelengths (Eq. (4)):

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH; \quad \lambda < 580\,\text{nm} \quad (3)$$

$$H_2O_2 + h\nu \rightarrow 2 \cdot OH; \quad \lambda < 310\,\text{nm} \quad (4)$$

The photo-generated ferrous ions enter Fenton reaction (Eq. (1)) to produce supplemental hydroxyl radicals. Consequently, the oxidation rate of ph-F is accelerated compared to Fenton process [33]. In addition to higher oxidation rate, there is a sizable drop in total iron utilization and sludge generation in ph-F compared to Fenton reaction [34]. Furthermore, it has been established that ph-F using both solar or UV light, has significant effects on inactivation of microorganisms in polluted water bodies for sustainable reuse for drinking and/or irrigation purpose. However, the efficacy of the process is greatly dependent on the microorganism present [35,36] and the type of water under treatment [23,37]. For illustration, in a study, the spores of *F. solani* were found to be more resistant to solar treatment compared to the vegetative cells of *E. coli* [35,36]. In another study, clarithromycin resistant bacteria could be completely removed from distilled and simulated wastewaters but the removal efficiency dropped to 77% in real effluent [37]. In addition, it has been reported that Fe^{3+} (5 mg L^{-1}) in combination with H_2O_2 (10 mg L^{-1}) and Solar Energy (2.5 kJ L^{-1}) had the highest inactivation rate within 60 min for *Phytophthora capsici* zoospores in distilled water in a solar-bottle-reactor followed by H_2O_2/solar > Fe^{2+}–H_2O_2/solar ≥ Fe^{3+}/solar > Fe^{2+}/solar > solar photo-inactivation [38].

Hydroxyl radicals, with high oxidation potential (E_0 = 2.80 V), are able to break down recalcitrant compounds such as phenolic and chlorinated compounds [11,39,40]. Several studies have been conducted to examine the effectiveness of ph-F for degradation of various recalcitrant compounds. Table 1 provides an overview of the recalcitrant compounds degraded by photo-Fenton process and the mineralization efficiency of these chemical pollutants under studied optimum conditions.