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Heterogeneous fluidized-bed Fenton process: Factors affecting iron removal and tertiary treatment application

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HIGHLIGHTS

- Key factors affecting iron removal in fluidized-bed Fenton have been revealed.
- Removal of organics and iron could be obtained by fluidized-bed Fenton reactor.
- Fluidized-bed Fenton was an effective tertiary treatment for pulp & paper wastewater.

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ABSTRACT

In this research, the factors affecting iron removal were determined for a fluidized-bed Fenton reactor using construction sand as the medium. Most of the particulate iron could be removed by the fluidized-bed Fenton process under optimum conditions. The surface area of the fluidized media available for iron crystallization via heterogeneous nucleation and hydraulic retention time were found to be the key factors controlling the iron removal efficiency. Bed expansion of 50% was sufficient for satisfactory iron removal. Further bed expansion did not provide any significant improvement, and could deteriorate the iron removal performance through scouring effect and increase energy consumption. Formic acid, one of the carboxylic intermediates from organic pollutant oxidation with hydroxyl radicals, remarkably deteriorated the iron removal performance. This is because it not only increased iron solubility through complexation but also hindered heterogeneous nucleation of ferric hydroxide onto the fluidized material. Therefore, in terms of iron removal, the fluidized-bed Fenton process should be applied to treat low-strength wastewater or to serve as a polishing unit to limit the formation of Fe^{3+}-chelating intermediates. As a tertiary treatment unit, the fluidized-bed Fenton reactor could successfully and consistently reduce the COD and color of secondary effluents from pulp and paper mills to below the new and more stringent standards of 120 mg/L and 300 ADMI, respectively. Depending on the water characteristics, total iron removal of 53–81% could be achieved at the optimum retention time.

1. Introduction

The Fenton process is an advanced oxidation process that produces powerful and effective hydroxyl radicals ($OH^{\cdot}$) [1,2]. It has been increasingly used in the treatment of contaminated water and soil. The reagents of the conventional Fenton process include H_2O_2 and Fe^{2+}, which can react to generate highly reactive hydroxyl radicals in a complicated and sequential manner according to Pignatello [3]. Only the equations related to this study are shown below.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3} + OH^{\cdot} + OH^{-};\ k_1 = 76\,M^{-1}s^{-1} \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^{+};\ k_2 = 0.02\,M^{-1}s^{-1} \quad (2)$$

$$OH^{\cdot} + Pollutant \rightarrow \rightarrow\rightarrow CO_2 + H_2O \quad (3)$$

$$Fe^{3+} + 3OH^{-} \rightarrow Fe(OH)_{3(s)}/FeOOH.\ H_2O_{(s)};\ K_{sp} = \{Fe^{3+}\}\{OH^{-}\}^{3} = 4 \times 10^{-38} \quad (4)$$

The Fenton reagents are environmentally friendly. Iron is very abundant and non-toxic; H_2O_2 is relatively easy to transport and handle and is environmentally benign at low concentrations [4]. The conventional Fenton process is simple, effective, and requires low capital investment [5]. However, the process has a few drawbacks. One of the most serious disadvantages of the Fenton process is the generation of large amounts of ferric hydroxide ($Fe(OH)_3$) sludge from the neutralization reaction (Eq. (4)), which requires further separation,

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Table 1
Performance of the fluidized-bed Fenton reactor for pollutant and iron removal.

Targeted pollutant	Removal efficiency (%)		Reference
	Organic	Total iron	
Dimethyl sulfoxide	95	34	Matira et al. [7]
Monoethanolamine	99	21	Su et al. [8]
Monoethanolamine	99	44	Anotai et al. [9]
2,4-dichlorophenol	99	14	Muangthai et al. [10]
Nitrobenzene	> 95	< 52	Anotai et al. [11]

dewatering, and disposal. The use of a fluidized-bed reactor addresses this problem. Ferric ions generated from the Fenton reaction can precipitate and crystallize onto the surface of fluidized media to reduce the amount of floppy iron sludge. Iron coated particles contain less moisture. This makes it much easier to reduce their moisture content than with floppy iron sludge, which even with thickening and dewatering has a moisture content of 70% or higher. This leads to high handling and disposal costs. Garcia-Segura et al. [6] thoroughly reviewed and summarized the operational parameters influencing the pollutant removal performance of the fluidized-bed Fenton process. According to their review, this process could effectively remove the organic pollutants present in several industrial wastewaters; unfortunately, data related to iron removal was not included. Table 1 shows the results from studies that reported both pollutant and iron removal performance. It can be seen that removal efficiencies for the target compound (95% or higher) was exceptional. This is similar to results gathered by Garcia-Segura et al. [6]. However, the iron removal efficiency, which is the most obvious advantage of the fluidized-bed Fenton over the ordinary Fenton process, was not very high (less than 52%) even when treating simple synthetic solutions. Boonrattanakij et al. [12] showed that the removal of total iron in a heterogeneous fluidized-bed reactor was not solely dependent on iron solubility (i.e., free ferric ions and complexes) but was also largely influenced by crystallization mechanisms, crystallite characteristic, and nucleation pathways. The present study was an attempt to further elucidate the factors that affect iron crystallization onto the fluidized material in order to improve iron removal performance. Fluidized carrier quantity, bed expansion, ferro-organic complexes, and operating mode (batch versus continuous) were thoroughly investigated. In addition, the heterogeneous fluidized-bed Fenton process was also applied as a tertiary treatment for the secondary effluent of a pulp and paper mill to remove chemical oxygen demand (COD) and color, in order to observe the behaviors of organic oxidation and iron crystallization in a real and complex solution. The results from this study could be directly applied to a full-scale fluidized-bed Fenton reactor to achieve removal of both organic pollutants and iron.

2. Materials and methods

2.1. Chemicals

All chemicals used in this work were analytical reagent grade. The fluidized material was construction sand (CS), which is superior to silica and alumina according to Boonrattanakij et al. [12]. The particles were between 0.42 and 0.59 mm in diameter (passing sieve #30 but retained on sieve #40) and had a surface area of 68.87 m^2/g. The XRD profile revealed that it mainly consisted of SiO_2. Prior to use, the CS was soaked in a pH 1 HCl solution for 24 h and subsequently rinsed with deionized water until the pH of the rinsed water was around 7. Demineralized water from a Millipore Mill-Q system was used to prepare all solutions.

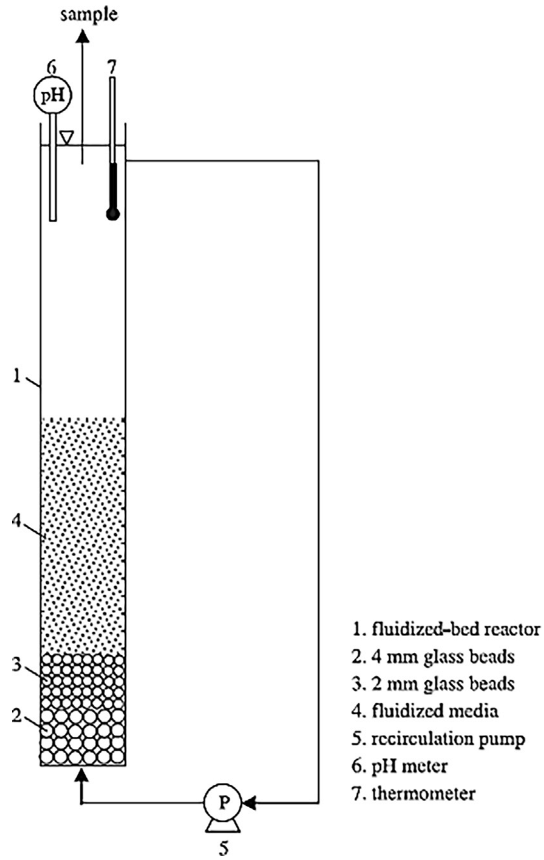

Fig. 1. Fluidized-bed reactor (not to scale).

2.2. Secondary effluent from pulp and paper mill

In addition to the synthetic solution, the secondary effluents from a selected pulp and paper mill were also used to characterize the behavior of the fluidized-bed Fenton process when treating a complex composition solution. The selected pulp and paper mill used activated sludge in the main process for treating its wastewater. The wastewater treatment plant (WWTP) consisted of a primary clarifier to separate settle-able pulp and solids, an aeration tank to remove biodegradable organic pollutants, and a secondary clarifier to separate active biomass from the treated effluent prior to discharge into the receiving water. Secondary effluents were periodically collected, and stored in plastic containers at 4 °C until use. Additionally, raw wastewater and primary effluent were also collected once to evaluate the performance of the existing WWTP.

2.3. Fluidized-bed reactor

A 1.4 L (1.3 L effective volume) glass-cylinder reactor with an inlet, outlet, and a recirculation pump, as shown in Fig. 1, was used as the fluidized-bed reactor (FBR). The bed expansion was varied from the original bed height by adjusting the internal recirculation rate. The FBR was controlled at 25 ± 0.2 °C by air recirculation using two air conditioners and gel freeze-packs.

2.4. Experimental procedure

For the batch investigation, a working solution was prepared by dissolving an appropriate amount of $FeSO_4{\cdot}7H_2O$ in demineralized water, or using secondary effluent from the pulp and paper mill. In the experiment examining the effect of ferro-organic complexation, formic acid (the simplest carboxyl product from $OH^{\cdot}$ oxidation of aromatic compounds [13–16]), was added to the ferrous solution. The working