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Dynamic simulation of degradation of toluene in waste gas by the photo-Fenton reaction in a bubble column

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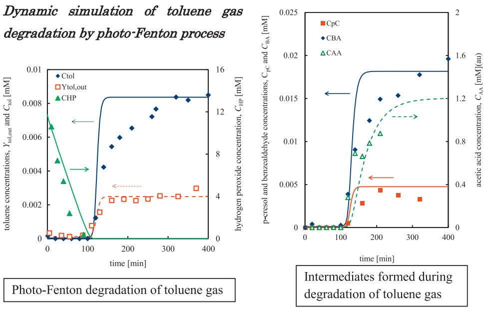
HIGHLIGHTS

- A dynamic simulation model for toluene gas photo-Fenton degradation was developed.
- Reaction kinetics and mass transfer were combined with the nonideal mixing model.
- Experiments were conducted to elucidate the reaction kinetics.
- The model could satisfactorily represent the rather complicated dynamic behaviors.

GRAPHICAL ABSTRACT



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ABSTRACT

A dynamic simulation model for the novel toluene gas removal chemical-absorption process based on the photo-Fenton reaction has been developed. It can predict the unsteady- and steady-state performance of a bubble column reactor for photo-Fenton degradation of toluene in a waste gas. In modeling, reaction kinetics in the liquid phase and gas–liquid mass transfer were combined with the tanks-in-series model for nonideal mixing in the gas and liquid phases. The rate equations for Fenton reagents (Fe ions and H_2O_2), OH radical and the intermediates were included besides those for toluene in the gas and liquid phases. The iron redox cycle generating hydroxyl radical is a key process in the photo-Fenton process. In the simulation model, therefore, the iron redox cycling was taken into account. Experiments for toluene gas photo-Fenton degradation in a semi-batch bubble column were conducted to elucidate the reaction kinetics and to verify the capability of the proposed dynamic simulation model. The proposed simulation model could satisfactorily represent the rather complicated dynamic changes of toluene concentrations in the gas and liquid phases, hydrogen peroxide, iron ions and intermediates during the course of the photo-Fenton process controlled by the iron redox cycle, which was established firstly by the Fenton reaction with the presence of H_2O_2 and subsequently by the UV light and dissolved oxygen after the complete consumption of H_2O_2.

1. Introduction

Volatile Organic Compounds (VOCs) are the common air pollutants emitted by the chemical and petrochemical industries and include most solvent thinners, degreasers, cleaners, lubricants and liquid fuels. Control of VOCs emission is a major concern of the industries' commitment towards the environment.

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In recent years, increasing attention has been focused on complete oxidation of organic compounds to harmless products of CO_2 and H_2O. Of the available oxidation technologies, advanced oxidation processes (AOPs) offer a promising technology in the treatment of recalcitrant organic compounds due to their greater efficiency in complete removal of organics. Therefore, the photocatalytic oxidation of VOCs in waste gas has been studied by several authors (e.g., D'Hennezel et al., 1998; Kim and Hong, 2002; Bouzaza et al., 2006; Zuo et al., 2006). Recently the use of the Fenton reaction to generate hydroxyl radicals and as a result to degrade organic contaminants has received extensive attention. Photoassisted Fenton process has been reported as an improvement to classic Fenton treatment (Wadley and Waite, 2004). In our previous studies (Tokumura et al., 2008; Handa et al., 2012), a novel process for removal of VOC gas by applying the photo-Fenton reaction in the liquid phase was proposed. The major advantage of photo-Fenton process is that the reagent components are safe to handle and environmentally benign. Highly complicated apparatus and pressurized systems are not required. Therefore, the photo-Fenton process is a feasible technology for applying directly from laboratory scale to large scale. The present paper focuses on the simulation of toluene gas degradation using the photo-Fenton process. Toluene, which is one of pollutants usually found in many industrial effluents and is extremely toxic and refractory in nature, was chosen as a typical example of VOCs in this study.

The OH radical generation being characteristic of the photo-Fenton degradation process is significantly affected by the rate of iron redox cycling between the +2 and +3 state (Wadley and Waite, 2004; Maezono et al., 2011; Tokumura et al., 2011). The photo-Fenton process mainly consists of two reactions, the Fenton reaction (Reaction (1)) and the photo-reduction (Reaction (2)):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \cdot OH \text{ (Fenton Reaction)} \tag{1}$$

$$Fe^{III}OH^{2+} \xrightarrow{h\nu} Fe^{2+} + \cdot OH \quad \text{(photo−Fenton Reaction)} \tag{2}$$

Here Fe^{III} denotes the sum of all iron species having an oxidation state of 3+. The Fenton reaction, which is the decomposition of hydrogen peroxide catalyzed by a ferrous ion and leads to oxidation of Fe^{2+} to Fe^{3+}, produces an OH radical in acidic aqueous solutions. Subsequently, the photo-reduction of Fe^{3+} by ultraviolet or visible light also produces an OH radical, which enables to continue the photo-Fenton catalytic cycle process, in which iron is cycled between the +2 and +3 oxidation states. In the photo-Fenton process, iron catalyzes the formation of OH radicals. Therefore, the photo-Fenton oxidation process is controlled by the amounts of iron and hydrogen peroxide in the solution.

When hydrogen peroxide exists, the iron redox cycling is mainly driven by the Fenton and photo-Fenton reactions. For the absence of hydrogen peroxide, on the other hand, the oxidation of Fe^{2+} by dissolved oxygen and the photo-Fenton reaction operate the iron redox cycling (Tokumura et al., 2011). The oxidation of Fe^{2+} by dissolved oxygen may take place via the following two reactions (Kang et al., 2002; Torres et al., 2008; Tokumura et al., 2011):

$$Fe^{II}\text{-(organic compounds: acetaldehyde and intermediates such as organic acids)} + O_2 \rightarrow Fe^{III} + \text{oxidative intermediates} \tag{3}$$

$$4Fe^{2+} + 4H^+ + O_2 \rightarrow 4Fe^{3+} + 2H_2O \tag{4}$$

It has been recently established that complexes of Fe^{II} and/or Fe^{III} with organic ligands significantly affect the photo-Fenton process (Pignatello et al., 1999). The iron redox cycling driven by the dissolved oxygen is rather weak as compared with that by the Fenton and photo-Fenton reactions. Even without hydrogen peroxide, in other words, the weak iron redox cycling takes place and a small amount of hydroxyl radicals are generated.

Hydroxyl radicals attack the organic molecules and mineralize them through the formation and decomposition of intermediates:

$$\text{Pollutant} \xrightarrow{\cdot OH} \text{intermediates} \xrightarrow{\cdot OH} \text{products } (CO_2, H_2O, \text{mineralization products}) \tag{5}$$

The mineralization of an organic pollutant usually involves a series of oxidation reactions. During the toluene photo-Fenton degradation process, firstly the breakage of the aromatic ring yields carboxylic acids and finally organic compounds are mineralized to CO_2 and H_2O (Mo et al., 2009). It should be noted that the complete destruction of the organic contaminant is sometimes not possible.

The aim of this study is to develop a dynamic simulation model for photo-Fenton degradation of toluene in a waste gas using a semi-batch bubble column. The dynamic simulation can provide valuable information for reaction kinetics, mass transfer, start-up and shutdown operations, operability studies and a steady-state performance as well. By taking account of reaction kinetics in the liquid phase and gas–liquid mass transfer combined with the tanks-in-series model for nonideal mixing in the gas and liquid phases, the dynamic simulation model was developed. Besides the degradation of toluene dissolved in the liquid phase, the decomposition of H_2O_2, the redox reactions of Fe, the formation and decomposition of OH radical and the formation and degradation of intermediates were considered in the proposed simulation model. In our previous paper (Tokumura et al., 2008) in which the liquid-phase mixing was assumed to be perfect mixing for simplification, the redox reactions of Fe, the formation and decomposition of OH radical and the formation and degradation of intermediates were not simulated. Their dynamic behaviors are very important in elucidating degradation of toluene gas by the photo-Fenton reaction. The parameters describing nonideal mixing in the tanks-in-series model with backflow are the numbers of hypothetical tanks in the gas and liquid phases and the backflow rate through the hypothetical tanks in the liquid phase, and usually they are adjustable parameters. In this study, they were determined using a multiple circulation cell model proposed by Joshi (1980) and the central plume model for the liquid velocity profiles in a bubble column proposed by Ulbrecht et al. (1985), respectively. Experiments were conducted to analyze the reaction kinetics of the photo-Fenton degradation driven by the iron redox cycle generating OH radicals and to validate the proposed dynamic simulation model.

2. Experimental

Experiments were carried out in a bubble column photoreactor which was made of Pyrex glass and its working volume was 7 L (Tokumura et al., 2008). The diameter of the column was 98 mm and its height was 1.40 m. Three 40 W UV light lamps having the radiation peak at 352 nm (FL15T8BLB, Sankyo Electronics, Co., Japan) for illumination were located around the photoreactor. The reaction temperature was kept constant at room temperature (298 ± 1 K). Using sulfuric acid the solution pH was adjusted to 3.0, which is the optimum pH for the photo-Fenton reactions (Wadley and Waite, 2004). Photo-Fenton degradation reactions were started by addition of known amount of H_2O_2 and injection of gas effluent containing toluene to water including iron(II) sulfate heptahydrate as a source of iron with UV light irradiation. At the beginning of degradation process, therefore, water in the photoreactor contained no toluene. For the continuous toluene treatment, hydrogen peroxide which is consumed by the photo-Fenton reaction has to be continuously and adequately supplied to the liquid-phase. In this