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Degradation of *p*-nitrophenol by Fe^0/H_2O_2/persulfate system: Optimization, performance and mechanisms

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ABSTRACT

In this study, a Fe^0/H_2O_2/persulfate system was developed to degrade *p*-nitrophenol (PNP) in aqueous solution, and 7 control experiments were setup to evaluate the synergistic effects in Fe^0/H_2O_2/persulfate system. First, effects of Fe^0 dosage (0–4.0 g/L), H_2O_2 dosage (0–30.0 mM), persulfate dosage (0–25.0 mM) and initial pH value (3.0–13.0) on PNP removal by the Fe^0/H_2O_2/persulfate system were investigated through single-factor experiments. Furthermore, the optimal parameters (*i.e.*, 1.3 g/L Fe^0, 24.8 mM H_2O_2, 6.7 mM persulfate and initial pH of 5.1) were obtained through response surface methodology (RSM). Meanwhile, a high PNP removal (99.9%) obtained under the optimal conditions was mainly ascribed to the strong synergistic effects among Fe^0, H_2O_2 and persulfate. Furthermore, PNP degradation pathway was proposed according to the detected intermediates. In addition, the reaction mechanism of Fe^0/H_2O_2/persulfate system was proposed according to iron corrosion products detected by using SEM-EDS, XRD and XPS. In a word, all the results suggest that Fe^0/H_2O_2/persulfate system should be recommended as a valid method for the treatment of toxic and intractable industrial wastewater.

1. Introduction

Nowadays, the refractory wastewaters from industrial production present a large challenge to the environment, since the intermediates and some steady forms of these typical refractory compounds discharged into the ecosystem are hard to be degraded completely. *p*-Nitrophenol (PNP), a typical poisonous, mutagenic and biorefractory nitroaromatic compound, has been widely used as raw materials in industries producing explosives, pharmaceuticals, pesticides and rubber chemicals etc [1]. PNP could pose a threat to the environment and the public since repeated exposure may lead to injury to blood cells and the nervous central system. Meanwhile, long-term exposure could cause large damage to kidney and liver [2]. Consequently, PNP has been regarded as a priority pollutant, and its concentration is restricted to below 10 ng/L in natural water by the U.S. EPA [3]. Considering the above-mentioned, PNP has been selected as the model pollutant in this study.

Zero valent iron (ZVI or Fe^0, $E^\theta = -0.44$ V) has been extensively applied to the treatment of intractable pollutants due to its effectiveness, low cost and benign environmental impact, and the removal of contaminants by ZVI is mainly attributed to the common effects of reduction, oxidation, adsorption and co-precipitation etc [4,5]. Over the last decades, several studies have demonstrated that ZVI effectually reduces the concentration of several organic and inorganic pollutants [6,7]. Aerobically, ZVI can degrade a series of organic compounds since Fe^{2+} and H_2O_2 were formed (Eq. (1)). The H_2O_2 produced is either reduced to water (Eq. (2)), or is converted into $HO^{\cdot}$ by reaction with Fe^{2+} (Eq. (3)) [8]. However, oxidative processes exhibit limited efficiency for the removal of contaminants in Fe^0/air system because less than 5% of the iron added is converted into oxidant capable of degrading contaminants and the yields of oxidants formed are low [9–11]. Meanwhile, it has been reported that the addition of H_2O_2 would improve the removal of pollutants [12].

$$Fe^0 + O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O_2 \tag{1}$$

$$Fe^0 + H_2O_2 + 2H^+ \rightarrow Fe^{2+} + 2H_2O \tag{2}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + OH^- \tag{3}$$

In most AOPs, it is well-known that hydroxyl radical ($HO^{\cdot}$) ($E^\theta = 2.8$ V) is a powerful oxidant which can react with various organic pollutants at near-diffusion controlled rates [13]. The classical homogeneous Fenton reaction process (H_2O_2 catalyzed by ferrous ions) was described as a series of chain and radical reactions, and hydroperoxyl radical ($HO_2{}^{\cdot}$) and its conjugated base, superox-

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ide anion ($O_2{}^{\cdot-}$) are usually accompanied by $HO^{\cdot}$ [14]. Although the conventional homogeneous Fenton reaction has been used widely in the treatment of contaminated wastewater, it suffers from some major drawbacks, such as the instability of Fe^{2+}, short life span and high consumption of Fe^{2+} [8]. In recent years, heterogeneous Fenton process has been developed as an alternative method and ZVI has shown to be a valid Fenton catalyst [15]. It has been found that phenol [16] and 4-chlorophenol [17] could also be rapidly degraded in ZVI/H_2O_2 system.

Recently, persulfate (PS, $S_2O_8{}^{2-}$, $E^{\theta} = 2.01$ V) has been regarded as an emerging oxidant to degrade pollutants in water. In addition, persulfate can be activated to produce the active sulfate radical ($SO_4{}^{\cdot-}$, $E^{\theta} = 2.6$ V). Compared with $HO^{\cdot}$, the generated $SO_4{}^{\cdot-}$ has been proven to be much more stable and effective for oxidizing unsaturated bonds and aromatic constituents [18]. Persulfate is a common source of $SO_4{}^{\cdot-}$ through activation processes that include heat, UV, base and transition metals [19,20]. In particular, the chemical activation of persulfate by transition metal ions is shown in Eq. (4). In addition, Fe^0 can activate persulfate to produce $SO_4{}^{\cdot-}$ (Eqs. (5)–(8)). Meanwhile, it has been reported that bisphenol A, phosphate [21] and bentazon [22] could be removed by the Fe^0 activated persulfate oxidation process.

$$S_2O_8{}^{2-} + Me^{n+} \rightarrow SO_4{}^{\cdot-} + Me^{(n+1\ )} + SO_4{}^{2-} \tag{4}$$

$$2Fe^0 + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^- \tag{5}$$

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + 2OH^- + H_2 \tag{6}$$

$$Fe^0 + 2S_2O_8{}^{2-} \rightarrow 2SO_4{}^{\cdot-} + Fe^{2+} + 2SO_4{}^{2-} \tag{7}$$

$$2Fe^{3+} + Fe^0 \rightarrow 3Fe^{2+} \tag{8}$$

Since ZVI can catalyze H_2O_2 and activate persulfate according to the above discussion, there might be strong synergistic effects among Fe^0, H_2O_2 and persulfate. In this study, therefore, the Fe^0/H_2O_2/persulfate system was developed to degrade PNP in aqueous solution (500 mg/L). In particular, the objectives of this paper are to: (i) optimize the key parameters of Fe^0/H_2O_2/persulfate process through single-factor experiments and response surface methodology (RSM); (ii) ascertain the synergistic effects in Fe^0/H_2O_2/persulfate system; (iii) propose the reasonable degradation pathway and mechanism of PNP in Fe^0/H_2O_2/persulfate system. The results of this study could help to develop a new application for the treatment of toxic and intractable industrial wastewater.

2. Materials and methods

2.1. Reagent

Details pertaining to reagent in this study are provided in the Supporting Information.

2.2. Experimental procedure

PNP aqueous solution (500 mg/L) was prepared by simple dissolution in deionized water. In each experiment, 300 mL PNP aqueous solution was added in a 500 mL beaker. The pH of PNP aqueous solution was adjusted with 0.1 M H_2SO_4/NaOH solution. The reaction was initiated after the simultaneous addition of Fe^0 powder, H_2O_2 and persulfate. During the reaction, the solution was stirred by a mechanical stirrer (350 rpm) and the experimental temperature was controlled by water batch heating. Besides, the samples were taken out at pre-determined time intervals, and filtered through PTFE syringe filter discs (0.45 µm). Firstly, the key operational parameters (*i.e.*, Fe^0 dosage, H_2O_2 dosage, persulfate dosage and initial pH) of Fe^0/H_2O_2/persulfate system were optimized by single-factor experiments. On the basis of single-factor experiments, the central composite design (CCD), one of the principal response surface methodologies used in experimental design, was done to obtain the optimal parameters (See Supporting Information). Furthermore, control experiments were setup to confirm the synergistic effects in Fe^0/H_2O_2/persulfate system for PNP removal. In addition, changes of H_2O_2, $S_2O_8{}^{2-}$ and Fe^{2+}/Fe^{3+} concentrations were determined, respectively. Finally, the reacted Fe^0 in Fe^0/H_2O_2/persulfate system were observed thoroughly through SEM-EDS, XRD and XPS analysis.

2.3. Analytical methods

Details pertaining to analytical methods (e.g., HPLC, SEM-EDS, XRD and XPS) in this study are provided in the Supporting Information.

3. Results and discussion

3.1. Parameters optimization

Details pertaining to parameters optimization in this study are provided in the Supporting Information. As a result, the optimal parameters (*i.e.*, 1.3 g/L Fe^0, 24.8 mM H_2O_2, 6.7 mM persulfate and initial pH of 5.1) were obtained through single-factor experiments and RSM analysis.

In addition, details pertaining to interactive relationship of Fe^0, H_2O_2, persulfate and initial pH in this study are provided in the Supporting Information. In short, strong mutual interaction was existed between the each two parameters (*i.e.*, Fe^0 and H_2O_2, Fe^0 and persulfate, Fe^0 and initial pH, H_2O_2 and persulfate, H_2O_2 and initial pH and persulfate and initial pH) according to 3D surface plots. The results further proved synergistic effect existed in the system, which was in accordance with the high PNP removal (99.9%).

3.2. Control experiments

To evaluate the synergetic effects in Fe^0/H_2O_2/persulfate process, 7 control experiments including (a) Fe^0 alone, (b) H_2O_2 alone, (c) persulfate alone, (d) Fe^0/H_2O_2, (e) Fe^0/persulfate, (f) H_2O_2/persulfate and (g) Fe^{2+}/H_2O_2/persulfate systems were setup under the same conditions (*i.e.*, Fe^0 dosage of 1.3 g/L, H_2O_2 dosage of 24.8 mM, persulfate dosage of 6.7 mM, initial pH of 5.1, $FeSO_4{\bullet}7H_2O$ dosage of 8.13 mM, stirring speed of 350 rpm, reaction time of 6 min, reaction temperature of 25 °C).

3.2.1. PNP removal analysis

Fig. 1(a) shows the performances of Fe^0 alone, H_2O_2 alone, persulfate alone, Fe^0/H_2O_2, Fe^0/persulfate, H_2O_2/persulfate, Fe^{2+}/H_2O_2/persulfate and Fe^0/H_2O_2/persulfate systems for PNP removal. In particular, the PNP removal (< 7.0%) obtained by Fe^0 alone, H_2O_2 alone, persulfate alone, Fe^0/H_2O_2 (initial pH = 5.1) and H_2O_2/persulfate could be neglected completely. Meanwhile, PNP removal (11.0%) obtained in the Fe^0/H_2O_2 system with initial pH of 2.4 was similar with Fe^0/H_2O_2 system (initial pH = 5.1) (see Fig. S4). In addition, the low PNP removal (29.6%) was obtained by Fe^0/persulfate system after 20 min. However, the PNP removal (99.9%) obtained by Fe^0/H_2O_2/persulfate system was much higher than the control experiments after 20 min treatment. Furthermore, the dissolved iron ions concentration in the effluent of Fe^0/H_2O_2/persulfate system was determined and the same concentration of Fe^{2+} was added in the Fe^{2+}/H_2O_2/persulfate control system. In other words, the heterogeneous system employing Fe^0 was also compared with a homogeneous system employing

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