Chlorine dioxide catalytic oxidation by zero valent iron for the degradation of PNP in aqueous solution

J Li¹ and B Lai¹

1Department of Environmental Science and Engineering, School of Architecture and Environment, Sichuan University, Chengdu 610065, China
E-mail address: dreamslijun@163.com (Jun Li)

Abstract. In order to evaluate the degradation of p-nitrophenol (PNP) in aqueous solution by chlorine dioxide oxidation process catalyzed by Fe⁰ micro-particles, the effects of Fe⁰ dosage (0-5.0 g/L), ClO₂ dosage (0-2.0 g/L), initial pH (3.0-13.0) and air flow rate (0-5.0 mL/min) on chemical oxygen demand (COD) removal of PNP in aqueous solution were investigated comprehensively. In particular, the maximum COD removal was obtained under the optimal conditions (i.e., Fe⁰ dosage of 4.0 g/L, ClO₂ dosage of 1.2 g/L, initial pH of 5.0, stirring speed of 300 rpm and reaction time of 30 min). Meanwhile, the two control experiments (i.e., Fe⁰ alone and ClO₂ alone systems) were carried out to confirm the performance of chlorine dioxide oxidation process catalyzed by Fe⁰ micro-particles. In a word, the study provided an effective and promising catalytic oxidation technology for toxic and refractory pollutants.

1. Introduction
Phenolic compounds are broadly produced in the chemical and processing industries [1]. In particular, p-nitrophenol (PNP), as one of the most widely used nitrophenolic compounds, is an important organic chemical raw material and intermediate used in manufacturing pesticides, dyestuffs, explosives, wood preservatives and rubber chemicals [2]. Although a widespread use has appeared in the production of the chemical industry, PNP is highly toxic both for the environment and humans, such as injury to blood cells caused by repeated exposure, damage to the central nervous system and mutagenic effects. Meanwhile, because of its high solubility, low biodegradability and persistency in wastewater, it is commonly detected in surface water, and both agricultural and industrial wastewater. Thus, the US and European Environmental Protection Agencies (EPA and EEA) have included it in their lists of priority pollutants to be monitored in industrial effluents [3]. In this study, PNP has been chosen as the model pollutant.

Chlorine dioxide is a powerful one-electron oxidant (E⁰ = 0.936V), which has comparable biocidal efficacy, but less pH dependence and DBP formation potential, compared with free chlorine [4]. In the 1940s, ClO₂ was firstly used in the United States for water treatment. Nowadays, ClO₂ in widely applied in drinking water treatment include disinfection, nitrification and bromate control [5] and broadly used to bleach flour and wood pulp [6]. According to the literatures, the application of ClO₂ in the wastewater treatment has been drew great attention [7], [8]. In addition, zero value iron (Fe⁰) has been has been extensively applied for the remediation/treatment of groundwater and wastewater because of its effectiveness, low cost and benign environmental impact[9]. In this study, the zero value iron micro-particles were used as catalyst in the ClO₂ catalytic oxidation process for the degradation of PNP in aqueous solution. Herein, the main objective of our work is investigating the effects of key parameters on chemical oxygen demand (COD) removal of PNP in aqueous solution and determining the...
optimal conditions of experimental parameters for the practical application of toxic organic wastewater by ClO$_2$ catalytic oxidation process.

2. Materials and methods

2.1. Reagent
$p$-Nitrophenol (PNP, 99.0%), zero valent iron (ZVI, Fe$^0$) powders from Chengdu Kelong chemical reagent factory were used in the experiments. Fe$^0$ particles have a mean particle size of approximately 120 μm, and their Fe content is above 99%. Other chemicals used in the experiment were of analytical grade. Distilled water was used throughout the whole experiment process. All solutions in the study were prepared by the distilled water. The preparation of different concentration of chlorine dioxide solution was through mixing the different concentration of reagent A and B reagent from Chengdu Kelong chemical reagent factory.

2.2. Experimental procedures
In our experiment, PNP stock solution (500 mg/L) was prepared by simple dissolution in distilled water. 300 mL solution of PNP was transferred into 500 mL beaker and the pH value of PNP aqueous solution was adjusted with 0.1 M sulfuric acid or sodium hydroxide solution. The reactions were initiated after adding the desired amount of Fe$^0$ microparticles and ClO$_2$ aqueous solution into the reactor synchronously. The experiment was performed at 25 ± 2°C by water batch heating and mixed by a mechanical stirrer (300 rpm). After the reaction process, aqueous samples were withdrawn with syringe and immediately filtered through a PTFE syringe filter disc (0.45 μm). All experiments were performed in triplicate, and all data in the figures were averaged values of 3 replicate samples and the error bars represented standard deviation of the means.

2.3. Analytical methods
The chemical oxygen demand (COD) of treatment effluents of the experiments were analyzed by COD analyzer (Lianhua, China). The solution pH was measured by a PHS-25 meter (Rex, China).

3. Results and discussion

3.1. Parameters optimization

3.1.1. Effect of Fe$^0$ dosage on COD removal
According to the literature [10], [11], as the catalyst, Fe$^0$ plays an important role in the catalytic oxidation process. In our study, effects of Fe$^0$ dosage (0, 1.0, 2.0, 3.0, 4.0, 5.0 and 5.5 g/L) on the COD removal of PNP in aqueous solution were evaluated comprehensively (experiment conditions: ClO$_2$ dosage of 1.2 g/L, initial pH of 5.3, reaction time of 30 min and stirring speed of 300 rpm). Figure 1 shows that COD removal dramatically increased from 49.2% to 62.2% with Fe$^0$ dosage enhancing from 0 to 2.0 g/L. The result shows that, in the presence of Fe$^0$ catalyst, the COD removal was much higher than without catalyst, which demonstrates that Fe$^0$ could improve the degradation of PNP in aqueous solution in ClO$_2$ oxidation system. In addition, the COD removal continually rose to maximum (64.3%) when Fe$^0$ dosage increased 4.0 g/L. The result could be explained that the amount of active sites increased with the increased Fe$^0$ dosage. What’s more, COD removal leveled off with the Fe$^0$ dosage further increasing to 5.5 g/L. Considering from the view of economic cost, the Fe$^0$ dosage of 4.0 g/L was selected in the following experiments.
3.1.2. Effect of ClO₂ dosage on COD removal
Effects of ClO₂ dosage (0, 0.2, 0.5, 0.8, 1.0, 1.2, 1.5 and 2.0 g/L) on the COD removal of PNP in aqueous solution were investigated (experiment conditions: Fe⁰ dosage of 4.0 g/L, initial pH of 5.3, reaction time of 30 min and stirring speed of 300 rpm). As shown as in Figure 2, in the absence of ClO₂, only 0.1% COD removal was obtained after 30 min treatment process, which proved that the adsorption of Fe⁰ micro-nanoparticles were weak and could be ignored in this system. Furthermore, when ClO₂ dosage added from 0 to 1.2 g/L, the COD removal dramatically increased after 30 min reaction time. In particular, the COD removal achieved the maximum value (74.9%) when ClO₂ dosage was 1.2 g/L. However, COD removal decreased to 51.4% with ClO₂ dosage further increasing to 2.0 g/L which might be due to the self-consumption between active species. Therefore, the optimal ClO₂ dosage was selected as 1.2 g/L in the subsequent experiments.

3.1.3. Effect of initial pH on COD removal
According to literature, the initial pH is an important parameter influencing the performance of ClO₂ oxidation process [5]. In order to investigate the influence of pH values on the oxidative process, effects of initial pH (3.0, 5.0, 7.0, 9.0, 11.0, 12.0 and 13.0) on the COD removal of PNP in aqueous solution were studied (experiment conditions: Fe⁰ dosage of 4.0 g/L, ClO₂ dosage of 1.2 g/L, reaction time of 30 min and stirring speed of 300 rpm). The results are presented in Figure 3, it shows that the COD removal depends strongly on the pH. The COD removal quickly increased from 69.5% to 74.9% when initial pH increased from 3.0 to 5.0. According to literatures [12], [13], based on the redox potential of ClO₂, chlorine dioxide is typically more reactive under acidic conditions than in neutral
and alkaline media. Meanwhile, the COD removal only changed slightly with the initial ranged from 5.0 to 11.0. Beyond pH value of 11.0, the COD removal begun to decrease, which was due to the fact that at alkaline conditions, ClO$_2$ reacts with OH$^-$ to form chlorite (ClO$_2^-$) and chlorate (ClO$_3^-$) species [14], leaving less ClO$_2$ available for pollutants removal. The above result indicates that the optimum pH value in catalytic system ranges from 3.0 to 11.0. Therefore, the optimal initial pH was selected at initial solution pH (5.3) without changing the pH.

![Figure 3](image_url)

**Figure 3.** Effects of initial pH value on the COD removal of PNP in aqueous solution.

3.1.4. Effect of air flow rate on COD removal
According to the literature [15], the influence of dissolved oxygen on the chlorine dioxide catalytic oxidation process for the degradation of pollutants was significant. Thus, effects of air flow rate (0, 1.0, 2.0, 3.0, 4.0 and 5.0 L/min) on the COD removal of PNP in aqueous solution were explored thoroughly (experiment conditions: Fe$^0$ dosage of 4.0 g/L, ClO$_2$ dosage of 1.2 g/L, initial pH of 5.3, reaction time of 30 min and stirring speed of 300 rpm).

As can be seen from Figure 4, the COD removal remained between 74.6% and 76.2% under different aeration conditions (i.e., air or without aeration). The results suggest that effect of dissolved oxygen (DO) on the COD removal by chlorine dioxide oxidation system catalyzed by Fe$^0$ micro-particles could be neglected completely. Therefore, the chlorine dioxide catalytic oxidation process was performed without aeration.

![Figure 4](image_url)

**Figure 4.** Effects of air flow rate on the COD removal of PNP in aqueous solution.

3.2. Control experiments
In our study, two control experiments (i.e., Fe$^0$ alone and ClO$_2$ alone systems) were performed to evaluate the performance of COD removal by Fe$^0$/ClO$_2$ catalytic oxidation system thoroughly under
the optimal conditions (i.e., Fe\(^0\) dosage of 4.0 g/L, ClO\(_2\) dosage of 1.2 g/L, initial pH of 5.3, reaction time of 30 min and stirring speed of 300 rpm).

Figure 5 shows the COD removal of PNP in aqueous solution in Fe\(^0\) alone, ClO\(_2\) alone and Fe\(^0\)/ClO\(_2\) systems. In particular, the combination of Fe\(^0\) and ClO\(_2\) enhanced the COD removal significantly, achieving a COD removal of 74.9\% after 30 min treatment, whereas the only addition of Fe\(^0\) led to the COD removal of 0.2\% and ClO\(_2\) alone system achieved a COD removal of 55.0\%. Considering the above result, the Fe\(^0\) micro-particles could be used as catalyst in the chlorine dioxide oxidation and improve the performance of degradation of pollutants.

![Figure 5](image-url)

**Figure 5.** Comparative study of different systems.

4. Conclusions
In this study, we investigated the performance of degradation of PNP in aqueous solution by ClO\(_2\) catalytic oxidation process. Meanwhile, Fe\(^0\) micro-particles as the catalyst exhibited the excellent catalytic activity in the ClO\(_2\) catalytic oxidation process (i.e., Fe\(^0\)/ClO\(_2\) system). Firstly, key parameters (i.e., Fe\(^0\) dosage, ClO\(_2\) dosage, initial pH and air flow rate) were investigated to obtain the optimal conditions. It shows that a high COD removal (74.9\%) was obtained after 30 min treatment under the optimal experiment conditions (i.e., Fe\(^0\) dosage of 4.0 g/L, ClO\(_2\) dosage of 1.2 g/L, initial pH of 5.3, stirring speed of 300 rpm). Compared with Fe\(^0\) alone and ClO\(_2\) alone systems, it was noted that the COD removal (74.9\%) achieved in ClO\(_2\) oxidation process catalyzed by Fe\(^0\) micro-particles was much higher than others (i.e., Fe\(^0\) alone (0.2\%) and ClO\(_2\) alone (55.0\%) systems), which indicated that the Fe\(^0\) could efficiently improve the performance of pollutant removal in ClO\(_2\) oxidation process. In conclusion, the results manifested that the ClO\(_2\) catalytic oxidation process with Fe\(^0\) micro-particles was an efficient and cleaning technology for the toxic and refractory industrial wastewater.

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