



## Inhibitory effect of inorganic ions on nitrobenzene oxidation by fluidized-bed Fenton process

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### ABSTRACT

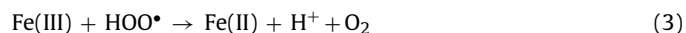
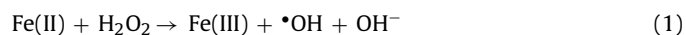
This study investigated the effects of inorganic ions including chloride ions, dihydrogen phosphate ions and nitrate ions on the oxidation of nitrobenzene by the fluidized-bed Fenton process. The nitrobenzene degradation decreased with increasing chloride, dihydrogen phosphate and nitrate concentrations. Dihydrogen phosphate and chloride ions significantly inhibited nitrobenzene degradation. However, the inhibition caused by chloride ions could be overcome by extending the reaction time if the concentration of chloride ions was low. Nitrate did not have significant effect on nitrobenzene removal. The inhibition effect of each inorganic ion on the nitrobenzene degradation was in the order:  $\text{H}_2\text{PO}_4^- \gg \text{Cl}^- > \text{NO}_3^-$ . In addition, the results also show that the removal efficiency of nitrobenzene by fluidized-bed Fenton process was higher than traditional Fenton process.

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### 1. Introduction

Nitrobenzene is an organic chemical compound that has been categorized as hazardous waste. It is widely used in several industries such as dye manufacturing, pesticides, rubber chemicals, and pharmaceuticals. However, it is believed to be a human carcinogen [1]. At low nitrobenzene concentration, a bioreactor can be used successfully to remove this contaminant [2], but at high concentrations, it is toxic to microorganisms and resistant to oxidation by biological processes. Therefore, powerful oxidation methods are needed for efficient treatment [3].

The Fenton process (or traditional Fenton process) is an advanced oxidation process (AOP) that uses hydrogen peroxide and ferrous ions to form hydroxyl radicals that can efficiently degrade many kinds of pollutants into environmentally friendly compounds [4–7]. A Fenton reaction can involve many steps, as shown below:



However, its application has been limited due to the generation of the excess amount of ferric hydroxide sludge that requires

additional separation processes and disposal [8]. To deal with this problem, several new Fenton modifications have been developed. One of these is the use of a fluidized-bed reactor in which the carriers can initiate the iron precipitation via a crystallization process [9]. In a fluidized-bed Fenton reactor (FBR), several important processes occur simultaneously including: (1) homogeneous chemical oxidation ( $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ), (2) heterogeneous chemical oxidation ( $\text{H}_2\text{O}_2/\text{iron oxide}$ ), (3) fluidized-bed crystallization, and (4) reductive dissolution of iron oxides.

As Fig. 1 illustrates, the Fenton's reagent can produce the non-selective oxidant,  $\text{OH}\cdot$ , via homogeneous reaction (a). This strong oxidant attacks the aromatic hydrocarbon to initiate ring opening in an oxidation reaction (b). Then the intermediate products from the previous reaction appear, and these lead to further oxidation (c).  $\text{Fe}^{3+}$  can be converted by reducing one electron of  $\text{Fe}^{2+}$  in Fenton's reaction (d). Some  $\text{Fe}^{3+}$  can also be converted back to  $\text{Fe}^{2+}$  and initiate further Fenton reaction as reaction (h). However, in the presence of a solid carrier, the ferric hydrolysis product of Fenton's reaction can also crystallize and grow on the surface of the carrier (reaction (e)), which, decreases the precipitation in puffy ferric hydroxide forms [10]. At the same time, the synthesized ferric oxide can also serve as a catalyst for hydrogen peroxide decomposition in a heterogeneous reaction (i). Iron oxide on the surface carriers can also re-dissolve via reductive dissolution (g) or heterogeneous reaction (f) to become  $\text{Fe}^{2+}$  form. In an acidic environment, ferric ions can be reduced to ferrous ions (d). Furthermore, the  $\text{Fe(III)}$  hydrolysis product of a Fenton's reaction can crystallize and grow on the surface of this carrier to reduce the precipitation of  $\text{Fe(OH)}_3$ .

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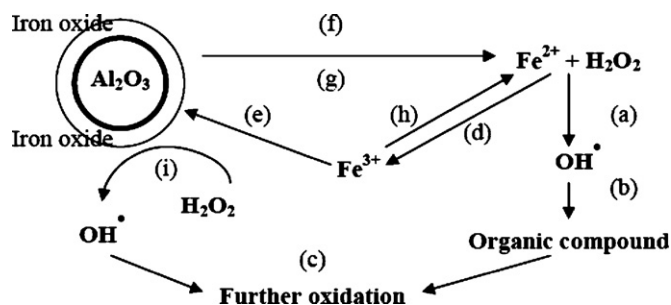


Fig. 1. Fluidized-bed Fenton reactions.

The concentration of hydroxyl radicals is affected by the background impurities present in the wastewater stream. Scavenging of hydroxyl radicals by anions is also likely to take place, when inorganic radicals are formed that are less reactive than hydroxyl radicals. However, in previous research, the effects of inorganic ions on the degradation of organic compounds have been generally overlooked, and some studies were conducted on only one anion. Therefore, this study was undertaken in order to compare the effects of anions such as chloride, phosphate and nitrate on the degradation of nitrobenzene. These inorganic ions are very common in most wastewaters [11] and might inhibit the Fenton reaction [12]. This study investigated the effect of inorganic ions on the degradation of nitrobenzene by a fluidized-bed Fenton process.

## 2. Materials and methods

Nitrobenzene ( $\text{C}_6\text{H}_5\text{NO}_2$ ), ferrous sulfate hepta-hydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) and 35% hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) were purchased from the Merck Company. Sodium chloride was obtained from the Showa Company. The other reagents used were at least of reagent grade.  $\text{Al}_2\text{O}_3$ , which is the main carrier in the FBR, was white and round with average particle diameter of 2.50 mm. A 1.35 l fluidized-bed reactor (FBR) was used in all experiments. The FBR was a cylindrical glass vessel having outlet, inlet and recirculating sections.

Nitrobenzene stock solution and inorganic ions (chloride ion, dihydrogen phosphate and nitrate) solutions were prepared with pure water at room temperature and poured into a circulating fluidized-bed reactor. The recycling pump was turned on to mix the solution at the desired bed expansions. Then the desired pH was adjusted by 1:4  $\text{H}_2\text{SO}_4$ , which took approximately 10 min before the pH reading was stable. Pre-calculated ferrous ion solution was added at the 5th minute after the recycling pump was switched on. The solution was rechecked again before adding  $\text{H}_2\text{O}_2$  solution to start the reaction. At selected time intervals of 0, 2, 5, 10, 20, 30 and 60 min, samples were taken from the FBR and analyzed immediately. The Fenton's reaction was stopped instantly by adding  $\text{NaOH}$  to the reaction mixture after sampling. The samples were then filtered on cellulose acetate membranes with 0.45  $\mu\text{m}$  pore size to remove precipitates. Nitrobenzene was analyzed using an HP 4980II gas chromatograph with a flame ionization detector and an HP-5 column (0.53 mm inside diameter, 15 m long).

For traditional Fenton process (or conventional Fenton process), the same procedure was conducted, however, without applying carrier ( $\text{Al}_2\text{O}_3$ ) into the reactor.

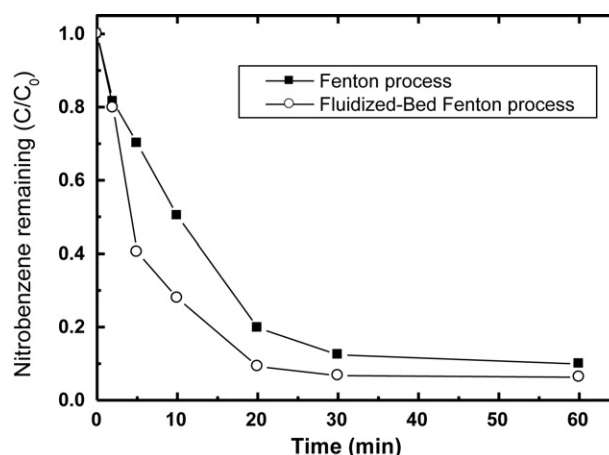


Fig. 2. Comparison between traditional Fenton and fluidized-bed Fenton process on the degradation of nitrobenzene.  $[\text{NB}] = 10 \text{ mM}$ ,  $[\text{H}_2\text{O}_2] = 50 \text{ mM}$ ,  $[\text{Fe}^{2+}] = 1 \text{ mM}$ ,  $\text{Al}_2\text{O}_3 = 100 \text{ g/l}$ , and  $\text{pH}_i = 2.8$ .

## 3. Results and discussion

### 3.1. Comparison between traditional Fenton and fluidized-bed Fenton processes

This part of the study evaluated the performance of traditional Fenton and fluidized-bed Fenton processes on the oxidation of nitrobenzene when using 10 mM of nitrobenzene, 50 mM of  $\text{H}_2\text{O}_2$ , 1 mM of  $\text{Fe}^{2+}$  and 100 g of  $\text{Al}_2\text{O}_3$  at pH 2.8. Effects of fluidized-bed Fenton and traditional Fenton processes on the nitrobenzene degradation are compared in Fig. 2.

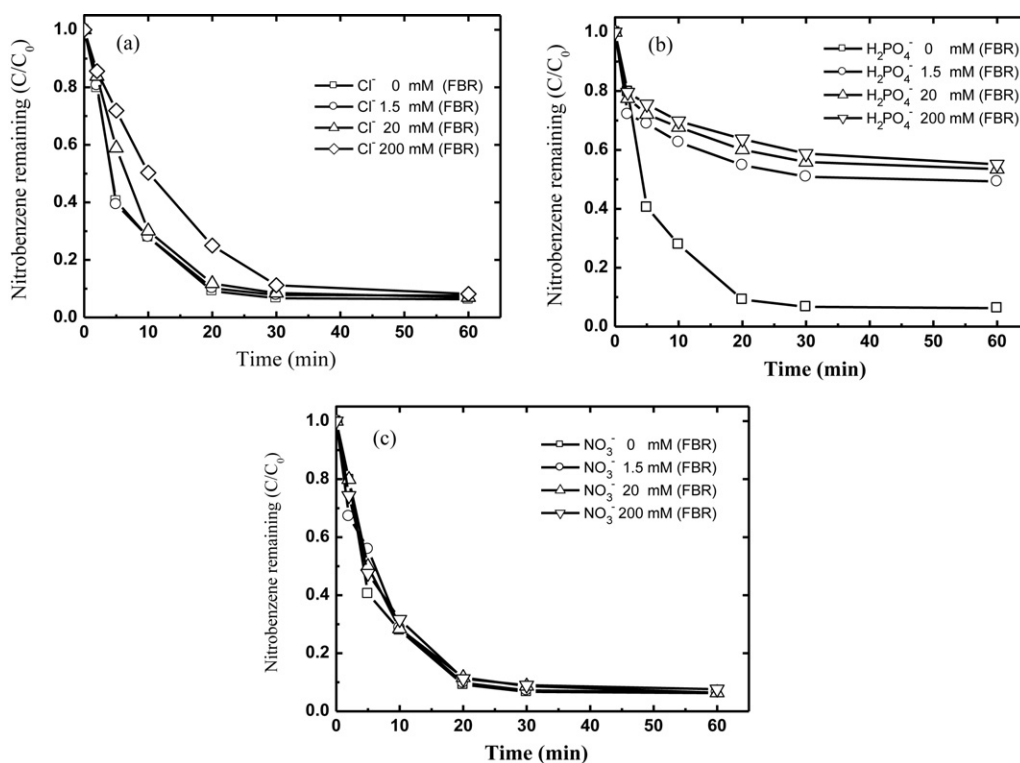
Within the first 2 min, the nitrobenzene oxidation was quite similar in both processes. However, the degradation of nitrobenzene in Fenton and fluidized-bed Fenton processes began to differ after 2 min. The nitrobenzene rapidly disappeared in the first 5 min with the fluidized-bed Fenton process. Nitrobenzene removal efficiency of the fluidized-bed Fenton process was higher than the traditional Fenton process. The removal efficiencies were 88% and 94% in the Fenton and the fluidized-bed Fenton processes, respectively.

The higher removal efficiency of nitrobenzene by fluidized-bed Fenton process is probably because (a) hydroxyl radicals produced from the Fenton's reagent in Eq. (1) can oxidize nitrobenzene; (b) some  $\text{Fe}^{3+}$  can convert back to  $\text{Fe}^{2+}$  and the ferrous ions can then react with hydrogen peroxide to further produce hydroxyl radicals; (c) in the presence of a solid carrier, the ferric ion can also crystallize and grow on the surface of the carriers, reducing the precipitation of  $\text{Fe}(\text{OH})_3$ , and at the same time, the synthesized ferric oxide can serve as a catalyst in a heterogeneous reaction [9].

### 3.2. Effect of chloride ions on the fluidized-bed Fenton process

The Fenton reaction is extremely sensitive to chloride ions ( $\text{Cl}^-$ ) remaining in the solution and this inhibition may be due to the complexation and radical scavenging. As shown in Eqs. (5) and (6), chloride ions create competition between hydroxyl radicals and organics, inhibiting the oxidation. This may result in a complex reaction with ferric ions. In addition, chloride ions interact with hydroxyl radicals, competing with organic compounds and slow down the oxidation [11,13]:





**Fig. 3.** Effect of (a) chloride ion, (b) dihydrogen phosphate and (c) nitrate on the degradation of nitrobenzene by fluidized-bed Fenton process. [NB] = 10 mM, [H<sub>2</sub>O<sub>2</sub>] = 50 mM, [Fe<sup>2+</sup>] = 1 mM, Al<sub>2</sub>O<sub>3</sub> = 100 g/l, and pH<sub>i</sub> = 2.8.

According to the effect of complexation, Cl<sup>-</sup> ions may undergo a complex reaction with ferrous and ferric ions, which hinders the reaction causing hydroxyl radicals production. The complex reactions are shown in Eqs. (7)–(11) [14]:



Based on the reactions above, the Fenton reaction has been inhibited because the ferrous and ferric complexes cannot catalyze hydrogen peroxide to produce hydroxyl radicals as efficiently as their free types.

This part examines the effect of chloride ion on nitrobenzene degradation by fluidized-bed Fenton process, where the chloride ion concentration was set at 0, 1.5, 20 and 200 mM. Fig. 3(a) shows that the oxidation of nitrobenzene decreased with increasing chloride ion concentration, indicating that the degradation efficiency of

nitrobenzene decreases as the Cl<sup>-</sup> ion concentration increases. The removal efficiencies of nitrobenzene in the presence of 0, 1.5, 20 and 200 mM of chloride ion were 93.70%, 92.40%, 93.00% and 91.80%, respectively. The pseudo-second-order rate constants are shown in Table 1. Good fit of the linear model to the data was obtained with  $R > 0.95$  in all cases. The inhibition effect of chloride ion was slightly increased with increasing chloride ion concentration. This is due to the competition between chloride ions and organic compounds in the reaction with hydroxyl radicals, leading to the inhibition of the oxidation. Chloride ions can also react with ferrous ions and ferric ions, as described in Eqs. (7) and (9). In addition, chloride ions can also interact with hydroxyl radicals, and slowing down the oxidation rate. However, there was almost no difference in the amount of nitrobenzene remaining after 60 min of reaction time when the chloride ion concentrations were in the range of 0–1.5 mM. This reveals that the inhibition can be overcome by extending the reaction time if the concentration of chloride ions is less than 20 mM as also shown in Fig. 3(a).

### 3.3. Effect of dihydrogen phosphate on fluidized-bed Fenton process

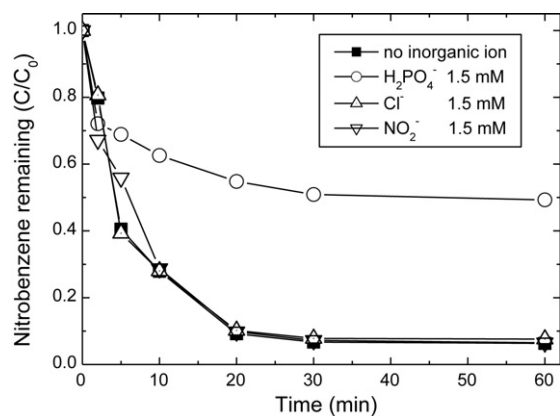
In this experiment, the effect of dihydrogen phosphate on a fluidized-bed Fenton process was investigated. The Fenton reaction is extremely sensitive to inorganic anions present in the solution, and in the case of dihydrogen phosphate ions, oxidation is clearly inhibited. The dihydrogen phosphate ion concentration was operated at 0, 1.5, 20 and 200 mM. Fig. 3(b) shows that the nitrobenzene removal increased with decreasing dihydrogen phosphate ion concentration.

When dihydrogen phosphate was introduced into the reactor, the nitrobenzene degradation efficiency fell from 93.7% to 50.1%. The removal efficiencies of nitrobenzene in the presence of 0, 1.5, 20 and 200 mM of dihydrogen phosphate were 93.7%, 50.1%, 46.5%

**Table 1**

Pseudo-second order rate constant of nitrobenzene under different inorganic ion concentrations by fluidized-bed Fenton process. [NB] = 10 mM, [H<sub>2</sub>O<sub>2</sub>] = 50 mM, [Fe<sup>2+</sup>] = 1 mM, Al<sub>2</sub>O<sub>3</sub> = 100 g/l, and pH<sub>i</sub> = 2.8.

Inorganic ions (mM)	Rate constant (M <sup>-1</sup> min <sup>-1</sup> )		
	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>
0	0.49	0.49	0.49
1.5	0.03	0.42	0.46
20	0.02	0.38	0.37
200	0.02	0.25	0.36



**Fig. 4.** Comparison between inorganic ions on the removal of nitrobenzene by fluidized-bed Fenton process. [NB]=10 mM, [H<sub>2</sub>O<sub>2</sub>]=50 mM, [Fe<sup>2+</sup>]=1 mM, Al<sub>2</sub>O<sub>3</sub>=100 g/l, and pH<sub>i</sub>=2.8.

and 44.9%, respectively, indicating that nitrobenzene degradation was slow in the presence of dihydrogen phosphate. The complexation reactions with ferrous ion could be occurring here, which can affect the distribution of iron species and their reactivity with hydrogen peroxide in the reaction solution. The presence of dihydrogen phosphate ions leads to competition between the organics and the hydroxyl radicals, which retards the degradation of nitrobenzene.

The rate constant of nitrobenzene degradation followed the same trend as nitrobenzene removal efficiency. The pseudo-second-order rate constants obtained under different experimental conditions are shown in Table 1. The inhibition effect of dihydrogen phosphate increased with increasing dihydrogen phosphate concentration from 0 to 0.2 M. It is obvious that the nitrobenzene degradation was inhibited in the presence of dihydrogen phosphate. The phosphate ions reaction in the solution depended on the cation species and the pH of the solution. The pH-phosphate distribution diagram [15] shows that at pH 3, phosphate primarily exists in the form of H<sub>2</sub>PO<sub>4</sub><sup>-</sup> which will react with ferrous and ferric ions to form the complex compounds, as shown in Eqs. (12) and (13). These complexes retard the reaction and the rate of the oxidation falls [16]:



Ferrous ions mainly exist in the form of FeH<sub>2</sub>PO<sub>4</sub><sup>+</sup> during the first stage of a Fenton reaction. It is still possible to oxidize nitrobenzene in the first stage since FeH<sub>2</sub>PO<sub>4</sub><sup>+</sup> may react with hydrogen peroxide and produce radicals. However, in the second stage, nitrobenzene was hardly decomposed. In the second stage, ferric ions undergo a complex reaction with H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, becoming (FeH<sub>2</sub>PO<sub>4</sub><sup>2+</sup>). This causes ferric ions to lose the ability to catalyze hydrogen peroxide since FeH<sub>2</sub>PO<sub>4</sub><sup>2+</sup> reacts slowly or not at all with hydrogen peroxide [11]. Furthermore, the concentration of the free ferric ions remaining in the solution is too low, so that the decomposition reaction of nitrobenzene cannot be observed. This suggests that in the presence of dihydrogen phosphate ions the nitrobenzene degradation decreased because ferrous ions were inhibited by formation of unreactive ferric complexes.

### 3.4. Effect of nitrate on fluidized-bed Fenton process

The effect of nitrate on fluidized-bed Fenton process was also examined in this study. The nitrate ions were at 0, 1.5, 20 and 200 mM, as shown in Fig. 3(c). The removal efficiency of nitrobenzene

was between 92.4% and 93.7% when nitrate concentrations varied from 0 to 200 mM, respectively. The removal efficiency of nitrobenzene in the presence of nitrate was almost the same in all experiments. The presence of nitrate ions on the removal efficiency of nitrobenzene using fluidized-bed Fenton process was not obvious in this study, even when the nitrate concentration was as high as 200 mM. The degradation rate of nitrobenzene also followed a pseudo-second order behavior and the rate constant had the same trend as nitrobenzene removal efficiency, as illustrated in Table 1.

These results show that the inhibition effect of nitrate on the nitrobenzene degradation was not significant in this study. Nitrate ions are not known to form complexes with either ferrous or ferric ions. Generally, there are two reasons why NO<sub>3</sub><sup>-</sup> has less effect on nitrobenzene degradation than Cl<sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>: (1) NO<sub>3</sub><sup>-</sup> will not produce a complex reaction with ferric ions, so the reaction between ferric ions and hydrogen peroxide is not suppressed and (2) NO<sub>3</sub><sup>-</sup> will not react with hydroxyl radicals, so the degradation rate of nitrobenzene is not inhibited [17].

In summary, it appears that all anions affected the degradation of nitrobenzene, but to a varying degree as shown in Fig. 4. The effects of inorganic ions on the degradation of nitrobenzene by fluidized-bed Fenton process showed that chloride ion and dihydrogen phosphate had a significant effect on the inhibition of nitrobenzene degradation. However, nitrate had no significant effect. Their sequence according to the inhibition reaction was H<sub>2</sub>PO<sub>4</sub><sup>-</sup> ≫ Cl<sup>-</sup> > NO<sub>3</sub><sup>-</sup>.

## 4. Conclusion

The degradation of nitrobenzene using a fluidized-bed Fenton process is extremely sensitive to inorganic anions present in the reaction solution. In addition to chloride ions, dihydrogen phosphate and nitrate ions in the solutions have an adverse effect on the removal efficiency and degradation rates, but to a varying degree depending on the ions used. In the case of chloride and dihydrogen phosphate ions, oxidation is strongly inhibited, while the addition of nitrate ion had no significant effect. The complexation reactions with ferrous and ferric ions are postulated to be the main reason for the inhibition of the degradation efficiency, though the scavenging of hydroxyl radicals and the formation of inorganic radicals may also play an important role. Their order of sequence according to the inhibition reaction was H<sub>2</sub>PO<sub>4</sub><sup>-</sup> ≫ Cl<sup>-</sup> > NO<sub>3</sub><sup>-</sup>. Moreover, this study revealed that the degradation of nitrobenzene is very fast for the Fenton process and becomes even faster for fluidized-bed Fenton process.

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