Oxidative Destruction of Phenolic Compounds in Water by Potassium Ferrate (VI)*

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Abstract: Oxidative destruction of phenolic compounds in real water and buffer with potassium ferrate was investigated by static shaking and jar tests. It was found that ferrate oxidation leads to rapid destruction of phenol in real water, while approximate 80% degradation was achieved in 10 minutes. Additional alum coagulation enhanced the phenol removal but the enhancements were insignificant. It was also found that the oxidation of phenols in pure water was highly pH-dependent. The maximum phenol degradation was obtained at neutral or weak alkaline pH conditions in the tests. Actually, the optimum degradation pH was suggested to be correlative to pKa of phenols. The different effects of nitro and chlorine substituent groups on the phenols degradation were also discussed in this paper.

Key words: Potassium ferrate; phenol; pH
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Phenol and its derivatives are important synthesis intermediates in the chemical industry and widely used as raw material in many petrochemical, chemical and pharmaceutical industries. At present, the importance of phenol is proved by its ever increasing production which reached 1900 million of kilograms in 1995 for the USA alone. As a result, phenols have been found in the wastewater of many industrial processes, and also found in wood, coal and household garbage to a lesser degree.

Phenols are considered as priority pollutants for they are harmful to organisms at low concentrations, and many of them have been listed in hazardous pollutants because of their potential harm to human health. Phenols are also precursors of halogenated by-products and lead to the formation of chlorophenols in drinking water disinfection process. Chlorophenols have strong organoleptic effects with rather low taste threshold (0.1 ppb) and thus deteriorate the finished water quality. Besides, chlorophenol compounds have been studied in recent years in view of their persistence and potential hazard in the environment.

Among the methods for removing phenol from aqueous wastes, solvent extraction is only economically attractive if the phenol concentration is high enough, i.e. over 1%. Likewise, biological treatment is appropriate for low phenol concentrations due to the bactericide properties of the phenolic compounds. However, these two methods are not suitable for phenols removal at the concentration level in surface water. Conventional coagulation-sedimentation processes are still the main approach for the particulates (e.g. clay, silica) and dissolved impurities (e.g. organic matters) removal from surface water. Unfortunately, many organic matters such as phenols are hardly removed by these processes.

Chemical pre-oxidation is seemed to be a promising way for phenol removal in drinking water treatment. Chlorine was widely investigated as pre-oxidants, but the negative effects of formation of disinfection by-products (DBPs) limit the wide application of pre-chlorination. Alternative pre-oxidants such as chlorine dioxide and ozone also have associated drawbacks. Ozone disinfection leads to the formation of bromate and bromoform in the presence of bromide ions[1]. After decomposition, chlorine dioxide gives rise to the formation of harmful chlorite and chlorate ions[2].

Ferrate (VI) is the higher oxidation state of iron and has a strong redox potential through the entire pH range (from −2.2 V in acid to −0.7 V in base)[3]. Ferrate has been studied as a disinfectant by many investigators, and it was found that ferrate inactivated wide varieties of microorganisms in buffered water. Ferrate (VI) can also destroy several priority pollutants in stimulated soft water[4]. We have found that ferrate pre-oxidation followed by aluminium coagulation effec-

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tively decreased residual algae concentration, co-precipitated heavy metal ions, aid the removal of turbidity in organic-rich water[5,6]. In addition, recent study found that ferrate treatment does not produce any remaining mutagenic by-products during the treatment process (Deluca et al., 1983b). The only product of ferrate decomposition in water is ferric hydroxide, which could be completely removed by the following alum coagulation-sedimentation[7]. Due to the unique characteristics of combining oxidant and coagulant qualities of ferrate (VI), it is a desirable pre-oxidant in drinking water treatment.

The objectives of this paper are to investigate the potential of ferrate oxidation against phenols in the water. Phenol and two substituted phenols, i.e. 2, 4-dechlorophenol (2, 4-DCP) and *p*-nitrophenol (*p*-NP), were selected as target compounds. The variables of changing experimental conditions included two water backgrounds, i. e. real water and buffer; ferrate dosage; reaction time; and pH. The impacts of substituted functional groups on the oxidation efficiency were also discussed.

1 Materials and methods

1.1 Chemicals and solutions

Potassium ferrate [K_2FeO_4] was prepared by the modification of the method of reaction between OCl⁻ and Fe(OH)$_3$ (gel) in strongly basic media and isolated from saturated KOH solution, and stored in the desiccators. The purity was determined by the Arsenite-Bromate method. Phenol, 2, 4-dechlorophenol (2, 4-DCP) and p-nitrophenol (*p*-NP) (+99% purity, Beijing chemical Ltd, Beijing, China) were purified before use. The phenols were dissolved into double distilled water to make a stock solution and stored in the refrigerator at 4 oC. The stock solutions were freshly diluted to 100 μg/L to make testing solutions just before tests. The pH of phenol testing solutions was adjusted to a certain values just before tests by KH_2PO_4 – K_2HPO_4 buffer (0.05M, pH 5.0, 6.0, 7.0, 8.0, 9.0), $Na_2B_4O_7 \cdot 10H_2O$ – Na_2CO_3 buffer (0.05M, pH 10.0, 11.0) and 0.1N HCl (pH 3.0, 5.0). Organic buffers were not adopted in the tests in order to avoid the undesirable reaction between ferrate and organics. Real river water from northern plain area was collected and stored in the refrigerator at 4 ℃. The water was brought back to room temperature (22 ℃) before tests. All chemical solutions and buffer solutions were prepared in double distilled water. The water quality of real water was listed as follows: turbidity 12 NTU; Color 16 CU; pH 7.1; total hardness 120 mg/L $CaCO_3$; total alkalinity 55 mg/L $CaCO_3$; DOC 5.3 mg/L.

1.2 Batch tests

Batch tests including shaking tests and jar tests were conducted in the laboratory. Ferrate solution was prepared by dissolving potassium ferrate solid in double distilled water just before use in order to minimize the loss of ferrate in water. In the case of shaking test, an aliquot of potassium ferrate solution at 3 mg/L were injected into a series of glass bottles (200 mL) containing 100 mL buffered phenol testing solutions; then the bottles were shook at 275 times/min for a period at ambient temperature (22 ℃). After that, the reaction was quenched by adding excess sodium sulfite at various time intervals. And then, the water samples were subjected to phenol measurement. The jar tests were carried out with a six-unit stirrer apparatus. Real water was first spiked with 50 μg/L phenol and transferred into 1000 mL bakers. Aliquot of ferrate solution was mixed with water samples in each beaker for a period before the addition of alum. Some of the water samples were subjected to coagulation with the addition of specific volume of alum solution at 300 rpm for 1 min. Thereafter, the samples were slowly stirred for 10 min at 60 rpm, and then settled for 30 min. The residual phenol concentration of supernatant was measured.

1.3 Analytical methods

Concentration of phenols was analyzed by a standard method based on spectrophotometric analysis at 510 nm of the developed color results from the reaction of phenol with 4-aminoantipyrene[8]. The Ferrate (VI) working solutions were prepared by dissolving ferrate solid in double distilled water just before use in order to minimise the loss of ferrate. A molar absorption coefficient $\varepsilon_{510\ nm} = 1\ 150\ M^{-1}\ cm^{-1}$ was used for the calculation of ferrate decomposition in buffer solutions[9].

2 Results and discussion

Figure 1 presents the phenol degradation by ferrate oxidation under natural condition. The results from the trials with additional alum coagulation are also presented in the same figure for comparison. The initial concentration of phenol in real water was 50 μg/L, and the dosage of ferrate was ranged from 1 to 5 mg/L. Ferrate oxidation led to rapid destruction of phenol in real water; the residual phenol further decreased with increasing ferrate dosage (Fig. 1a). The lowest phenol residual (16.2 μg/L, about 67% reduction) was obtained at the dosage of 5 mg/L. The residual concentration was not proportional to the dosage of ferrate. This may be attributable to the consumption of ferrate by other reductive materials or the products from phenol

oxidation in the water. The residual phenol concentration from the trials with additional alum coagulation was lower than that from solely ferrate oxidation, but the difference was not significant. This is because alum coagulation is not effective in removing phenol from water.

The residual phenol also varied with reaction time (Fig. 1b). The residual phenol dropped rapidly within the first period of reaction time (5 min), and then gradually decreased with prolonged contact time and then reached the lowest plateau at 10 min (about 80% degradation). This indicated a quick oxidation of phenol by ferrate in real water. Additional alum coagulation led to slight enhancement in phenol removal.

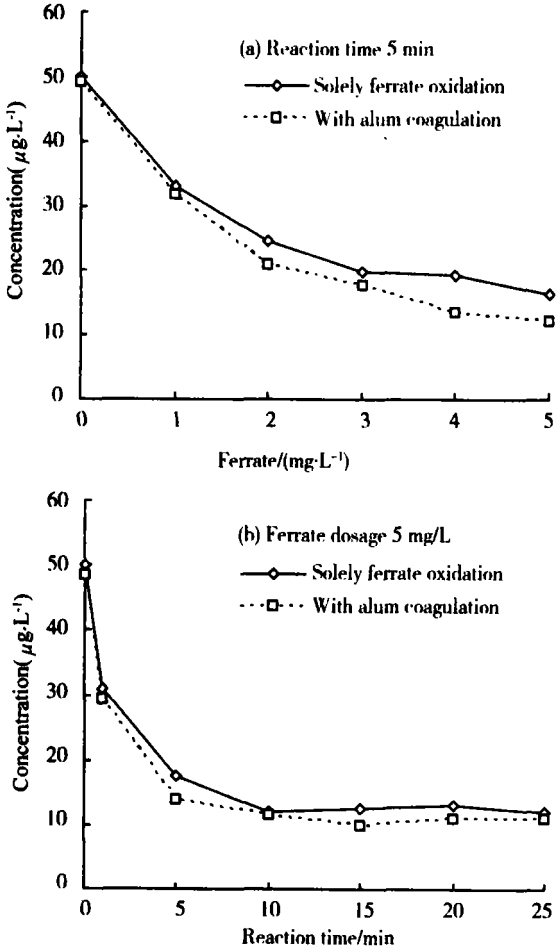

Fig. 1 Phenol degradation by ferrate oxidation in real water

Figure 2 illustrats the variation of residual phenol in pure water with reaction time at various pH values. The dosage of ferrate was selected to be 3 mg/L as normally used in surface water treatment. Generally, "two-stage" time-dependent pattern in residual phenol with steep slope in the first stage (within early 5 minutes) follows a slow slope within prolonged reaction time in the secondary stage was observed. The "two-stage" pattern was much clear at pH 3, 5 and 11, in which an obvious inflexion was obtained. This phenomenon is consistent with the results in the real water (see Fig 1b). The initial sudden drop of residual phenol indicated the rapid reaction rate between ferrate and phenol, especially in the case of low pH conditions. It is worth to note that the decrease in the first oxidation stage at low pH condition was larger than that at high pH condition, for example the residual phenol concentration at different pH condition after 3 min oxidation was in the order of pH 3 < pH 5 < pH 7 < pH 9 < pH 11. It seemed that there exists correlation between the first stage oxidation efficiency and the redox potential of ferrate, for ferrate has higher oxidative potential in acid solution than in base[10].

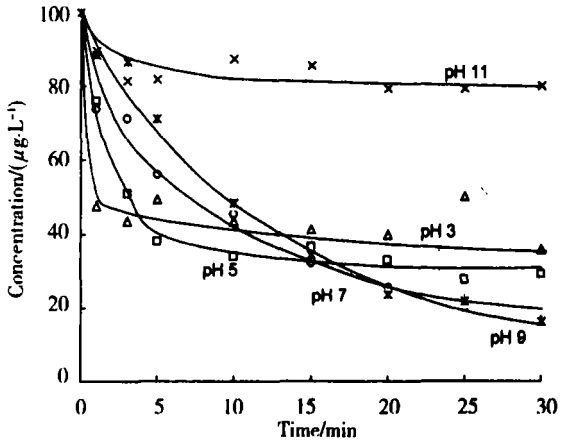

Fig. 2 Phenol degradation by ferrate oxidation under various pH conditions (ferrate 3 mg/L, as K_2FeO_4)

The residual phenol further decreased in the secondary stage within the prolonged reaction time, but the decreasing rate varied largely among various pH conditions. Slowly reducing rate in phenol residual at pH 3, 5 and 11 were observed, in contrary relative higher reducing rate were obtained at pH 7 and 9. The higher oxidation rate in the secondary stage resulted in relative lower residual phenol at pH 7 and 9, compared to that at pH 3, 5 and 11.

The data of these trials were reorganized and plotted in Figure 3 to illustrate the function of pH at various reaction times. It was quite clear that the higher phenol destruction was achieved at longer reaction time (more than 10 minutes) under neutral pH conditions, for example at pH 9 the residual phenol dropped from 88 μg/L to 16 μg/L as reaction time extended from 1 min to 30 min. Whilst under acid and alkaline conditions, only small improvements in reduction were obtained with prolonged reaction time. The phenol residual concentration with the function of pH at longer reaction time could be best described by "U" shape curves. This phenomenon was mainly attributable to the changing

stability of ferrate in water

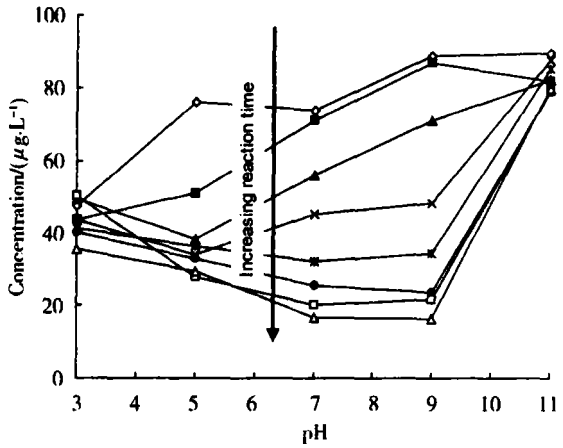

Fig. 3　Phenol degradation by ferrate oxidation with the function of pH (ferrate 3 mg/L as K_2FeO_4)

Figure 4 shows that the decay of ferrate in aqueous system at various pH values with initial concentration 3 mg/L. The existence of reductive materials in the solution may accelerate the decomposition of ferrate. In this study, the decomposition of ferrate while co-existed with phenol was not monitored. Ferrate becomes more and more stable in the water with the increasing pH value, this agrees with the findings of many other researchers[11]. Higher stability provides sufficient long oxidation in neural and alkaline conditions (pH 8 – 10), therefore leads to substantial reduction of phenol (see Fig. 2).

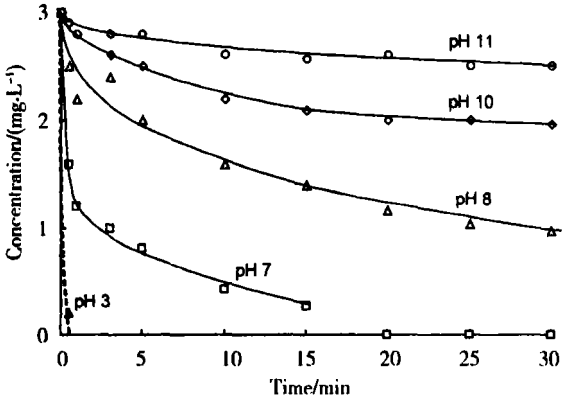

Fig. 4　Decomposition of ferrate under various pH values

It was concluded that the redox potential and the stability were two key factors influencing the phenol degradation efficiency in the ferrate-phenol reaction system. The stability increases with increasing pH value while the oxidative potential of ferrate drops off from 2.2 to 0.7 in aqueous system. In the case of low pH condition, e.g. pH 3 and 5, higher oxidative potential of ferrate led to fast phenol oxidation and resulted in sudden drop in residual concentration in the first stage (see Fig. 2). After that, the rapid decomposition of ferrate almost ceased the reaction and left an inflexion in reduction curve. It is worth to note that the residual phenol further decreases to a small extent after complete decomposition of ferrate, for quick decay of typical violet color of ferrate was observed (within several minutes). This indicates that ferrate decomposition may generate some intermediate oxidative materials such as Fe^{5+} and Fe^{4+} species, and caused further oxidation.

While in the neutral and alkaline conditions, lower redox potential of ferrate led to slow oxidation rate and consequent gradual reduction in phenol residual. Rather low phenol degradation at pH 11 in the first stage was obtained, together with the low decreasing rate in the long reaction time, indicating the slow reaction rate of ferrate and phenol within the whole reaction period. Actually, the characteristic violet color of ferrate persisted throughout the whole reaction time while ferrate co-existed with phenol in alkaline solution (pH 11) because of the extreme high stability of ferrate at pH 10 – 11[3].

In addition, the relative distribution of phenol and phenate species (C_6H_5OH /$C_6H_5O^-$) is suggested to be another important factor, as the phenate ion is much more susceptible to oxidation than phenol[12]. The large formation of the ionized species at higher pH values could increase the activity of phenol to ferrate oxidation and supplementary contribute to the phenol degradation with the increasing pH. This will be discussed later based on the following results.

The oxidation of two substituted phenols, i.e. 2, 4-dichlorophenol (2, 4-DCP) and *p*-nitrophenol (*p*-NP), was also conducted in this study. The variations of residual concentration at different reaction time were similar to those of phenol and not shown in this paper. The residual concentrations of two substituted phenols as the function of pH at various reaction times are illustrated in Figure 5. The data from phenol are also presented in the same figure to compare and facilitate the discussion. It is obvious that the pattern of oxidation curves of *p*-NP and 2, 4-DCP was similar to that of phenol except for the optimum phenol degradation pH. This indicates that the oxidation of *p*-NP and 2, 4-DCP by ferrate is also pH-dependent.

It is worth to notice the apparent differences in optimum degradation pH between three kinds of phenols. The optimum pH was around 8 for 2, 4-DCP, 7 for *p*-NP, and a narrow range around 9 for phenol, respectively. The different pKa value (the negative logarithm expression of the acidity constant) of 2, 4-DCP, *p*-NP and phenol could be the reasonable explanation for above differences for the optimum oxidation pH ap

peared around their own pKa value. The pKa values for phenol, 2, 4-DCP and p-NP are 8.98, 7.8 and 7.25, respectively, which corresponds to the optimum oxidation pH (see Fig. 6). The pH determines the degree of dissociation of the phenol and substituted phenols, and this impacts the reaction to some certain extent. In the weak acid conditions below pKa, phenol molecule dominates the species in the solution. The concentrations of phenate ions increase with pH value and reach the equal level to phenol molecule at pKa, after that the phenate ions prevail in the weak alkaline conditions above pKa. The deprotonated compounds, refered to phenate ions in this paper, have been found to be more reactive in oxidation. The increments of phenate ions in solution could contribute to the degradation efficiency by ferrate oxidation. In the case for phenol oxidation, as the pKa of phenol (9.89) is close to the pH zone 10-11, where ferrate is much stable, a lower optimum degradation pH appeared (around 9). Since the redox potential and stability of ferrate, pKa of phenols was all pH-dependent, pH was believed to be the most important factor influencing the oxidation efficiency of phenols and shape the phenol residual curve pattern along reaction time (see Fig. 2).

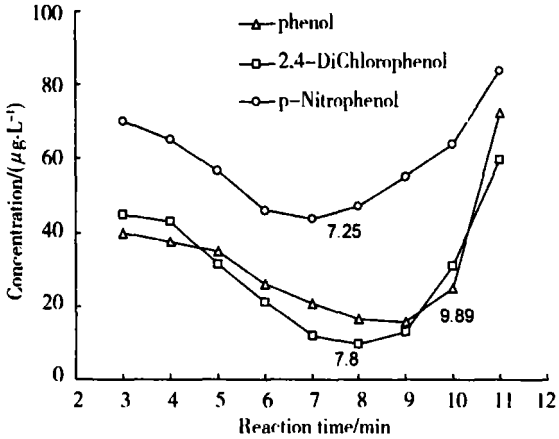

Fig. 5 Phenol, 2, 4-dichlorophenol and p-nitrophenol degradation by ferrate oxidation with the function of pH (ferrate 3 mg/L, as K_2FeO_4)

The figure also showes the big difference in phenol degradation efficiency among three phenols (see Fig. 6). The residual concentrations at optimum degradation pH were 15.8, 13 and 55 μg/L for phenol, 2, 4-DCP and p-NP, respectively. 2, 4-DCP is the most susceptible one than phenol and p-NP. The reasons for this phenomenon are not quite clear at current stage but it may be attributable to the substituted groups. It was assumed that the electro-withdrawing effect of nitro group lowered the reactivity of p-NP to the ferrate oxidation. Besides, electron-donating resonance effect of chlorine substitution may also lead to the increase of reactivity[13], which resulted in the faster degradation by ferrate oxidation.

3 Conclusions

The static tests were conducted to evaluate the ferrate oxidation of phenol, 2, 4-dichlorophenol and *p*-nitrophenol in real water and pure water. It was found that ferrate oxidation led to rapid degradation of phenol in real water condition. Higher ferrate dosage and longer contacting time resulted in higher phenol degradation. Additional aluminium coagulation enhanced the phenol removal to a small extent. Two stage oxidation curve of phenol degradation (rapid decrease followed by slow reduction) along reaction time was obtained. Redox potential, stability of ferrate and pKa of phenols in aqueous system were believed to be key factors that influence the degradation efficiency. The phenols oxidation by ferrate as the function of pH could be described by U-shape curves at long reaction time. The optimum degradation pH for three kinds of phenols was confirmed to be correlative with their pKa. In addition, substituent chlorine and nitro groups on the aromatic ring enhanced or hindered the phenols oxidation by ferrate.

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高铁酸盐氧化去除水中酚类化合物的研究

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摘　要：采用实验室试验研究了高铁酸盐氧化分解水中酚类化合物的效果。研究发现，高铁酸盐能够在短时间内氧化地表水中的苯酚，10 min可以分解 80%以上。后续采用硫酸铝混凝可以强化苯酚的去除。另外，高铁酸盐氧化酚类化合物受 pH影响较大，在中性和弱碱性条件下，高铁酸盐的氧化速率最高。酚类化合物的最优氧化速度 pH区间与其 pKa相关。酚类化合物苯环上的硝基和氯取代基也是影响氧化速度的主要因素。

关键词：高铁酸盐；酚类化合物；pH；取代基

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