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Effect of sodium dodecyl benzene sulfonate on the process of Fenton degradation of 4-chlorophenol

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ABSTRACT

The Fenton process has been shown to be very successful in removing highly toxic chlorinated phenols from water. However, the influence of other constituents in industrial wastewater, such as sodium dodecyl benzene sulfonate (SDBS) surfactants should be intensively researched. In this study, the effects of SDBS on the kinetics of 4-chlorophenol (4-CP) degradation undergoing Fenton process have been studied. Results showed that 4-CP degradation ratio decreased as SDBS concentration increased. The 4-CP degradation ratio declined from 98.3 to 84.5% when the SDBS concentration increased from 0 to 2.0 mmol L^{-1} after 10 min reaction. This experimental result was attributed to the hydration between 4-CP and SDBS and the consumption of hydroxyl radicals ($^{\cdot}OH$) by surfactants. The SDBS had amphiphilic structure in water environment with hydrophilic and hydrophobic entities. It could interact with 4-CP functional groups via hydrophilic groups (benzene sulfonate) by hydration in the aqueous phase. The kinetics modeling indicates that the 4-CP degradation reaction followed the pseudo-first-order reaction for 4-CP concentration. The SDBS also had affirmative effects on the hydrophilic and organic acid intermediate organic matter mineralization. The SDBS existence could reduce the maximum concentrations of intermediate products. For example, the organic acids intermediate maleic acid concentration was descend from 2.59 to 0.21 mmol L^{-1} when the SDBS concentration increased from 0 to 2.0 mmol L^{-1}. In a word, the surfactants SDBS can reduce the 4-CP degradation ratio and encourage the intermediate products mineralization.

Keywords: Fenton; Degradation; Hydrogen peroxide; 4-chlorophenol; SDBS; Surfactants

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1. Introduction

Phenolic compounds could pose serious risks to the environment once they are discharged into natural water for their degradation-resistant and low biodegradability characteristic [1]. The 4-chlorophenol (4-CP) is one of the most toxic chlorinated phenols which could cause grave problems for a wide range of organisms. 4-CP has been widely used as intermediates in the synthesis of the higher chlorinated congeners, certain dyes, pesticides, pulp, and paper industries [2,3]. Many satisfactory results have been

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demonstrated in the advanced oxidation processes (AOP) in aqueous phase [4,5]. In the AOP, Fenton process has been widely researched for its fast response speed, high mineralization rate, and low secondary pollution [6,7]. But in most Fenton process research works, only single phenolic compound was used as the model waste substance presently [8–10]. This greatly limits the practical application of Fenton process in wastewater treatment because it's efficiency is largely impacted by the presence of other chemical compounds in wastewater, such as surfactants, organic dyestuff, and chelation agents. Although chemical oxygen demand and total organic carbon are the parameters to evaluate the wastewater quality and efficiency of the treatment process [11,12], both parameters only represent the macroscopical thinking and hardly provide the microcosmic characteristics of different structures and species of multifarious contamination in the wastewater [13].

In our opinion, microcosmic characteristics of different structures and species of multifarious contamination in wastewater are very critical to develop useful treatment technologies for practical applications. In this work, the sodium dodecyl benzene sulfonate (SDBS) was chosen as the representative of the surfactants because it was often applied to paper, dye, and pesticide production. The influences of the surfactant on the kinetic process of Fenton process degrading 4-CP, the intermediate species and the degradation pathway are discussed. Through experiments we inferred the impact of SDBS on microscopic mechanism and characteristics of the degradation of 4-CP, which no doubt will provide the theoretical basis for actual industrial wastewater treatment by Fenton process.

2. Experimental procedure

The experiments were performed in 200 mL beaker with continuous stirring (100 rpm) at room temperature (18 ± 2℃). The initial concentration of 4-CP was maintained 1 mmol L^{-1} and the initial concentration of SDBS was 0 mg L^{-1}. Series of experiments were conducted in order to obtain the optimal parameters such as pH, Fe^{2+} initial concentration, and H_2O_2 concentration. At the beginning of the experiment, pH was adjusted with 25% (V/V) sulfuric acid to set value. Then ferrous iron catalyst (ferrous sulfate, $FeSO_4{\cdot}7H_2O$), SDBS, and hydrogen peroxide (30% W/W) were joined to the 4-CP solution in turn. Under the optimal concentrations of ferrous iron catalyst and hydrogen peroxide, the SDBS concentration was subsequently varied from 0 to 2.0 mmol L^{-1}. Samples were collected every 15 s. The concentrations of 4-CP and aromatic intermediates, such as maleic acid (MA), oxalic acid (OA), hydroquinone (H), Pyrocatechol (P), Resorcinol (R), and Benzoquinone (BQ), were analyzed by HPLC (Shimadzu LC-6A Kyoto, Japan) with a reversed phase C18 column (Agilent, 150 mm × 4.6 mm, 5 μm) and ultraviolet detector (The wavelength was set at 265 nm). The volume ratio of mobile phase of deionized water (containing 1% phosphoric acid) and methanol was kept at 40:60. Concentrations of 4-CP and intermediates were determined by a quantitative method of peak area.

3. Results and discussion

3.1. Influence of SDBS and kinetics of 4-CP degradation

The optimal parameters (pH, Fe^{2+} concentration and H_2O_2 concentration) of Fenton process treatment 4-CP solution (1 mmol L^{-1}) were studied by single-factor experiments at room temperature (Fig. 1). The results showed that the degradation ratio of 4-CP ($[4\text{-CP}]_0 = 1$ mmol L^{-1}) could reach 98.3% after 10 min reaction in the optimal concentrations ($[Fe^{2+}]_0 = 1$ mmol L^{-1}, $[H_2O_2]_0 = 5$ mmol L^{-1}) and pH 3.0. They were located in excellent agreement with the literature data [9].

In order to examine the effect of surfactant on the Fenton process, distinct concentrations of SDBS were dosed in a series of tests while other reaction conditions remained the same. Fig. 2 showed the time courses of 4-CP concentration with the change of SDBS concentration. Apparently, the degradation ratio was reduced by the presence of SDBS in the reaction solution. Higher concentrations of SDBS led to less 4-CP degradation rate by Fenton process. The degradation

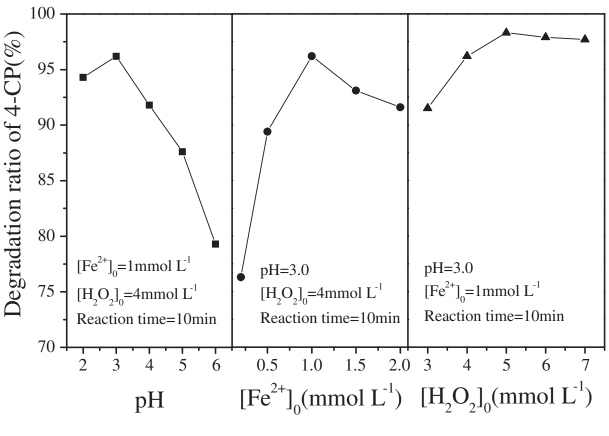

Fig. 1. The optimal reaction conditions of 4-CP degradation by Fenton process at room temperature.

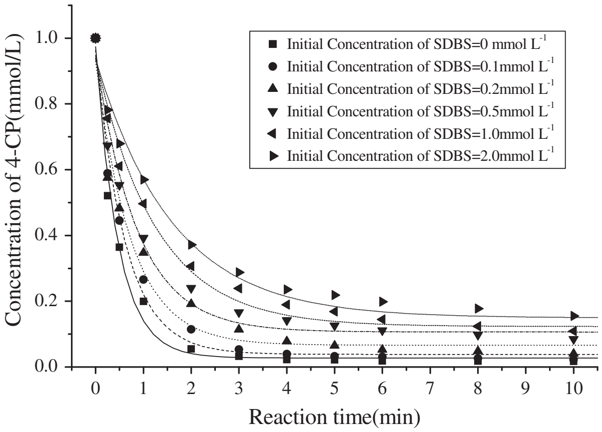

Fig. 2. The fitting curves of pseudo-first-order reaction for 4-CP degradation by Fenton process with different SDBS concentrations at optimal process conditions (pH 3.0, $[Fe^{2+}]_0 = 1$ mmol L^{-1}, $[H_2O_2]_0 = 5$ mmol L^{-1}).

ratio declined from 98.3 to 84.5% when the SDBS concentration increased from 0 to 2.0 mmol L^{-1} after 10 min reaction.

The kinetics of the reaction followed the pseudo-first-order reaction to 4-CP concentration. The fitting curves of pseudo-first-order reaction for 4-CP degradation by Fenton reaction with different SDBS concentration at optimal conditions were presented by the curves in Fig. 2. Table 1 presented the calculation of pseudo-first-order rate constants, *k*, of the 4-CP degraded by Fenton process for the 10 min reaction. The first-order kinetics of the degradation ratio was expressed as follows (Eq. (1)):

$$C = C_0 e^{-kt} \tag{1}$$

where *C* is the concentration of 4-CP at reaction time *t*, C_0 is the initial concentration of 4-CP. *k* is the pseudo-first-order rate constant of degradation, and *t* is time.

Table 1
Pseudo-first-order equations of 4-CP degradation by Fenton process with different SDBS concentrations

Concentration of SDBS (mmol L^{-1})	Pseudo-first-order equation: $C = C_0 \exp(-kt)$			
	k (min^{-1})	R^2	Number of points	Prob. > *F*
0	2.137	0.989	11	<0.0001
0.1	1.635	0.988	11	<0.0001
0.2	1.389	0.964	11	<0.0001
0.5	1.217	0.983	11	<0.0001
1.0	0.878	0.984	11	<0.0001
2.0	0.732	0.989	11	<0.0001

The dynamic process of 4-CP degradation follows the pseudo-first-order kinetics expression. It could be seen that the calculated value of *k*, for reactions in the absence of SDBS, was almost three times higher than that for reactions with the addition of SDBS of 2 mmol L^{-1}. These results indicated that SDBS as the common auxiliary in pulp and paper, dyestuff, pharmaceutical, and agrochemical industries had negative effects on the Fenton process at low concentration, which was reported earlier.

3.2. Discussion of reaction process

The experiments in the present work indicated that the presence of SDBS affected the degradation

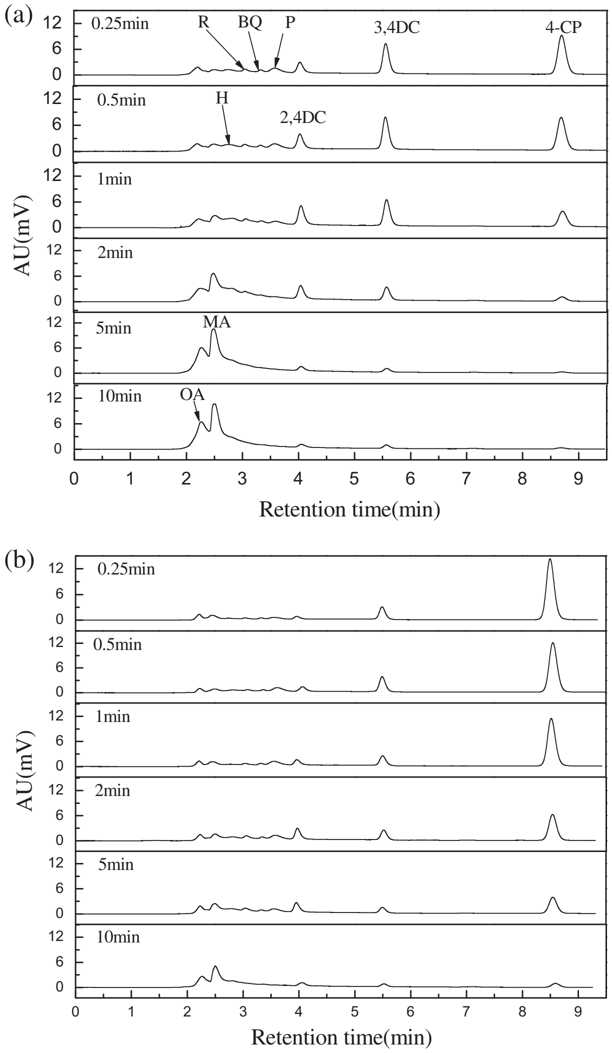

Fig. 3. HPLC chromatogram of 4-CP solution treated with Fenton process. (a) Initial SDBS concentration is 0 mmol L^{-1} and (b) initial SDS concentration is 1 mmol L^{-1} (pH 3.0, $[Fe^{2+}]_0 = 1$ mmol L^{-1}, $[H_2O_2]_0 = 5$ mmol L^{-1}).

efficiency of Fenton process. Yang and Wang [14], showed that the sodium dodecyl sulfate (SDS) surfactant had a negative effects on the Fenton process treatment of methyl orange solution even at low concentration. They mentioned that SDS had amphiphilic structure in water environment with hydrophilic and hydrophobic entities, and a shell of SDS molecules surrounding methyl orange was created and functioned as a protective layer for methyl orange via hydrophobic groups (dodecyl) of SDS which interact with the methyl orange functional groups by Van der Waals force. Therefore, the methyl orange degradation ratio declined sharply even though minimal concentration of SDS exists in the aqueous phase.

In this study, the SDBS surfactant also had amphiphilic structures and could combine with hydrophobic molecules by Van der Waals force. However, 4-CP had few hydrophobic characters. Then, SDBS could interact with 4-CP functional groups via hydrophilic groups (benzene sulfonate) by hydration in the aqueous phase. Nevertheless, the hydration between the SDBS and 4-CP was not strong enough to form a

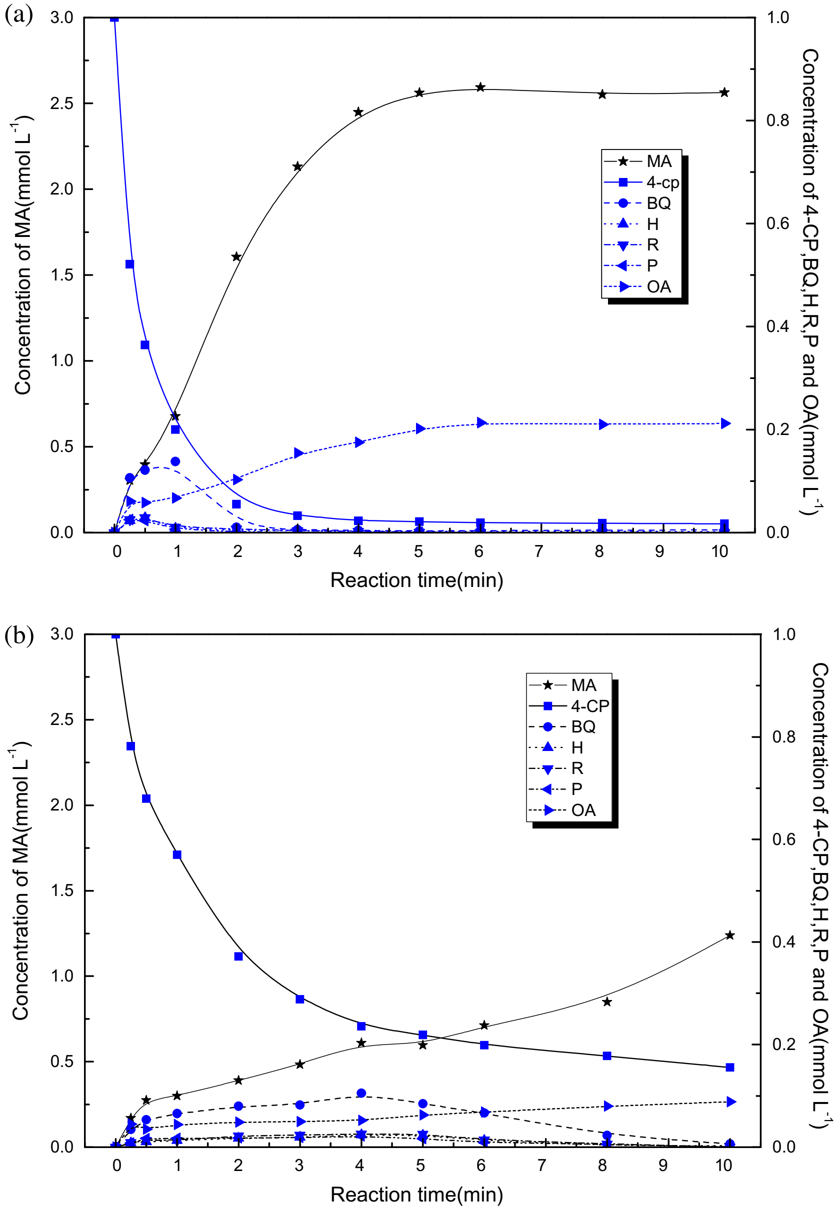

Fig. 4. Intermediates of 4-CP against the treatment time with Fenton process. (a) Initial SDBS concentration is 0 mmol L^{-1} and (b) initial SDBS concentration is 2.0 mmol L^{-1} (pH 3.0, $[Fe^{2+}]_0 = 1$ mmol L^{-1}, $[H_2O_2]_0 = 5$ mmol L^{-1}).

surfactant shell to block the hydroxyl radical attacking. At the same time, hydroxyl radicals were consumed through the reaction with free SDBS and other intermediate in the aqueous phase. Overall, 4-CP degradation by Fenton process was hampered by the presence of SDBS.

The intermediate products of the reaction were identified by HPLC. The retention times of compounds by HPLC were presented in Fig. 3. Fig. 3(a) shows the 4-CP degradation process in separate reaction time without the SDBS present. The results indicated that after 10 min reactions, the aromatic components concentrations were very low, but the organic acids such as MA and OA were found utilizing the standard addition method.

In the Fenton process, due to the stronger ortho/para directory effect of the OH^- group than that of the Cl^- group, ·OH adds to the ortho/para position of OH^- to form 4-chlorohydroxycyclohexadienyl ($C_6H_4(OH)_2Cl·$) radicals. Then the Cl^- position of 4-CP was replaced by OH to form dechlorinated aromatic product H, P, and R. The $C_6H_4(OH)_2Cl·$ radicals also could form 3, 4 dihydroxy chlorophenol (3,4DC) and 2, 4 dihydroxy chlorophenol (2,4DC). Then, the intermediate products could further react with ·OH to form C_1–C_6 ring cleavage products, such as MA and OA. The pathway of 4-CP degradation by Fenton process was shown in Fig. 5 which was in accord with the literature data [8,15,16].

Fig. 3(b) displays the 4-CP degradation process in diverse reaction time with 2 mmol L^{-1} SDBS in experimental aqueous phase. Even the 4-CP degradation by Fenton process was hampered by SDBS, the intermediate products were similar as the condition of in absence of SDBS. However, the aromatic components intermediate products such as 3,4DC and 2,4DC maintain low concentration comparing to the condition of without SDBS. Fig. 4 showed the time course of concentrations of intermediate products with 0 mmol L^{-1} (Fig. 4(a)) and 2.0 mmol L^{-1} (Fig. 4(b)) SDBS initial concentrations.

The results indicated that the SDBS also had affirmative effects on the intermediate hydrophilic organic matter mineralization. On the one hand, the SDBS hydrophobic groups have a tendency to agglomeration in the aqueous phase. Then the hydrophilic groups of SDBS which combined with the hydrophilic organic intermediate could easily stretch to the aqueous phase. Then ·OH radicals could easily attack the intermediate organic matter and degrade them into organic acids, H_2O, and CO_2. Therefor, the maximum concentrations of intermediate products are also lower. The phenomenon of the lower concentrations of MA and OA in the condition of SDBS existence is explained by the above theory. On the other hand, 4-CP degradation by Fenton process was hampered by the presence of SDBS. The reaction velocity of 4-CP reaction with ·OH radicals was lower compared to the situation in the

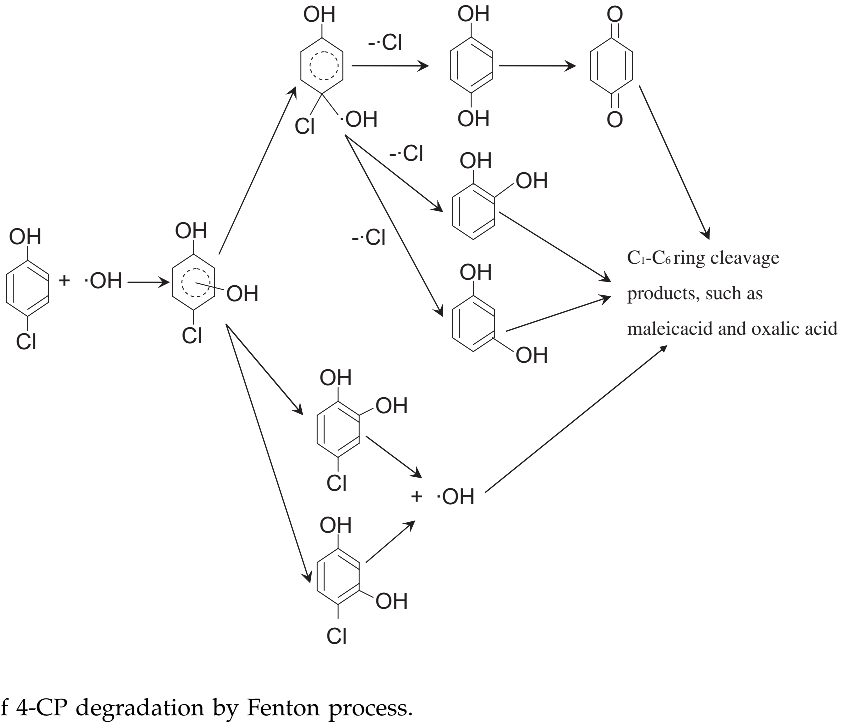

Fig. 5. The pathway of 4-CP degradation by Fenton process.

absence of SDBS. It is well known that ·OH radicals were more inclined to electrophilic attack on the aromatic ring of intermediate products such as 3,4DC and 2,4DC. Therefore, the concentrations of 3,4DC and 2,4DC are maintained lower.

4. Conclusions

According to the experiments, the presence of SDBS was found to decrease 4-CP degradation ratios. The 4-CP degradation ratio declined from 98.3 to 84.5% when the SDBS concentration increased from 0 to 2.0 mmol L^{-1} after 10 min reaction. The SDBS had amphiphilic structures and could combine with 4-CP, which had few hydrophobic characters by hydration in the aqueous phase. The hydration between the SDBS and 4-CP was not strong enough to form a surfactant shell to block the ·OH radical attacking. But, ·OH radicals were consumed through the reaction with free SDBS and other intermediate in the aqueous phase. In a word, 4-CP degradation by Fenton process was hampered by the presence of SDBS. The kinetics of 4-CP degradation reaction followed the pseudo-first-order reaction to 4-CP concentration. The reaction rate constants of 4-CP reduced with increasing concentrations of SDBS. The 4-CP degradation pathway by Fenton process had been presented. SDBS also accelerated the hydrophilic and organic acid intermediate organic matter mineralization. The SDBS existence could decrease the maximum concentrations of intermediate products.

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