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Research Article

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Degradation of 2-naphthalenesulfonic acid by Fenton oxidation

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ABSTRACT

In this study, the degradation of 2-naphthalenesulfonic acid (2-NSA) was investigated by homogeneous Fenton oxidation. The influence of reaction time, amounts of H_2O_2, ratio of $H_2O_2/FeSO_4$, solution pH and concentration of Na_2SO_4 was investigated on degradation of 2-NSA by homogeneous Fenton oxidation. The optimum conditions were obtained to be 120 min of reaction time, $H_2O_2/FeSO_4$ of 10 solution pH of 3 and H_2O_2 amount of 41.6 mg/L for a 2-NSA concentration of 50 mg/L with a COD removal of 96.0 %.

Keywords: Fenton Oxidation, hydroxyl free radical, 2-Naphthalenesulfonic acid, wastewater

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INTRODUCTION

2-NSA is a commercially important dye intermediate and is widely used in the direct and reactive dyes production. With the scale expanding of dye production, the amount of toxic and harmful organic waste water was also growing [1]. Organic substances in dye intermediate wastewater are often aromatic compounds substituted by some groups, such as $-NO_2$, SO_3^- etc, resulting in passivation of benzene ring [2, 3]. Thus the naphthalene ring connected to SO_3H is also made the ring stable. During 2-NSA manufacturing, wastewater released from the acidulation precipitation process exhibits very high COD, acidity and chroma [4]. 2-NSA wastewater may cause ecological and pose potential impact on drinking water quality if not be treated with proper and efficient methods before discharge. 2-NSA is a kind of difficult bio-degradation in natural conditions of organic matter [5, 6]. The wastewater of 2-NSA is usually pretreated by solvent complex extraction and over 90% COD and color could be removed [1]. However, there is still a certain concentration of 2-NSA compounds left. At present, the degradation pathway of 2-NSA in Fenton oxidation process receives more attention [7]. This study intends to use the Fenton oxidation for degradation 2-NSA in aqueous solution.

EXPERIMENTAL SECTION

Chemicals and reagents

2-NSA was from QiaoChang Chemical Co. Ltd.(Binzhou, China). Methanol used were of guaranteed reagent grade and obtained from SK Chemicals. Ulsan 680-160 Korea. Other chemicals used were of analytical reagent grade and obtained from Tianjin Hengxing Chemical Reagent Co. Ltd. (Tianjin, China).

Experiment methods

Orthogonal experiment

The influence of reaction time, amounts of H_2O_2, ratio of $H_2O_2/FeSO_4$, solution pH and concentration of Na_2SO_4 was investigated on degradation of 2-NSA by orthogonal test. Each factors divided into three levels, the L_9 (3^4) orthogonal table as Table 1.

Table 1 Factors and levels of orthogonal experiment

level	A	B	C	D
	H_2O_2 (mg/L)	$H_2O_2/FeSO_4$	pH	reaction time （min）
1	41.6	2.5	3	60
2	83.25	5	4	120
3	166.5	10	5	180

Single factor experiment

A certain amount of ferrous sulfate and H_2O_2 is added to the 2-NSA waste water (50mg/L), reaction of 120min, based on COD index. The effect of solution pH, reaction time, H_2O_2 dosage, $H_2O_2/FeSO_4$ dosage and Na_2SO_4 on degradation effect were investigated.

RESULTS AND DISCUSSION

The results of orthogonal experiment

As shown in table 2, the primary and secondary factors affecting the removal rate of COD are as follows: H_2O_2dosage > pH > $H_2O_2/FeSO_4$ > reaction time, the best combination is $A_1B_3C_3D_1$.

Table 2 The results of $L_9(3^4)$ orthogonal experiment

No.	Factor A	FactorB	FactorC	FactorD	The removal rate of COD
1	41.6	2.5	3	60	78.35
2	41.6	5	4	120	93.23
3	41.6	10	5	180	72.93
4	83.25	2.5	4	180	97.29
5	83.25	5	5	60	91.88
6	83.25	10	3	120	85.11
7	166.5	2.5	5	120	93.23
8	166.5	5	3	180	94.59
9	166.5	10	4	60	95.94
K_1	162.0300	90.8900	90.8900	98.8000	
K_2	75.0800	27.6600	39.5200	82.9900	
K_3	15.8100	134.3700	122.5100	71.1300	
COD k_1	54.0100	30.2967	30.2967	32.9333	
k_2	25.0267	9.2200	13.1733	27.6633	
k_3	5.2700	44.7900	40.8367	23.7100	
R	38.2000	25.0300	27.6633	9.2233	

Effect of reaction time

Figure 1 presents the effect of the reaction time varied from 30 min to 120 min on the degradation of 2-NSA. It can be seen that the removal rate of COD increased from 81.3% to 88.9%. When the reaction time continues to increase, there was no significant change in COD. So the optimum reaction time was fixed at 120 min and used in the following experiments.

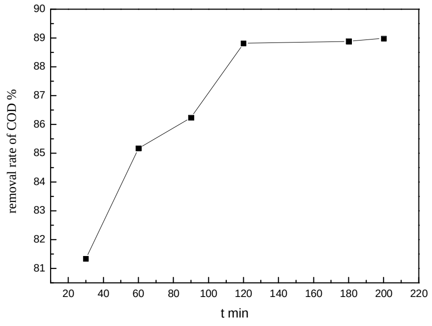

Figure 1 Effect of reaction time on the degradation of 2-NSA

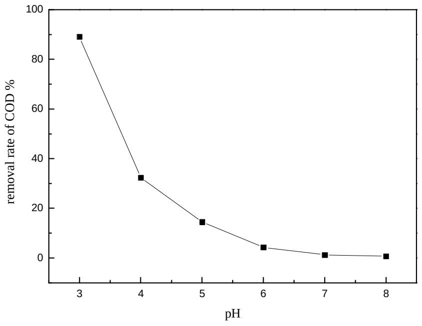

Figure 2 The effect of pH on the degradation of 2-NSA

Figure 2 presents the effect of the solution pH increased from 3 to 8 on the degradation of 2-NSA. It can be seen that the removal rate of COD reduced from 89% to 0.7%. The pH value of the solution is too low, the concentration of H^+ in the solution is too high, then Fe^{3+}cannot be successfully reduced to Fe^{2+}. When the pH value of the solution is higher, the higher OH^- concentration in the solution, the inhibition of formation of ·OH, the number of ·OH that generated by the reaction will decrease. Then the removal rate of COD decreased [8,9].With the reaction time increasing, there was no significant change in COD. So the solution pH was fixed at 3 and used in the following experiments.

Effect of the amounts of H_2O_2

Figure 3 presents the effect of the amount of H_2O_2 increased from 20.8mg/L to 41.6mg/L on the removal of 2-NSA. It can be seen from Figure 3 that the solution COD decreased with the increase of the amount of H_2O_2. With the amount of H_2O_2 increasing, there was no significant change in COD of solution. According to the CWPO reaction principle [10], the increasing of H_2O_2 will produce more hydroxyl radicals and increase the oxidation ability. So the removal rate of COD also will increase. But, when the dosage of H_2O_2 is excessive, H_2O_2 would react with the hydroxyl radical. It is a H_2O_2 self consumption phenomenon. The optimum amount of H_2O_2 was determined to be 41.6mg/L and used in the following experiments.

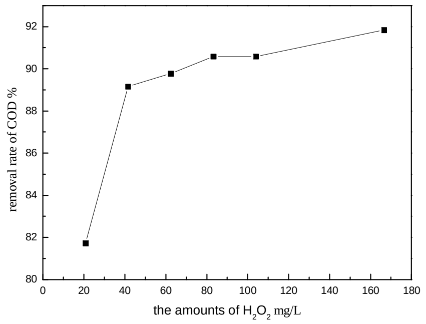

Figure 3 Effects of the amount of H_2O_2 on the degradation of 2-NSA

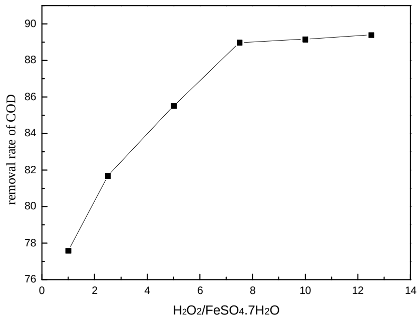

Figure 4 Effect of H_2O_2 to Fe^{2+} ratio on the degradation of 2-NSA

Figure 4 presents the effect of the H_2O_2 to $FeSO_4 \cdot 7H_2O$ mass ratio varied from 1:1 to 10:1 on the degradation of 2-NSA at fixed H_2O_2 dose of 41.6mg/L. It can be seen that the removal rate of COD increased from 77.5% to 89.1%. When the H_2O_2 to $FeSO_4 \cdot 7H_2O$ mass ratio continues to increase, there was no significant change in COD. The mass ratio of H_2O_2 to $FeSO_4 \cdot 7H_2O$ was fixed at 10:1 and used in the following experiments.

Effect of Na_2SO_4·

Figure 5 presents the effect of the amount of Na_2SO_4 increased from 30 g/L to 90 g/L on the degradation of 2-NSA. It can be seen that the removal rate of COD increased from 89% to 96%, showed that the solution COD increased with the increase of the amount of Na_2SO_4.With the amount of Na_2SO_4 increasing, there was no significant change in COD.

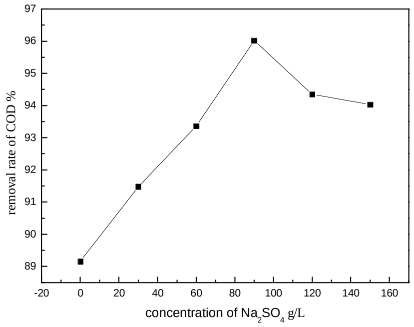

Figure 5 Effect of the amount of Na_2SO_4 on the degradation of 2-NSA

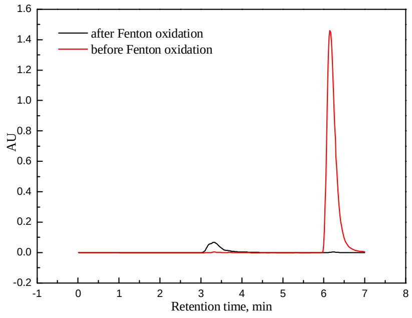

Figure 6 HPLC chromatogram of 2-NSA before and after Fenton oxidation

Fenton oxidation as one of advanced oxidation processes is effective in industrial wastewater treatment. During the Fenton process, hydroxyl radicals are generated by the decomposition of hydrogen peroxide catalyzed by ferrous ions [13]. From the above experimental results, the mechanism of Fenton oxidation of 2-NSA may be as follows [11, 12] :

$Fe^{2+}+H_2O_2 \longrightarrow Fe^{2+}+OH^-+OH\cdot$

$Fe^{3+}+H_2O_2 \rightarrow Fe^{2+}+HO_2\cdot+H^+$
$Fe^{2+}+OH\cdot \rightarrow Fe^{3+}+OH^-$
$Fe^{3+}+HO_2\cdot \rightarrow Fe^{2+}+O_2+H^+$
$OH\cdot+H_2O_2 \rightarrow H_2O+HO_2.$
$Fe^{2+}+HO_2\cdot \rightarrow Fe^{3+}+HO_2^-$

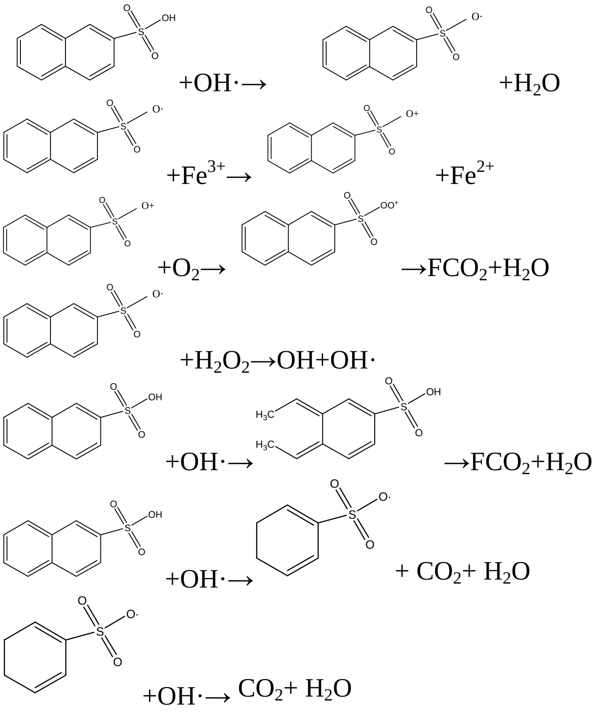

Figure 6 was the HPLC chromatogram analysis of the 2-NSA solution and after its degradated solution by Fenton oxidation method. As shown in Figure 6, 2-NSA in aqueous solution was degradated thoroughly.

CONCLUSION

In this work, Fenton oxidation was employed for the degradation of 2-NSA in aqueous solution.. The results showed that the optimum conditions were obtained to be 120 min of reaction time, solution pH of 3, H_2O_2 to $FeSO_4$ mass ratio of 10 and H_2O_2 amount of 41.6 mg/L for the 2-NSA concentration of 50 mg/L with a COD removal of 96.0 %.

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