Bull. Environ. Contam. Toxicol. (2002) 69:430–435

DOI: 10.1007/s00128-002-0080-z

Bulletin of Environmental Contamination and Toxicology

Treatment of H-Acid Wastewater by Photo-Fenton Reagent Combined with a Biotreatment Process: A Study on Optimum Conditions of Pretreatment by a Photo-Fenton Process

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Received: 17 May 2001/Accepted: 2 July 2002

The oxidation efficiency of a photo-Fenton reagent system can be enhanced significantly when UV or visible light is introduced into the system (Lipczynska-kochany 1991). Thus, among the advanced oxidation processes, the oxidation technique based on UV or visible light shows promise in the application of the treatment of toxic and refractory organic wastewater and non-biodegradable industrial wastewater (Oliveros et al. 1997, Zhu et al. 1996, Pignatello and Sun 1995), and has demonstrated by full-scale applications in Western countries (Pignatello 1992).

1-Amino-8-naphthol-3,6-disulfonic acid (H-acid) containing wastewater is one of the most important pollutants in industries producing acidic and active dyestuff and medicine. H-acid is highly toxic to microbe, and it is difficult to treat H-acid wastewater by a biological process (Chen and Pignatello 1997). Presently, a wet catalytic oxidation process has been successfully adopted to treat this kind of wastewater which contains a high concentration of H-acid. However, its strict operation conditions and high primary investment hinder its wider application for the treatment of H-acid wastewater of low COD_{cr} values. In recent years, increasing attention has been paid to photo-catalytic processes, which have certain obvious advantages in the treatment of low concentration bio-refractory organic wastewater. In this study, the UV-Fenton reagent system was employed to pretreat bio-refractory H-acid wastewater with a COD_{cr} of 300–500 mg/L. Optimal conditions suitable for diminishing COD_{cr}, as well as the biodegradability of the effluent, has been investigated.

MATERIALS AND METHODS

Both 10g/L $FeSO_4$ and 30% H_2O_2 were chemically pure reagents. m-TiO_2 was an analytically pure reagent. 5-TiO_2 and 6-TiO_2 were home-made reagents(CP). The active sludge was taken from a municipal wastewater plant in Dalian, China. After the large inert particles and debris in the sludge were removed, the sludge was cultured and tamed with a certain proportion of municipal sewage and pretreated wastewater (pH 7–8) for 7 days, then, further cultured with pretreated wastewater for 8 days before being used for the biodegradability test. The biodegradability was evaluated by the following procedure: a certain amount of wastewater was mixed with the active sludge (wastewater:sludge = 8:2), then cultured at 30°C in a shaker (HQL150-B, Wuhan, China) operated at 150 r/min, and centrifuged at 400

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r/min for 15min. Then the upper liquid sample was withdrawn before the COD_{cr} was determined according to the National Standard Method of China(Wei 1989). The COD_B was calculated by:

$$COD_B = COD_0 - COD_1 \qquad (1)$$

where COD_B is the biodegradable COD_{cr} of the wastewater, COD_0 is the COD_{cr} of the wastewater sample before cultivation in the shaker, while COD_1 is the COD_{cr} after cultivation.

The photo-catalytic reactor is illustrated in Figure 1. It consisted of a 200 cm^3 round-bottom Pyrex glass flask, with an inlet and an outlet for gas flow. A 6W and 365 nm high pressure mercury lamp was placed 5 cm from the flask. A N_2-O_2 gas mixture bubbled through the reactor. The solutions were magnetically stirred and maintained at a temperature of 25±1°C, using a cooler and a water bath .

A water sample containing 500 mg/L of H-acid wastewater and 300–500 mg/L COD_{cr} was prepared by diluting with distilled water. 150 c.c. of H-acid wastewater and Fenton reagents were added to the round bottomed flask. Titanium dioxide was then added to give a 1–5 w/v suspension. After attaining equilibrium in the dark for 15 min. under an oxygen atmosphere, the sample was irradiated with the mercury lamp. The suspensions were irradiated for time intervals ranging from 0–90 min. Prior to analysis, the titanium dioxide was removed from the suspensions by 13 mm X 0.2 um nylon syringe filters.

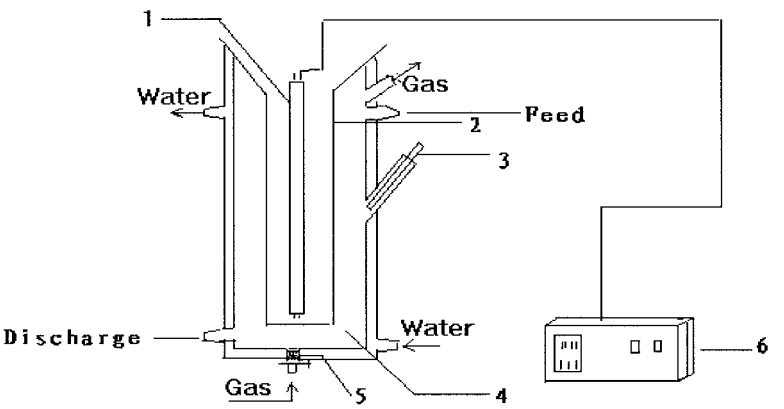

Figure 1. Photo-catalytic oxidation reaction system

1. 365 nm UV lamp(6W) 2. quartz tube 3. sample outlet 4. reaction mixture 5. stirrer 6. timer

The perpendicular test of a 3^K factorial design(Box et al. 1978) has been widely employed. In the experimental layout, we chose a 3^4 factorial design, a factorial arrangement with four factors each at three levels. The perpendicular test results were adopted by the maximum difference analysis process.

RESULTS AND DISCUSSION

The perpendicular test table was adopted to decide the effective factors on COD_{cr} removing efficiencies, so that the most crucial effective factors can be established. The chosen factors and levels in the perpendicular test are shown in Table 1. The experiment was arranged by the perpendicular test table of $L_9(3^4)$ (Li 1987).

Table 1. Factor and level of perpendicular test

	factor	Level 1	level 2	Level 3
A	dose of 10g/L $FeSO_4$ (%)	0.5	2.0	1.0
B	value of pH	7	6	5
C	dose of 3% H_2O_2 (%)	3	2	1
D	dose of TiO_2(‰)	1.0	2.0	0.5

The experimental results are given in Table 2. The order of all factors affecting the removing efficiency of COD_{cr} is D>C>A>B according to the values of maximum difference. The dosage of the TiO_2 is the most important effective factor for the removing efficiency of COD_{cr}. The dosage of H_2O_2 is another important effective factor for the removing efficiency of COD_{cr}.

Table 2. Perpendicular test results and maximum difference analysis

Number of experiment	Factor				Index of effluent		Removal efficiency of COD_{cr} (%)
	A	B	C	D	pH	COD_{cr}	
1	1	1	1	1	3.5	285.4	13.8
2	1	2	2	2	4.0	278.8	15.8
3	1	3	3	3	3.0	173.2	47.6
4	2	1	2	3	4.0	146.8	55.6
5	2	2	3	1	4.0	330.0	0.3
6	2	3	1	2	4.5	308.5	6.8
7	3	1	3	2	4.5	321.7	2.8
8	3	2	1	3	3.0	146.8	55.6
9	3	3	2	1	4.0	291.9	11.8
I	25.7	24.1	25.4	12.6			
II	20.9	23.9	27.7	8.5			
III	23.4	22.1	16.9	52.9			
R	4.8	2.6	10.8	44.4			

Note: COD_{cr} of influent=331 mg/l , color=500 pei , pH=5

The effectiveness of each factor on the removing efficiency of COD_{cr} is examined according to the tendency in Figure 2. The optimum experimental conditions of the removal efficiency of COD_{cr} is also discussed from the tendency in Figure 2. From the results of maximum difference analysis, the following conclusions can be drawn. 1). The dosage of the TiO_2 catalyst affects remarkably the removing efficiency of COD_{cr}. The optimum dosage of TiO_2 catalyst is 0.5‰ for the given 3 levels according to Figure 2. 2). The dosage of H_2O_2 also affects, obviously, the

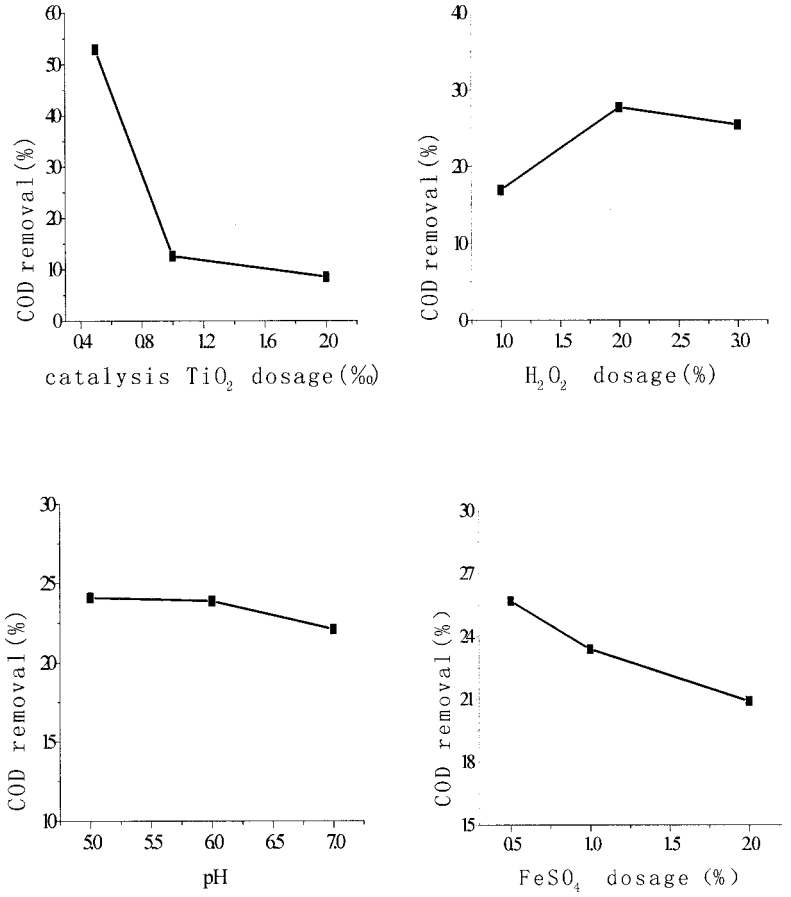

Figure 2. Tendency of effectiveness of factors on removing efficiency of COD_{cr}

removing efficiency of COD_{cr}. The optimum dosage of H_2O_2 is 2% for the given 3 levels. 3). The dosage of $FeSO_4$ affects the removing efficiency of COD_{cr} to a certain extent. The optimum dosage of $FeSO_4$ is 0.5% for the given 3 levels. 4) The pH value has little effect on the removing efficiency of COD_{cr}. The optimum pH value is 5 for the given 3 levels, based on the original pH value of the wastewater.

It can also be concluded from the results of the perpendicular test that the preliminary optimum parameters for the removing efficiency of COD_{cr} are 5, 0.5%, 2.0%, 0.5‰ and 90min for pH, 10g/L $FeSO_4$, 3% H_2O_2, photo-catalyst m-TiO_2 and reaction time, respectively, in treating H-acid wastewater with a COD_{cr} of 300–500mg/L. Single effect tests on the dosages of the main factors of H_2O_2 and the photo-catalyst m-TiO_2 were conducted in order to decide exactly the optimum experimental parameters.

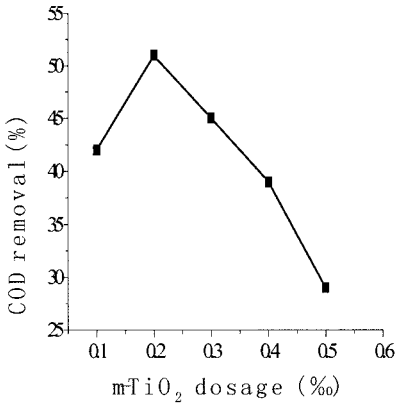

Figure 3. Effect of catalysis dosage on removal efficiency of COD_{cr}
Experimental conditions:
pH=5, $FeSO_4$=0.5%, 3%H_2O_2=2%, reaction time=90 min

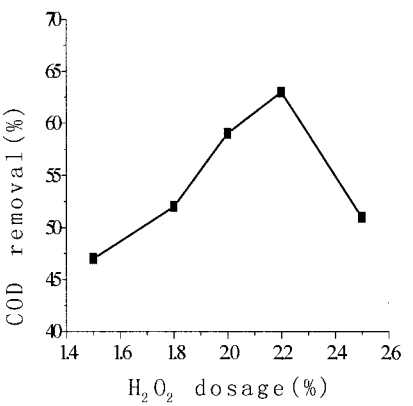

Figure 4. Effect of H_2O_2 dosage on removal efficiency of COD_{cr}
Experimental conditions:
pH=5, FeSO4=0.5%, m-TiO_2=0.2‰, reaction time=90 min

Figures 3 and 4 illustrate the effects of the single factor catalyst dosage and H_2O_2 dosage, respectively, on the experimental results. It can be seen from Figure 3 that when the dosage of m-TiO_2 is below 0.2‰, the removing efficiency of COD_{cr} increases with the m-TiO_2 dosage, but when the dosage of m-TiO_2 is over 0.2‰, the removing efficiency of COD_{cr} decreases with the m-TiO_2 dosage. Therefore, the optimum dosage of m-TiO_2 is set at 0.2‰. Figure 4 shows that when the dosage of 3% H_2O_2 is less than 2.2%, the removing efficiency of COD_{cr} increases with the H_2O_2 dosage, while the removing efficiency of COD_{cr} decreases with the H_2O_2 dosage when the dosage of H_2O_2 is more than 2.2%. Thus, the optimum dosage of H_2O_2 should be set to 2.2%.

Table 3 illustrates the removing efficiency of COD_{cr} under the conditions of optimum treatment for COD_{cr} removal. It can be seen from Table 3 that the results show the removing efficiency of COD_{cr} is 52.4–62.7% under the conditions of optimum treatment for COD_{cr} removal : pH =5, 10g/L $FeSO_4$=0.5%, 3% H_2O_2 =2.2%, m-TiO_2 =0.2‰ and reaction time = 90 min.

Table 3. Removal efficiency of COD_{cr} under optimum treatmental conditions

Influent COD_{cr} (mg/L)	447.5	413.7	387.5	312.9	254.5
Effluent COD_{cr} (mg/L)	212.8	182.9	166.0	121.1	94.6
Removal efficiency of COD_{cr} (%)	52.4	55.8	57.2	61.3	62.7

Table 4 gives the comparison tests of biodegradability under the condition of optimum treatment for COD_{cr} removal. It can be seen from Table 4 that the

biodegradability value COD_{B2}/COD_{cr} is enhanced greatly from 6.3–9.5% to 37.8–43.9%, and COD_{B4}/COD_{cr} from 9.2–14.5% to 59.1–63.6% under the condition for optimum treatment for COD_{cr} removal: pH =5, 10g/L $FeSO_4$=0.5%, 3% H_2O_2 =2.2%, m-TiO_2 =0.2‰ and reaction time = 90min.

Table 4. Comparison tests of biodegradability

Items	COD_{cr} (mg/l)	COD_{B2} (mg/l)	COD_{B2}/COD_{cr} (%)	COD_{B4} (mg/l)	COD_{B4}/COD_{cr} (%)
H-acid wastewater	447.5	28.2	6.3	41.1	9.2
	387.5	29.5	7.6	39.7	10.2
	254.5	24.3	9.5	36.9	14.5
Effluent of	212.8	80.4	37.8	125.7	59.1
pretreated H-acid	166.0	67.1	40.4	97.3	58.6
wastewater	94.6	41.5	43.9	60.2	63.6

Note : COD_{B2}, COD_{B4} illustrate biodegradability COD_{cr} of reaction time 2h & 4h respectively

The above experimental results show that the optimum experimental parameters of the removing efficiency of COD_{cr} are 5, 0.5%, 2.2%, 0.2‰ and 90min for pH, 10g/L $FeSO_4$, 3% H_2O_2, photo-catalyst m-TiO_2 and reaction time, respectively, in treating H-acid wastewater with a COD_{cr} of 300–500mg/L. The removing efficiency of COD_{cr} is 52.4–62.7% under the conditions of optimum treatment and the biodegradability value COD_B/COD_{cr} is enhanced significantly. It was found that the COD_{cr} and biological toxicity can be decreased, making the follow-up biologi -cal treatment possible and easier. Thus, it can be concluded from the tests that the effluents from the photo-Fenton process exhibit good biodegradability aerobically and are suitable for follow-up biotreatments.

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