

# Rapid determination of wastewater COD using $\text{Mn}(\text{H}_2\text{PO}_4)_2$ as catalyst

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**Abstract**—A new rapid determination method of wastewater COD in mixed acid solution  $\text{H}_2\text{SO}_4$ - $\text{H}_3\text{PO}_4$ , with  $\text{Mn}(\text{H}_2\text{PO}_4)_2$  as catalyst, has been proposed in this paper. Through orthogonal experiment, the optimal test conditions have been determined:  $\text{Mn}(\text{H}_2\text{PO}_4)_2$ : 0.3g,  $\text{H}_2\text{SO}_4$ : $\text{H}_3\text{PO}_4$ =6:1 (V/V), reflux time, 5 minutes. The results were similar to that of the standard method, but the test time was only 1/24 of that and the test cost decreased 85%.

**Keywords**: COD; catalyst; mixed acid; rapid determination.

## 1 Introduction

The standard potassium dichromate method (China NEPA, 1989) is a widespread used method in the determination of wastewater COD. The method has strong oxidation potentials and high accuracy, but the test cost is very high because the reflux (digest) time of wastewater amounts with two hours and the expensive reagent  $\text{Ag}_2\text{SO}_4$  is used as catalyst. It is necessary to find a method that not only the test cost of catalyst can be reduced, but also the COD can be determined rapidly. A rapid determination method of COD in  $\text{H}_2\text{SO}_4$ - $\text{H}_3\text{PO}_4$  mixed acid solution was proposed by Jeris (Jeris, 1967; Wells, 1970), but the test cost was not reduced because  $\text{Ag}_2\text{SO}_4$  was still used as catalyst. A rapid determination method of wastewater COD in mixed acid solution  $\text{H}_2\text{SO}_4$ - $\text{H}_3\text{PO}_4$ , with  $\text{Mn}(\text{H}_2\text{PO}_4)_2$  as catalyst, has been proposed in this paper. The results are similar to that of the standard method (China NEPA, 1989), but the reflux time is only 5 minutes and the test cost decreases 85%.

## 2 Experimental

### 2.1 Reagents

Solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  (0.15mol/L, 1000ml) was prepared and placed in volumetric flask.

Catalytic solution of  $\text{Mn}(\text{H}_2\text{PO}_4)_2$  was prepared with 14.0g  $\text{Mn}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  + 100ml concentrated  $\text{H}_3\text{PO}_4$  + 600 ml concentrated  $\text{H}_2\text{SO}_4$  and placed in a brown reagent bottle. The concentration is 0.3g  $\text{Mn}(\text{H}_2\text{PO}_4)_2$  per 15 ml catalytic solution.

Other reagents were prepared as the same as standard method (China NEPA, 1989).

## 2.2 Determination method

5.00 ml of sample aqueous solution was placed in a 250 ml reflux conic flask with ground glass neck. 10.00ml oxidative solution and some glass beads were added. 15.00ml catalytic solution was added to the conic flask slowly from the top of linked condenser. Placed the conic flask on electric stove to reflux about 5 minutes (from boil). If there was  $Cl^-$  in the wastewater, 0.1g  $HgSO_4$  was added into the conic flask and the following operations were the same as above.

70ml distilled water was used to wash the condenser wall after cooling.

2-3 drops indicator of o-phenanthroline were added to the moved conic flask. Titrating the solution from yellow to blue-green and then red-brown with standard  $(NH_4)_2Fe(SO_4)_2$ . At the same time, a blank test was operated as above with 5.00 ml distilled water and then recorded the volumes of  $(NH_4)_2Fe(SO_4)_2$  consumed. The results was calculated as the standard method (China NEPA, 1989).

## 3 Results and discussion

### 3.1 The selection of the optimal test conditions

The optimal test conditions, with potassium hydrogen phthalate ( $COD = 500mg.L^{-1}$ ) standard solution as test sample, were determined through orthogonal experiment. The planned experiment and results are listed in Table 1. The test values are the average of triplicate determinations. The absolute values of relative errors are examinational targets.

Table 1  $L_9(3^4)$  orthogonal experiment table

Test No.	Planned experiments			Test results		
	$Mn(H_2PO_4)_2 \cdot 2H_2O$ , (g)A	$H_2SO_4 \cdot H_3PO_4$ (V) B	Reflux time, (min.)C	COD true values, $mg.L^{-1}$	COD test values, $mg.L^{-1}$	Relative errors, %
1	1(0.2)	1(4+1)	1(5)	500	476.39	4.72
2	1(0.2)	2(5+1)	2(10)	500	481.54	3.69
3	1(0.2)	3(6+1)	3(20)	500	484.2	3.18
4	2(0.3)	1(4+1)	2(10)	500	489.23	2.15
5	2(0.3)	2(5+1)	3(20)	500	493.44	1.31
6	2(0.3)	3(6+1)	1(5)	500	498.06	0.39
7	3(0.4)	1(4+1)	3(20)	500	491.68	1.66
8	3(0.4)	2(5+1)	1(5)	500	495.10	0.98
9	3(0.4)	3(6+1)	2(10)	500	502.87	0.57
$k_1$	11.59	8.53	6.09			
$k_2$	3.85	5.98	6.41		$T=18.65$	
$k_3$	3.21	4.14	6.15			
$\bar{k}_1$	3.86	2.84	2.03			

Table 1 (Continued)

Test No.	Planned experiments			Test results		
	Mn(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O, (g)A	H <sub>2</sub> SO <sub>4</sub> ·H <sub>3</sub> PO <sub>4</sub> (V) B	Reflux time, (min.)C	COD true values, mg. L <sup>-1</sup>	COD test values, mg. L <sup>-1</sup>	Relative errors, %
$\bar{k}_2$	1.28	1.99	2.14	$\bar{T}=6.22$		
$\bar{k}_3$	1.07	1.38	2.05			
R	2.79	1.46	0.11			

According to the extreme difference *R*, the needs of Mn(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O is the most important factor that influences the test results. The volume ratio of H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> is the second factor and the reflux time is a small factor. According to the test results, the relative errors of No. 3, No. 6 and No. 9, which the volume ratios of H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> are the same, are very small. The relative error of No. 6 is the smallest with 0.3 g catalyst. So, A<sub>2</sub>B<sub>3</sub>C<sub>1</sub> was selected as the optimal test conditions, i. e. , Mn(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O=0.3g, H<sub>2</sub>SO<sub>4</sub>·H<sub>3</sub>PO<sub>4</sub>=6:1, the reflux time : 5 minutes.

### 3.2 Mechanism of catalytic oxidation

The catalytic mechanism (Ballinger, 1962) with Ag<sub>2</sub>SO<sub>4</sub> as catalyst in the former determination of waste water COD is as follows: The organic compounds in wastewater which contain hydroxyl groups are oxidized to fatty acids (RCOOH) with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in acid solution. The fatty acids react with Ag<sub>2</sub>SO<sub>4</sub> to form an unstable compound (RCOOAg). The elimination of carbon dioxide from the fatty acid silver will product a new fatty acid silver which carbon number is less than the former's. By a repetition and extension of the process, the final products will be CO<sub>2</sub> and H<sub>2</sub>O.

According to reference (Sun, 1982), the brown black Mn<sub>2</sub>O<sub>3</sub>, a strong catalyst in the oxidation of hydrocarbon, will be prepared when Mn(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> was placed in the solution of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, but there is no Mn<sub>2</sub>O<sub>3</sub> in our solution. Mn<sup>2+</sup> is oxidized to Mn<sup>3+</sup> only in the acid solution of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. As the action of Ag<sup>+</sup>, acting with fatty acid, Mn<sup>3+</sup> may be produces a unstable intermediate-free fatty acid manganese which accelerates the oxidation reaction from organic compounds to CO<sub>2</sub> and H<sub>2</sub>O. The detail mechanism need to be further studied.

The phosphoric acid in our test has two uses. One is that it can increase the digestive temperature suitably, the other is that the organic compounds can be drawn to its surroundings. The oxidation of organic compounds can be accelerated because the reactant concentrations are relatively high (Sun, 1982).

### 3.3 The interference and elimination of Cl<sup>-</sup>

If there is Cl<sup>-</sup> in wastewater, the Cl<sup>-</sup> will be oxidized to Cl<sub>2</sub> by K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in acid solution. The test results will be higher than its real values. So the Cl<sup>-</sup> must be covered before adding K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. We selected 0.1 g HgSO<sub>4</sub> as covering agent because Cl<sup>-</sup> acts with Hg<sup>2+</sup> to produce HgCl<sub>4</sub><sup>2-</sup> complex, which greatly reduces its ability to react with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. According to ratio

( $HgSO_4:Cl^- = 10:1$  (w/w) in standard method, 0.1 g  $HgSO_4$  can cover 10 mg  $Cl^-$ . If 5.00 ml waste water is used, the maximum of  $Cl^-$  is 2000 mg.  $L^{-1}$  that can be concealed. In general test of wastewater, 0.1 g  $HgSO_4$  is enough to concealed the interference of  $Cl^-$ .

### 3.4 The precision and accuracy of the method

#### 3.4.1 The precision

Sixteen parallel tests were done on standard COD water sample and real wastewater. The results are summarized in Table 2.

Table 2 The precision of experiments

Standard COD samples, mg. $L^{-1}$				Waste water COD samples, mg. $L^{-1}$			
No.	Test values	No.	Test values	No.	Test values	No.	Test values
1	496.78	2	495.42	1	243.20	2	245.16
3	498.10	4	496.39	3	244.53	4	243.44
5	495.94	6	497.88	5	242.38	6	242.81
7	496.36	8	498.14	7	243.46	8	244.64
9	494.89	10	496.70	9	245.05	10	241.98
11	497.67	12	497.53	11	243.51	12	242.72
13	498.21	14	498.06	13	243.29	14	244.36
15	496.55	16	497.47	15	244.12	16	243.51
Average		497.00				243.64	
Standard deviation		2.652mg. $L^{-1}$				0.936mg. $L^{-1}$	
Coefficient of variation		0.534%				0.384%	

As shown in Table 2, the standard deviation and coefficient of variation of standard COD sample are 2.652 mg.  $L^{-1}$  and 0.534% respectively. Those of wastewater are 0.936mg.  $L^{-1}$  and 0.384%.

#### 3.4.2 The accuracy

Different concentrations of standard COD samples of potassium hydrogen phthalate and sodium acetate were tested. The results are listed in Table 3.

Table 3 The results of recovery rates

Potassium hydrogen phthalate standard sample			Sodium acetate standard sample		
COD true values, mg. $L^{-1}$	Test values, mg. $L^{-1}$	Recovery rates, %	COD true value, mg. $L^{-1}$	Test values, mg. $L^{-1}$	Recovery rates, %
	196.31	98.15		198.45	99.22
200	203.05	101.52	200	195.35	97.68
	195.89	97.94		196.28	98.14
Average	198.42	99.21	Average	196.69	98.34
	407.12	101.78		392.30	98.08

Table 3 (continued)

Potassium hydrogen phthalate standard sample			Sodium acetate standard sample		
COD true values, mg. L <sup>-1</sup>	Test values, mg. L <sup>-1</sup>	Recovery rates, %	COD true value, mg. L <sup>-1</sup>	Test values, mg. L <sup>-1</sup>	Recovery rates, %
400	396.90	99.22	400	399.46	99.86
	394.76	98.69		404.98	101.24
Average	399.59	99.90	Average	398.91	99.73
800	789.50	98.69	800	810.66	101.33
	796.84	99.60		798.50	99.81
	808.10	101.01		791.71	98.96
Average	798.15	99.77	Average	800.29	100.04

As shown in Table 3, the recovery rates of two standard COD samples are between 97% and 102%. From Table 2 and Table 3, we can conclude that the precision and accuracy are very satisfactory.

### 3.5 Compared with standard method

#### 3.5.1 Comparison of practical wastewater COD

For comparison with standard method, 10 kinds of practical wastewater COD in Xinxiang City were tested. The results are summarized in Table 4.

Table 4 Comparison of test results of wastewater COD with standard method

Sources of waste water and names	This method, mg. L <sup>-1</sup> A	Standard method, mg. L <sup>-1</sup> B	Relative errors, $\frac{A-B}{B} \times 100\%$
Weihe River water	130.43	128.40	+1.58
Renmin Shengliqu water	62.14	61.65	+0.79
The 1st chemical plant mixed waste water	200.48	198.73	+0.88
Organic chemical plant mixed waste water	1116.34	1101.58	+1.34
Xinxing pharmaceutical factory waste water	1827.93	1893.25	-3.45
Silk plant dyeing waste water	958.71	967.69	-0.93
Silk plant destarch waste water	828.05	812.86	+1.87
Chemical fiber mill long silk waste water	489.22	487.27	+0.40
Chemical fiber mill cotton pulp waste water	4221.73	4324.66	-2.38
Chemical fiber mill exploded air pool water	960.62	971.50	-1.12

As shown in Table 4, the test results in our method are in good coincidence with that of standard method. The relative errors are less than 10% times of test errors of COD. It shows that the method is practicable.

#### 3.5.2 Comparison of test cost

Table 5 is shown the comparison of test cost in two methods. In our method, because

the cheap  $Mn(H_2PO_4)_2$  was used as catalyst, reflux time was 5 minutes and  $HgSO_4$  was reduced to 0.1 g, the test cost was decreased greatly. The test cost of a water sample is only 0.36 RMB Yuan. Compared with 2.40 Yuan of standard method, the test cost was decreased 85%.

Table 5 Comparison of test cost with standard method\*

Compared items	This method		Standard method	
	Needs	Cost $\times 100$ , Yuan	Needs	Cost $\times 100$ Yuan
$K_2Cr_2O_7$ , g	0.1470	0.51	0.2452	0.86
$(NH_4)_2Fe(SO_4)_2$ , **, g	1.0617	0.74	1.4812	1.04
$Mn(H_2PO_4)_2$ , g	0.6	0.77	0	0
$Ag_2SO_4$ , g	0	0	0.6	86.68
$HgSO_4$ , g	0.2	1.38	0.8	5.51
$HgSO_4$ , ml	25.72	24.18	60	56.40
$H_3PO_4$ , ml	4.28	4.80	0	0
Electricity, kWh	0.13	3.64	3.20	89.60
Total cost $\times 1\%$ , Yuan		0.36		2.40

\* Test one water sample (including blank test); \*\* needs of  $(NH_4)_2Fe(SO_4)_2$  change in different COD, in our method COD=500mg. L<sup>-1</sup>, blank COD = 0mg. L<sup>-1</sup>

## 4 Conclusions

As shown in our results,  $Mn(H_2PO_4)_2$  is a strong catalyst in the oxidation of  $K_2Cr_2O_7$  in  $H_2SO_4$ - $H_3PO_4$  mixed acid solution.  $Ag_2SO_4$  can be replaced by  $Mn(H_2PO_4)_2$  completely in the determination of wastewater COD. The reflux time is only 5 minutes and test cost is very cheap. Because its high precision and accuracy, this method is suitable in the rapid determination of wastewater COD.

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