

Influence of Nitrite on Chemical Oxygen Demand Determined by Potassium Permanganate at 100°C and on Dissolved Oxygen Determination by Azide Modification

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Abstract

A marked elevation in COD of the water treated by activated sludge was observed, which suggested the existence of nitrite-N in high concentration. In such a case, it was impossible to determine DO concentration with normal addition of alkali-iodide-azide reagent. In order to find an alternative method which could avoid this difficulty, the effect of nitrite on COD value determined by potassium permanganate at 100°C and on dissolved oxygen determination by azide modification was investigated.

Chemical oxygen demand of 1 mg/l nitrite-N solution was 1.1 mg/l that was equal to theoretical oxygen demand for oxidation of nitrite-N to nitrate-N. The above fact suggests that the increase of COD at the presence of nitrite-N has to be taken into consideration in determining COD.

With an addition of only 1 ml of alkali-iodide-azide reagent, the part exceeding over 2.15 mg of nitrite-N (about 15 to 20 mg/l nitrite-N) were found still liberating iodine continuously and preventing analysis of DO value. It is then found necessary to analyze concentration of nitrite-N before DO determination and to add adequate amount of alkali-iodide-azide reagent, if samples contain more than 15 to 20 mg/l nitrite-N.

INTRODUCTION

Recently many attempts have been made for improvement of water quality with the various kinds of biological waste treatment methods including nitrification. Since nitrite is the intermediate of nitrification, the existence of nitrite in high concentration is sometimes observed in biologically treated waters.¹⁻³⁾

On the other hand, it is well known that nitrite acts both oxidizing and reducing agents and sometimes gives incorrectness to several water quality indices, i. e., chemical oxygen demand and dissolved oxygen. Although permanganate value of nitrite was examined by Subrahmanyam *et al.*,⁴⁾ the validity of the use of this value for COD determination by the standard method in JIS is not known.

Azide modification is recommended if samples contain more than 50 µg/l nitrite-N,^{5,6)} but the limit of this method has not been elucidated by using actual water samples as yet. At the beginning of these analytical methods, perhaps, nitrite concentration of water was so low that special cautions were not necessary. Nitrite rich samples have become common along with the progress of such novel waste treating methods as biological nitrification, and now, establishment of alternative procedures for analyzing such samples are needed.

This paper reports the results of experiments on the influence of nitrite on chemical oxygen demand and on dissolved oxygen determination of waters, especially biologically treated water which contains considerable amount of nitrite-N.

MATERIALS AND METHODS

1. Chemicals

All chemicals used in the experiments were commercial products.

2. Analyses

Biochemical oxygen demand (BOD), chemical oxygen demand determination by potassium permanganate at 100°C (COD) and dissolved oxygen (DO) were analyzed by the methods of JIS K0102.⁷⁾ Nitrogen (nitrite-N) was determined according to the method of Griess Romijin.⁸⁾ Phosphorus and nitrogen in skim milk were determined by the methods of Allen⁹⁾ and micro Kjeldhal,¹⁰⁾ respectively.

3. Acclimation of activated sludge

Skim milk was inoculated with returned sludge from a dairy industry waste treatment plant and was acclimated by a fill-and-draw method at $24 \pm 1^\circ\text{C}$. The aeration time was 24 hr. Determination of nitrite-N concentration was started at 24th day. After 30 min's setting, supernatant was drawn and examined as treated water.

4. Chemical oxygen demand of nitrite-N

One and ten miligram per liter solutions of nitrite-N were prepared using sodium nitrite. Chemical oxygen demand of a suitable portion of the solution was analyzed by means of JIS method as mentioned above.

5. Effect of nitrite-N on DO determination

Solution of 0, 5, 10, 15, 20 or 25 mg/l nitrite-N was prepared and examined.

RESULTS AND DISCUSSION

1. Observation of increase in COD and in nitrite-N during acclimation of activated sludge

Curves of COD, COD removal (%), nitrite-N, pH, MLSS and fed BOD are shown in Fig. 1. Composition of skim milk is listed in Table 1. These figures correspond to the following conditions; BOD loading was 0.08 to 0.24 kg BOD/kg MLSS·day and skim milk provided the 72 : 5 : 1 ratio of BOD : N : P. The activated sludge exhibited very good settling properties, with a SVI around 100. Under microscope protozoa and rotifers were apparent in the system. The pH of treated water was found to

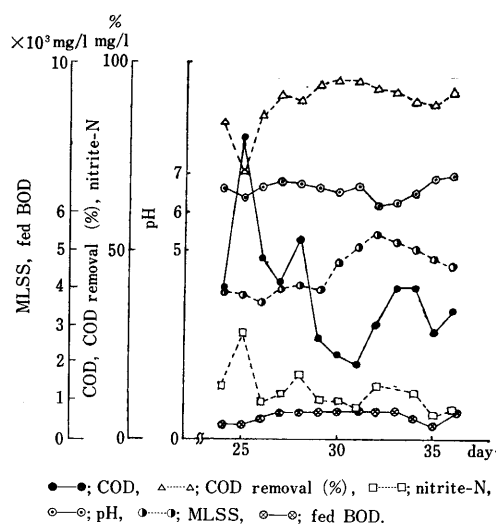


Fig. 1 Chemical oxygen demand, COD removal (%), nitrite-N, pH, MLSS and fed BOD during the experimental period.

Table 1 Analyses of skim milk

Skim milk (1000 mg/l)	
Chemical oxygen demand	552.3 (mg/l)
Biochemical oxygen demand	711.0
Nitrogen	52.3
Phosphorus	9.9

BOD : N : P, about 72 : 5 : 1.

be relatively constant ranging between 6.1 to 6.9 (mean 6.5) throughout the experiments.

Chemical oxygen demand of the water varied between about 20 and 80 mg/l and then nitrite-N concentration was remarkably high, max 28.4, min 7.6 and mean 13.2 mg/l. Such a high concentration of nitrite-N implies that the accumulation of the substance is derived from deficiency of oxygen and accordingly that the DO value should be determined by the azide modification method. However it is impossible to use this method because the liberation of iodine is continuous.

2. Chemical oxygen demand of nitrite-N

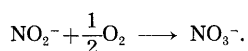
Chemical oxygen demand determined by the experiments and corresponding theoretical oxygen demand of nitrite-N are summarized in Table 2.

The oxidations of 1 and 10 mg of nitrite-N theoretically require 1.1 and 11.4 mg of oxygen, respectively, according to the following equation :

Table 2 Chemical oxygen demand and theoretical oxygen demand of nitrite-N.

Nitrite-N concentration	Chemical oxygen demand (mg/l)	Theoretical oxygen demand (mg/l)
1 mg/l	1.1±0.1 ¹⁾	1.1
10 mg/l	11.4±0.1 ¹⁾	11.4

1) Number of assays was 6 each.



The values determined by the experiments were found substantially equal to the theoretical values, namely, 1.1±0.1 and 11.4±0.1 mg/l, respectively. The result coincided with that obtained by Subrahmanyam *et al.*⁴⁾ In spite that nitrite-N is nearly oxidized, it still consumes adequate amount of oxygen that is considered to be COD.

The result of recovery test is summarized in Table 3. In this experiment, 50 mg/l glucose solution and 50 mg/l skim milk solution were used as the base solution of known COD. After adding nitrite to those samples, COD and nitrite-N were determined, net COD was calculated by subtracting COD of nitrite-N from total COD and recovery of COD was estimated. The recovery was approximately 100%. So it is possible to neglect an error due to the presence of nitrite.

Data in Fig. 2 show the contribution of nitrite-N to COD and COD removal (%). During the test period, COD of nitrite-N was max 32.4, min 8.7 and mean 15.1 mg/l, occupying max 54.8, min 26.9 and mean 39.0% of total COD. Nitrite-N was also caused incorrectness of COD removal, max 10.8, min 1.8 and mean 3.8%.

It is necessary to take account of a part of nitrite-N in obtained COD in the case of the water containing considerable amount of nitrite-N.

3. Effect of nitrite-N on dissolved oxygen determination by azide modification

Dissolved oxygen values of several degrees of concentration of nitrite-N are presented in Table 4.

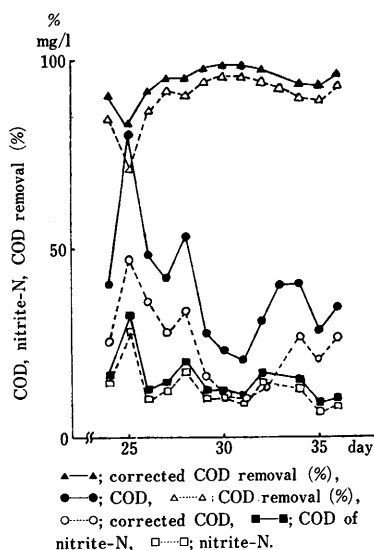
Table 3 Recovery of COD

	COD ¹⁾ (mg/l)	Nitrite-N ²⁾ (mg/l)	COD of ³⁾ Nitrite-N (mg/l)	Recovery ⁴⁾ (%)
50 mg/l glucose ^{A)}	38.2±0.4	—	—	—
50 mg/l glucose ^{B)} and nitrite	52.6±0.6	13.2	14.5	99.7
50 mg/l skim milk ^{A)}	26.9±0.4	—	—	—
50 mg/l skim milk ^{B)} and nitrite	41.0±0.7	12.9	14.2	99.6

1) Number of assays was 6 each.

2) Number of assays was 3 each.

3) Calculated from 2).

4) Recovery (%) = $\frac{\text{COD of A (or a)}}{\text{COD of B (or b)} - \text{COD of nitrite-N}} \times 100$ **Fig. 2** COD value and COD removal before and after correction

When a sample contained more than 15 to 20 mg/l nitrite-N, it was impossible to recognize the end point of the iodine-thiosulfate titration because excess nitrite-N might act as oxidizing agent and continuously liberated iodine by the following process:¹¹⁾



The color of sample solution after addition of 1 ml of 36 N sulfuric acid was dark brown resulting from a large quantity of free iodine.

Sodium azide reacts with nitrite in acid solution as hydrogen azide as follows:¹²⁾



According to this reaction, one milliliter of alkali-

Table 4 Dissolved oxygen values of sodium nitrite solution

Nitrite-N concentration (mg/l)	Dissolved oxygen ¹⁾ (mg/l)
0	7.26±0.04
5	7.28±0.05
10	7.21±0.04
15	7.21±0.04

1) Data were statistically analyzed according to the t test ($P<0.05$). Number of assays was 6 each. There were no statistical difference between DO values.

iodide-azide reagent which contains 10 mg of sodium azide can decompose 7.08 mg of nitrite or 2.15 mg of nitrite-N. The concentration is 15 to 20 mg/l if water in incubation bottles of 110 to 140 ml capacity contains 2.15 mg of nitrite-N.

In order to avoid the effect of nitrite-N in high concentration, DO of the water containing 25 mg/l nitrite-N was determined by the following methods: one was to add the suitable amount of alkali-iodide-azide reagent for about 130 ml of 25 mg/l nitrite-N, namely 2 ml. The other was to add the alkali-iodide-azide reagent containing two times the concentration of sodium azide.

Table 5 shows DO values of water containing 0 and 25 mg/l nitrite-N examined by azide modification (JIS method) and by modified methods. When addition of alkali-iodide-azide reagent was increased, same volumes of manganese sulfate solution and 36 N sulfuric acid were added. Both methods turned out a success. There were scarcely any difference between DO values.

If a sample contains more than 15 to 20 mg/l nitrite-N, it is necessary to analyze concentration of nitrite-N before DO determination and to add adequate quantity of alkali-iodide-azide reagent.

CONCLUSION

Influence of nitrite on chemical oxygen demand determined by potassium permanganate at 100°C and dissolved oxygen determination by azide modification was examined.

1. Chemical oxygen demand of 1 mg/l nitrite-N solution is equal to theoretical oxygen demand of the solution, namely, 1.1 mg/l.

Table 5 Dissolved oxygen values of water containing 0 or 25 mg/l nitrite-N determined by modified methods.

Addition	Nitrite-N	
	0 mg/l	25 mg/l
	Dissolved oxygen (mg/l)	
JIS method	7.49±0.05 ³⁾	—
2 ml of alkali- ¹⁾ iodide-azide reagent	7.53±0.06 ³⁾	7.54±0.08 ³⁾
1 ml of alkali- ²⁾ iodide-azide reagent	7.50±0.03 ³⁾	7.49±0.07 ³⁾

- 1) Addition of MnSO_4 solution and 36N H_2SO_4 were 2 ml.
- 2) This reagent was prepared to contain two times the concentration of sodium azide.
- 3) Data were statistically analyzed according to the t test ($P<0.05$). Number of assays was 10 each. There were no statistical difference between DO values.

2. Existence of more than 15 to 20 mg/l nitrite-N (2.15 mg of nitrite-N) hinders the analysis of DO by azide modification with normal addition of alkali-iodide-azide reagent. Inhibition of nitrite-N can be prevented by adding the amount of alkali-iodide-azide reagent sufficient to fully decompose the dissolved nitrite-N out.

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