MISASSUMPTIONS IN COD MEASUREMENT IN WASTEWATERS CONTAINING HIGH CONCENTRATION OF VFA [TELEMAC CONTRIBUTION #9]

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Abstract
Volatile fatty acids (VFAs) are only partially oxidised in the COD analyses. This could cause underestimation of the organic load applied to an anaerobic wastewater treatment plant as well as effluent quality estimation.
This paper presents the results of an interlaboratory exercise for COD measurement of a set of solutions containing VFAs. The results confirm the partial oxidation of VFAs using standarized COD analytical procedures. Better results were obtained using the closed reflux method instead of the open reflux one. Moreover, the highest oxidation is achieved using the lowest headspace in the tubes.

Keywords anaerobic wastewater treatment; chemical oxygen demand (COD); intercalibration; interlaboratory; monitoring; tele-control; tele-monitoring; VFA; Acetic acid

INTRODUCTION

Several analytical methods are used to describe the pollution capability of wastewaters. In particular tree methods are mainly used to give a general description of the level of pollution. These methods are BOD (Biological Oxygen Demand), TOC (Total Organic Carbon) and COD (Chemical Oxygen Demand). Each one of these methods gives an information that is complementary to that of the others and is not able to completely describe the level of pollution of wastewaters. In particular COD give a value of the amount of the oxygen necessary to chemically oxidize the substances presents in wastewater.

The methods proposed by the Standard Methods for the Examination of Water and Wastewater (1995), are not able to oxidize every organic compounds that may be present in wastewaters. In particular, volatile fatty acids (VFAs) are not completely oxidized. This aspect has a particular importance in anaerobic digestion wastewater treatment process because, in the presence of high amount of VFAs, the wastewater COD content may be greatly underestimated. During anaerobic wastewater treatment processes a large amount of VFAs is usually produced: therefore, a wrong analytical COD evaluation can bring a wrong evaluation of the process performances, especially under overload periods, causing several problems in plant management and decrease biogas production.

In this paper the results of an interlaboratory exercise for COD measurement of samples containing VFAs are presented. The study shows the influence of different analytical methods used for the COD determination in four different laboratories involved in the TELEMAC project (TELEmonitoring and Advances teleControl of high yield wastewater treatment). These methods proposed for COD determination by the Standard Methods as well as commercial kits have been tested.

METHODS

The interlaboratory exercise has been carried out among four laboratories involved in the TELEMAC project: one in Italy at ENEA (L1), one in France at INRA (L2) and two in Spain at Universidade de Santiago de Compostela (L3) and at AGRALCO (L4).

COD measurements were conducted according to Standard Methods (1995), using both the open and the closed reflux method. Because the objectives of the exercise was to verify the oxidation procedures on volatile fatty acids (and not the dichromate measurement by titration or colorimetry), for the closed reflux method only the titrimetric one was used. For more analytical details see sections 5220B and C of the Standard Methods (1995). Moreover two (L1 and L2) of the four laboratories have also used commercial COD test kits.

For the COD measurements potassium hydrogen phthalate (KHP) was used as standard assuming a theoretical COD (TOD) of 1.176 gO_2/g. Among the several VFAs produced in anaerobic processes, acetic acid (both liquid and as sodium acetate trihydrate), propionic acid and butyric acid were used for the interlaboratory exercise. Every chemicals used were ACS reagents. TOD assumed in this study was 1.07, 0.47, 1.51 and 1.82 gCOD/g for acetic acid, sodium acetate trihydrate, propionic acid and n-butyric acid, respectively (Pitter and Chudoba, 1990).

RESULTS AND DISCUSSION

The interlaboratory exercise shows that the concentration of the VFA greatly affects the result of the COD measurements with errors that can reach even 50%, in the case of tests with acetic acid (Tables 1 to 6). Better results are obtained using kit tests available on the market, and the worst using the open reflux method. This can be due to the volatilisation of VFAs to the headspace of the digestion tubes. By this way the volatile compounds will not react in the liquid face. The better results obtained by the market kit (Tables 4 and 6) and at L3 (Table 2) can be attributed to the lower headspace volume that has (probably) increased the contact of the volatile compounds with the oxidant. The worst results were presented using the open reflux methods or using a high headspace volume.

Both acetic acid and sodium acetate were tested to evaluate the possible effect of VFAs volatilisation during the preparation of the standards. The results show that the COD underestimation may not be justified by acid volatilisation (during the preparation of the standard solutions) because relevant errors were also presented where sodium acetate was used for standard preparation. The results in the COD analysis carried out with potassium hydrogen phthalate confirm the efficiency in oxidation of “common” organic substances (Tables 1 to 6).

Table 1 Results obtained using the open reflux method at L2. Values are arithmetical means of three replicates. Units in mgO_2/L. In brackets the relative error (%).

TOD	KHP measured COD	Acetic acid measured COD	Na Acetate measured COD
100	100(0)	90(-10)	46(-54)
200	208(+4)	162(-19)	148(-26)
400	392(-2)	351(-12)	297(-25)
800	760(-5)	677(-15)	501(-37)

Table 2 Results obtained using the closed reflux method at L3 with 3.5 mL headspace in the tubes. Units in mgO_2/L. In brackets the relative error (%).

TOD	KHP measured COD	Acetic acid measured COD	Na Acetate measure COD
100	119(+19)	92(-8)	108(+8)
200	216(+8)	189(-6)	200(0)
400	411(+3)	384(-4)	395(-1)
800	816(+2)	751(-6)	773(-3)

Table 3 Results obtained using the open reflux method at L4. Values are arithmetical means of three replicates. Units in mgO_2/L. In brackets the relative error (%).

TOD	KHP measured COD	Acetic acid measured COD	Na Acetate COD
100	84(-16)	87(-13)	102(+2)
200	180(-10)	179(-11)	181(-10)
400	393(-2)	384(-4)	372(-7)
800	798(0)	744(-7)	728(-9)

Table 4 Results obtained using commercial kits at L2. Values are arithmetical means of three replicates. Units in mgO_2/L. In brackets the relative error (%).

KHP		Acetic acid		Sodium acetate	
TOD	meas. COD	TOD	meas. COD	TOD	meas. COD
100	102(+2)	111	114(+3)	100	103(+3)
200	205(+3)	222	237(+7)	201	214(+6)
400	415(+4)	444	475(+7)	402	430(+7)
800	834(+4)	888	951(+7)	804	870(+8)

The COD underestimation is also confirmed when other VFAs are measured (Tables 5 and 6). Also in this case, using tubes with a minor headspace (as in the commercial kits) can increase the VFAs oxidation (Table 6).

The better results of the kits could also be explained with a better seal of the screw-cap on the tube because of the "single-use" of the kit vials.

Table 5 Results obtained using the closed reflux method at L1. 10 mL headspace in the vials. Values are arithmetical means of (*)three, (**)five, (***)four, (****)two replicates. Units in mgO_2/L. In brackets the relative error (%).

	TOD	measured COD
Acetic acid	214	211*(-1.4)
Acetic acid	856	594**(-30)
Sodium Acetate	365	299***(-18)
Propionic acid	302	267***(-11)
n-butyric acid	364	334****(-8)
KHP	234	254*(+8)

Table 6 Results obtained using commercial kits L1. Vales are arithmetical means of two replicates. Units in mgO_2/L. In brackets the relative error (%).

	TOD	Measured COD
Acetic acid	107	95(-11)
Acetic acid	214	213(-1)
Acetic acid	428	428(0)
Acetic acid	856	825(-4)
Propionic acid	151	149(-1)
Propionic acid	302	395(-2)
Propionic acid	604	598(-1)
Propionic acid	1208	1180(-2)
n-butyric acid	182	176(-3)
n-butyric acid	364	344(-6)
n-butyric acid	728	628(-14)
n-butyric acid	1456	1366(-6)
KHP	118	118(+1)
KHP	232	243(+3)
KHP	471	469(0)
KHP	941	923(-2)

To improve the chemical oxidation of VFAs, the increase of the digestion time using the closed reflux method has been tested. The oxidation time was increased from two (standard oxidation time) to 6 and 24 hours. The results (Table 7) shows that increasing the oxidation time increases the value of the measured COD for the acetic acid standards. It has to be highlighted the very low COD values with the two hour of oxidation. On the contrary, the prolonged oxidation time has caused a COD overestimation (of the lowest standard concentrations). A possible explanation could be that the longer oxidation time could remove part of the rubber in the caps or could oxidize some dirty material previously present in the vials.

Table 7 COD measured oxidising acetic acid using the closed reflux method and increasing the digestion time from 2 to 6 and 24 hours at L1 using 10 mL headspace digestion tubes. Values are arithmetical means of two replicates. Units in mgO_2/L. In brackets the relative error (%).

TOD	2 h	6 h	24
50	32(-36)	56(+12)	75(+50)
100	46(-54)	105(+5)	110(+10)
200	85(-58)	182(-9)	203(+2)
400	159(-60)	340(-15)	399(0)

CONCLUSIONS

The results of the interlaboratory exercise on the COD measurement of VFAs have confirmed that the standard methods usually adopted could underestimates the true COD concentrations. To increase the accuracy of the COD measurement of VFAs the closed reflux method has to be preferred than the open reflux one. Attention must be paid to leave the lowest headspace in the digestion tubes to increase the contact of the volatile compounds with the oxidant. Even though the best resuts were obtained with commercial kit, similar results were obtained with closed reflux method and low head sapace (3.5 mL).

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