

Reagents and Reaction Time Reduction in the Determination of Chemical Oxygen Demand (COD).

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SUMMARY

The assesment of water quality typically involves the determination of its chemical oxygen demand (COD). This method is performed in an acidic medium, using potassium dichromate as oxidizing agent, mercury(II) sulfate as halide inhibitor, and silver sulfate as catalyst. Samples are digested for two hours, and the resulting absorbances are read in a spectrophotometer. Unfortunately the required reagents used are harmful and the reaction times are rather long. We have reported earlier the sucessful use of H₂O₂ as an alternative, environmentally friendlier oxidizing agent. In the present work a protocol has been devised and tested to halve the amount of silver sulfate required, and with a judicious use of UV light this greatly reduces the reaction time thus yielding a faster and more environmentally sound technique.

Keywords: COD, Hydrogen Peroxide, UV light, Silver Sulfate.

INTRODUCTION

Despite the undeniable economic importance of key industries, the concomitant effluent production often increases the amount of toxic substances released into water bodies that affects aquatic ecosystems [Ledakowics et al. 2001; Kusic et al. 2006]. Some industrial effluents are rich in dissolved organic matter, a fraction of which is difficult to degrade and remains after biological treatment [Quintero and Cardona 2010].

Among the different techniques that measure water quality, the chemical oxygen demand (COD) is prominent as a measure of the amount of oxygen required to oxidize the organic matter present [Domini et al 2009; Zhang et al. 2009]. The standardized method involves the use of $K_2Cr_2O_7$ ($E^0 = 1.36$ V) in the presence of a catalyst (Ag_2SO_4) for the oxidation of organic compounds under acidic conditions (H_2SO_4). Certain inorganic substances present in the environment interfere since they are also susceptible to oxidation, thus elevating the COD results. To prevent this, $HgSO_4$ is added as halide and pseudohalide inhibitor (e.g., chloride, iodide, sulfur, sulfites, etc.) [Ai et al. 2004; Chen et al. 2005; Zhu et al. 2006]. The procedure involves the addition of a known amount of oxidizer to the sample; the resulting mixture is then subjected to heat treatment in a digester for two hours at 150 °C [Sousa et al. 2007; Su et al. 2007; Yao et al. 2009; Berenguer, 2015].

Alternative methods have been developed, although many pose their own challenges (including higher costs) [Raposo et al. 2008; Domini et al. 2009; Vyrides & Stuckey, 2009; Zhang et al. 2009]. A greener alternative has been developed based on the use of hydrogen peroxide ($E_0 = 1.78$ V) to achieve the desired oxidation without the need for toxic chromates [Gogate et al. 2003; Quintero et al. 2010; Carbajal-Palacios et al. 2012].

The combination of oxidizing agents and UV irradiation is particularly interesting [Alnaizy and Akgerman, 2000; Benítez et al. 2011, Litter et al. 2012] since for example the UV/ H_2O_2 combined method generates $\cdot OH$ radicals, capable of transforming various toxic organic compounds into less dangerous, biodegradable products [Gogate et al. 2004] or even into CO_2 . In fact, Advanced Oxidation Processes (AOPs) rely on this radical generation for the treatment of effluents. Examples of AOPs include the use of ozone (O_3), hydrogen peroxide (H_2O_2), and ultraviolet radiation (UV) [Chidambara et al. 2005; Kusic et al. 2006; Farmer and Cardona, 2009; Benitez et al. 2011].

Hydrogen peroxide has been used for several years for the treatment of industrial effluents and potable water, mainly with the aim of removing organic matter [USP technologies 2015]. H_2O_2 is a versatile oxidant, with an oxidation potential greater than that of chlorine, chlorine dioxide or potassium permanganate and is capable of producing hydroxyl radicals via catalysis either in the

presence or absence of radiation [Luis de Mattos et al. 2003]. By simply adjusting factors such as pH, temperature, dose, reaction time and the nature and amount of catalysts, H₂O₂ can oxidize different complex organic compounds into simpler, less toxic and more biodegradable species [Nilsun, 1999; Alnaizy and Akgerman, 2000]. The generation of highly oxidizing and reactive species in the reaction medium like the superoxide anion radical (O₂^{•-}), the hydroperoxide anion (HOO⁻) and the highly reactive and non-selective hydroxyl radical (•OH) increases such degradation rates. These species firstly attack unsaturated centers (e.g., chromophores) and then the rest of the organic moieties [Gogate 2004].

The purpose of the present work was to verify the viability of using hydrogen peroxide as oxidizing agent for the COD determination in order to reduce reaction times with the help of UV light and to decrease the required amounts of the harmful Ag₂SO₄ catalyst.

EXPERIMENTAL

The preparation of solutions and the experimental procedures for the proposed COD determination are described next.

1. Preparation of solutions.

1.1 Method #1 (Standardized technique). The solutions for the standard COD determination were prepared in accordance with international standards [APHA, 1998] using K₂Cr₂O₇ (Reasol, 99.0%), H₂SO₄ (Fermont, 96.1%), HgSO₄ (Fermont, 98.4%), and Ag₂SO₄ (Fermont, 98.4%).

1.2 Method #2 (H₂O₂ as the oxidizing agent). Solutions were prepared as in 1.1, except that K₂Cr₂O₇ was replaced by H₂O₂. The stoichiometric amount of H₂O₂ required for the oxidation of the sample with the largest COD in the range of interest of this work was used throughout this procedure. The oxidizing solution was prepared by adding 5.2 mL H₂O₂ (J. T. Baker, 30%) to 500.0 mL of the water sample, followed by 167.0 mL of H₂SO₄ and 33.3032 g of HgSO₄. This mixture was then diluted to 1000 mL with distilled water [Carbajal-Palacios et al. 2012]. The acidic catalyst solution was prepared as in 1.1.

1.3 Method #3 (Decreased amount of Ag₂SO₄). The catalytic solution for the experiments aimed at achieving a silver sulfate decrease was prepared dissolving 7.5015 g of Ag₂SO₄ in 1 L of H₂SO₄. Complete dissolution was achieved after two days and the resulting solution was stored in an opaque container to prevent its photodecomposition. The oxidizing solution was prepared as in 1.2.

1.4 Method #4 (With UV irradiation). The oxidant solution was prepared as in 1.2 and the catalyst solution was prepared as in 1.3. UV light (Mineral light camp, model UVGL-58, multiband UV-254/366 nm, 18 W) was then irradiated onto the sample to decompose H₂O₂ and reduce reaction time. Several exposure time were tested in triplicate: 30, 40, 50 and 60 min.

2. COD Determination

2.1 Decrease of the Ag₂SO₄ concentration (Method #3).

Two different concentrations of Ag₂SO₄ were tested: 0.0481 M (standard concentration) and 0.0241 M.

2.2 Decrease of reaction time with UV light (Method #4).

Samples were exposed to UV light during 30, 40, 50 or 60 min.

2.3 Tube preparation and absorbance readings

i) 1000 mg_{COD}/L-stock solutions were prepared for each of the four methods described above by drying potassium hydrogen phthalate (KHP, 100%, J.T. Baker) at 110 °C during 2 h and dissolving 0.8514 g in distilled water to a final volume of 1000.0 mL. Standard dilutions were then prepared from such stock solutions as follows: 30, 40, 50, 70, 90, 100, 200, 300, 400, 500, and 600 mg of COD / L.

ii) The final digestion solution was prepared for each method by mixing 1.5 mL of the corresponding oxidizer, 3.5 mL of the catalyst solution and 2.5 mL of water or sample.

iii) For the standard COD determination a calibration curve was obtained as described in the international standard [APHA, 1998] using a UV-Vis spectrophotometer (Perkin Elmer, Lambda 25) as follows:

- Method #1: The solutions were digested for 2 h and their absorbances read at 620 nm.
- Methods #2 and #3: The solutions were digested for 2 h at ambient temperature.
- Method #4: The solutions were digested for 1 h at ambient temperature under UV radiation and their absorbances read at 420 nm.

iv) A calibration curve was developed for each COD range (low/high, see below) by analyzing selected dilutions of the KHP standard solution using a 1-cm optical path quartz cell in the UV-Vis spectrophotometer.

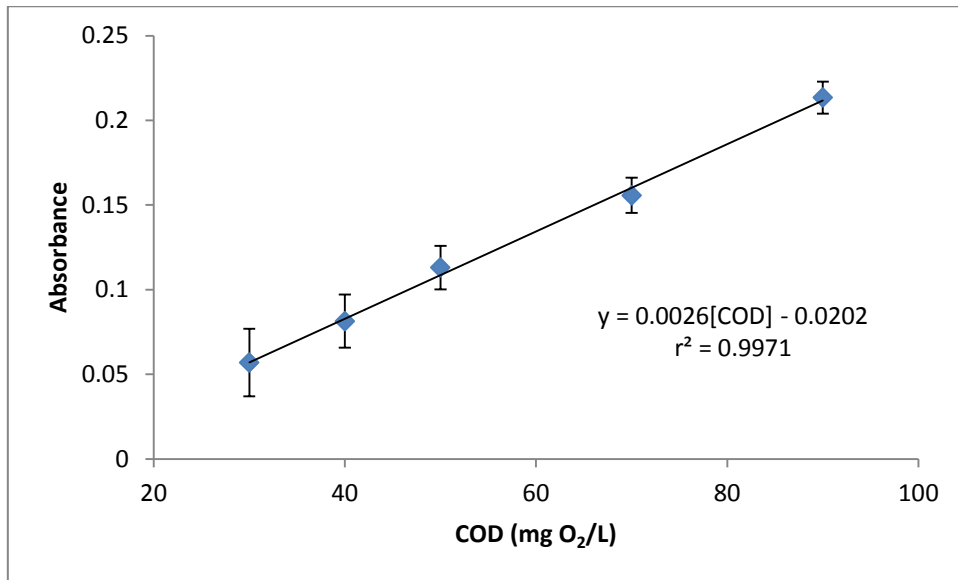
v) These four COD determination methods were applied to real industrial wastewater samples and the results are compared below.

RESULTS AND DISCUSSION

Decrease of the Ag_2SO_4 concentration

Quintuplicate tests were performed with the two different Ag_2SO_4 concentrations. Halving the original concentration to 0.024 M yielded a very good linear correlation, as shown in Figures 1a (low COD range, 30-90 mg O_2/L) and 1b (high COD range, 100-600 mg O_2/L). It is noteworthy that the standard deviations are larger in the low range determinations; nonetheless these values are still small.

(a)



(b)

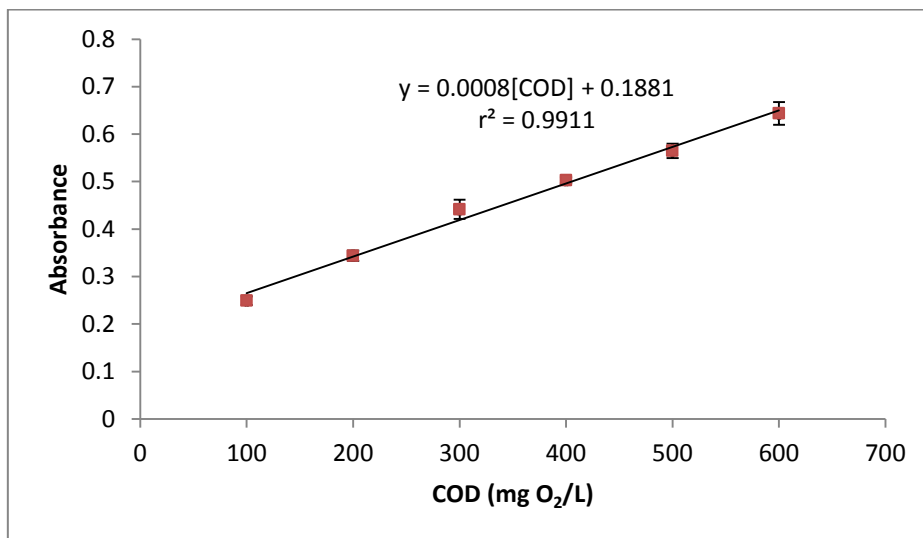


Figure 1: Calibration curves for two COD ranges:

a) low COD range, 30-90 mg O₂/L and b) (high COD range, 100-600 mg O₂/L)

Attempts to halve the standard HgSO₄ concentration yielded a nonlinear response with COD concentration and therefore were not pursued any further.

Industrial samples

The following industrial wastewater samples were tested from: (a) cattle slaughterhouse, (b) municipal wastewater plant (Toluca North Plant), (c) municipal wastewater plant (Cerro de la

Estrella), (d) chocolate production, and (e) wastewater combined from diverse industries (undisclosed upon request). (Due to the high DQO concentrations, a 1/10 dilution had to be performed before analysis **EN LOS 5 CASOS?** la del rastro, chocolatera y la última, no tengo el nombre ni ubicación, la de la planta norte así se llama, es un planta de agua residua municipal de toluca, el cerro de la estrella, es otra planta tratadora de agua en Iztapalapa). **MI PREGUNTA NO ES POR LOS NOMBRES DE LAS PLANTAS, SINO QUE SI EN TODAS SE HIZO LA MISMA DILUCIÓN QUE MENCIONAS.** COD results (including averages and standard deviations) are shown in Table 1.

Table 1. Quintuplicate COD determinations of industrial wastewater samples (methods #1, 2 and 3).

	COD, mg/L		
	Method 1	Method 2	Method 3
(a) Cattle slaughterhouse			
test1	1880	1823	1723
test 2	1743	1810	1823
test 3	1620	1692	1637
test 4	1586	1743	1586
test 5	1734	1702	1578
Average	1712	1754	1669
Standard deviation	116.0	60.5	103.5
(b) Municipal wastewater plant (Toluca North Plant)			
test1	1093	1234	1035
test 2	1283	1178	1321
test 3	950.0	1235	1173
test 4	1132	1089	1245
test 5	1265	1157	1087
Average	1144	1179	1172

Standard deviation	136.5	60.8	115.5
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(c) Municipal wastewater plant (Cerro de la Estrella)

test1	1616	1734	2135
test 2	2023	1823	2046
test 3	1784	1935	1939
test 4	1801	2021	2178
test 5	1698	1690	1724
<i>Average</i>	1784	1841	2004
Standard deviation	152.3	137.3	181.5

(d) Chocolate production wastewater

test1	3303	3358	3548
test 2	3440	3194	3465
test 3	3270	3254	3239
test 4	3281	3246	3294
test 5	3343	3134	3198
<i>Average</i>	3327	3237	3349
Standard deviation	68.8	82.8	151.0

(e) Wastewater combined from diverse industries

test1	2126	2135	2235
test 2	2116	2198	1944
test 3	1906	2045	2176
test 4	1973	1987	2198
test 5	2054	2233	2231
<i>Average</i>	2035	2120	2157
Standard deviation	94.5	102.9	121.4

The results obtained with methods #2 and #3 are compared below to those with the standard method #1 by means of Fisher's test (i.e., comparison of variances) to evaluate their performance with respect to the standardized test. The results are shown in Table 2.

Table 2. Fisher's test for methods #2 and #3 with different wastewater samples.
(F from tables at the 95% confidence level = 6.388).

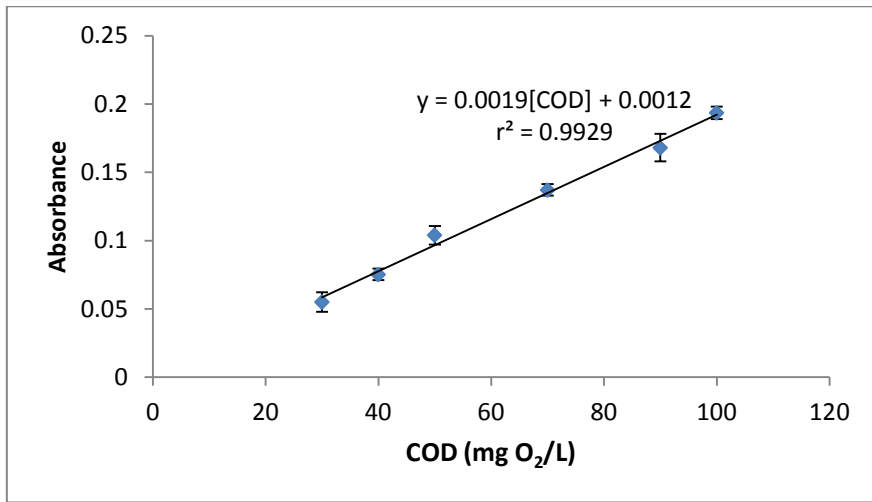
Plant/Method:	Slaughterhouse	North Plant	Cerro de la Estrella	Chocolate Company	Diverse Industries
Method 2	3.681	5.042	1.231	1.450	1.187
Method 3	1.256	1.396	1.419	0.207	1.651

As observed in Table 2, all of the F-values obtained from the experiments are considerably smaller than the reference value obtained from tables (i.e., $F = 6.388$ at the 95% confidence level) which validates the procedures of the proposed greener methods that use H_2O_2 and reduce the Ag_2SO_4 requirement.

Decrease of reaction time with UV light

In order to decrease the reaction time required for method #3, samples were irradiated with UV light (i.e., method #4) during different times: 30, 40, 50 and 60 min. Linear results were only obtained at 60-min irradiation times. Calibration curves were obtained for both COD ranges: (a) low range, 30-90 mg O_2/L , and (b) high range, 100-600 mg O_2/L with the corresponding standard solutions. Good linear correlations were obtained, as shown in Figures 2a and 2b. Again, it is noteworthy that the standard deviations are larger in the low range determinations; nonetheless these values are still small.

(a)



(b)

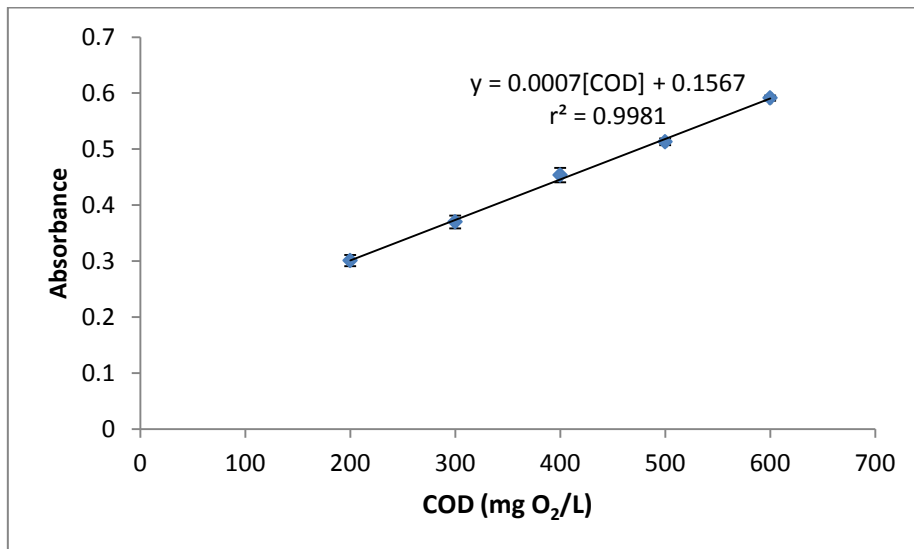


Figure 2: Calibration curves for the UV-irradiated (60 min) samples for two ranges: a) low COD range (30-100 mg O₂/L) and (b) high COD range (from 200-600 mg O₂/L).

Quintuplicate tests were then conducted with industrial wastewater samples from the same sources as above. COD results (including averages and standard deviations) obtained with the four methods are shown in Table 3.

Table 3. Quintuplicate COD determinations of real wastewater samples. Comparison of results obtained with the four methods described above.

COD, mg/L

	Method 1	Method 2	Method 3	Method 4
(a) Cattle slaughterhouse				
test1	1698	1731	1332	1156
test 2	1805	1609	1270	1525
test 3	1709	1721	1358	1193
test 4	1584	1768	1418	1028
test 5	1592	1635	1135	1429
Average	1678	1693	1303	1266
Standard deviation	91.9	67.5	108.0	204.9

(b) Municipal wastewater plant (Toluca North Plant)

test1	1032	817	910.0	985
test 2	984	1072	1060	1039
test 3	1038	893	1222	1076
test 4	1062	1143	952	939
test 5	976	1088	1102	1115
Average	1018	1002	1049	1031
Standard deviation	37.2	140.1	124.2	70.5

(c) Municipal wastewater plant (Cerro de la Estrella)

test1	1726	1770	1744	1815
test 2	1805	1773	1646	1602
test 3	1694	1623	1746	1595
test 4	1685	1886	1784	1912

test 5	1807	1772	1721	1695
Average	1744	1765	1728	1724
Standard deviation	59.1	93.1	51.4	137.8

(d) Chocolate production wastewater

test1	2632	2750	2521	2597
test 2	2781	2763	2570	2844
test 3	2590	2802	2618	2671
test 4	2652	2591	2675	2737
test 5	2811	2802	2757	2788
Average	2693	2741	2628	2727
Standard deviation	97.0	87.0	92.0	97.0

(e) Wastewater combined from diverse industries

test1	1867	1863	2021	1885
test 2	1998	1941	1807	1974
test 3	2007	1870	1895	2054
test 4	1986	1929	2018	1984
test 5	1897	1966	1951	1850
Average	1951	1914	1938	1949
Standard deviation	64.1	45.4	90.2	81.8

From Table 3 it is clear that the results are very similar among the four methods. As above, the results obtained with methods #2, #3 and #4 are compared below to those with the standard method #1 by means of Fisher's test (i.e., comparison of variances).

**Table 4. Fisher's test for methods #2, #3 and #4 with different wastewater samples.
(F from tables at the 95% confidence level = 6.388).**

Plant/Method:	Slaughterhouse	North Plant	Cerro de la Estrella	Chocolate Company	Diverse Industries
Method 2	1.856	14.18	2.487	1.245	1.996
Method 3	1.381	11.15	1.319	1.113	1.976
Method 4	4.969	3.592	5.448	1.001	1.627

As observed in Table 4, all of the F-values obtained from the experiments (except those of the unusually turbid North Plant wastewaters) are smaller than the reference value obtained from tables (i.e., $F = 6.388$ at the 95% confidence level) which validates the procedure of this proposed greener method that uses UV-irradiated H_2O_2 .

Some of the results in Tables 1 and 3 obtained with different methods are rather similar. This is possibly due to the presence of simpler organic compounds that are easily oxidizable and thus display a similar behavior with different methods, while greater differences mean a greater resistance to oxidation.

In order to better assess the practicability of the different methods, a summary is now presented of the reagents and quantities used in each one as well as the reaction times and the use of electrical energy or lamps See Table 5.

Table 5. Comparison of reagents and materials used in each technique.

Reagents and materials	Method 1 (Standard)	Method 2 (Peroxide)	Method 3 (Peroxide and half Ag_2SO_4)	Method 4 (Peroxide, half Ag_2SO_4 and UV light)
$K_2Cr_2O_7$	Yes	No	No	No
$HgSO_4$	Yes	Yes	Yes	Yes
H_2SO_4	Yes	Yes	Yes	Yes
H_2O_2	No	Yes	Yes	Yes

Ag_2SO_4	Yes	Yes	Half concentration	Half concentration
Waste generated (mL)	75	75	75	75
Heating time (min)	120	0	0	0
Reaction time (min)	120	120	120	60
Use of UV light	No	No	No	Yes
Additional electrical power required	Yes	No	No	Yes
Goodness (F-test, see text)	Good	Good	Good	Good
Cost of 10 Tests (\$USD)	1.54	1.46	1.02	1.02

CONCLUSIONS

A greener, faster and cheaper method for COD determination is validated which decreases the toxicity of the standard method by replacing the oxidizing agent $\text{K}_2\text{Cr}_2\text{O}_7$ with H_2O_2 , and by halving the concentration of Ag_2SO_4 . The reaction time is also halved with the help of the UV light.

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