

A Greener UV and Peroxide-Based Chemical Oxygen Demand Test


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Abstract Water quality assessment typically includes the determination of chemical oxygen demand (COD) by oxidation of organic matter with Cr(VI) in an acidic medium followed by digestion. Unfortunately, the required reagents are harmful and the reaction times are rather long. We investigated earlier the use of H₂O₂ as a more environmentally friendly oxidizing agent to replace the hazardous chromates. In the present study, we have furthered this possibility by incorporating the use of H₂O₂ in the presence of UV light. A protocol has been devised and tested with standards and real samples that replaces toxic Cr(VI), halves the amount of silver sulfate required, and greatly reduces the necessary reaction time, thus yielding a faster and more environmentally sound method.

Keywords Chemical oxygen demand · Ultraviolet · Hydrogen peroxide · Chromate replacement

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1 Introduction

Industrial effluent production often increases the amount of toxic substances released into bodies of water (Ledakowics et al. 2001; Kusic et al. 2006). Some industrial effluents are particularly rich in dissolved organic matter, a fraction of which is difficult to degrade and persists even after biological treatment (Quintero and Cardona 2010).

Among the different methods that assess water quality, chemical oxygen demand (COD) is prominent as a measure of the amount of oxygen required to oxidize the organic matter that is present (Domini et al. 2009; Zhang et al. 2009a, b). The standard method involves the use of K₂Cr₂O₇ ($E^0 = 1.36$ V) in the presence of a catalyst (Ag₂SO₄) for the oxidation of organic compounds under acidic conditions (H₂SO₄). Certain inorganic substances in the environment interfere because they are also susceptible to oxidation, thereby elevating the COD results. To prevent this interference, HgSO₄ is added as a halide and pseudo halide inhibitor (e.g., chlorides, iodides, sulfides, and sulfites) (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 later subjected to heat treatment in a digester for 2 h at 150 °C (Sousa et al. 2007; Yao et al. 2009; ISO 1989, 2002).

In view of the hazardous nature of most of the required chemicals in the standard method as well as its long heating time and high temperature, alternative methods have been developed based primarily on electrochemical, photocatalytic, or photolytical strategies.

Electrochemical alternatives include amperometric detection at novel electrodes such as boron-doped diamond (BDD) (Yu et al. 2007; Yu et al. (2016) Bogdanowicz et al. 2012, 2013), Cu (normal electrocatalytic type) (Silva et al. 2009), nanoparticulated Cu (Yang et al. 2011), and chronocoulometry at Ti/TiO₂ electrodes (Ge et al. 2016).

Photocatalytical alternatives (PC) typically rely on the decomposition of organics by the UV-produced holes at semiconducting TiO₂ surfaces. Portable devices utilize for example LED technology and nanostructured TiO₂ (Zhang et al. 2009a, b). Another PC approach involves the use of KMnO₄ as a supporting oxidizer (Zhu et al. 2006). Analyte detection can be effected by fluorescence (Li and Song 2009) and quantum dot-assisted chemiluminescence (Silvestre et al. 2011). Fast and sensitive chemiluminescence detection has also been used for the monitoring of radical generation during UV photolysis (Su et al. 2007).

A relatively novel approach for the measurement of COD involves the examination of TOC as a cleaner alternative whereby good results have been reported (Dubber and Gray 2010). The use of faster heating sources (e.g., closed microwaves, open microwaves, and ultrasound) alleviates the problem of time consumption (Domini et al. 2006, 2009; Dharmadhikari et al. 2005). All of these alternative methods have particular advantages and challenges (Domini et al. 2009; Zhang et al. 2009a, b; Raposo et al. 2008; Vyrides and Stuckey 2009).

In the present approach, the combination of oxidizing agents and UV irradiation is particularly promising (Alnaizy and Akgerman 2000; Benitez et al. 2011) because the combined UV/H₂O₂ method generates $\cdot\text{OH}$ radicals capable of transforming most toxic organic compounds into less dangerous and more biodegradable products (Gogate and Pandit 2004) or even into CO₂. Advanced oxidation processes (AOPs) rely on this radical generation for the treatment of effluents. Examples of AOPs include the use of ozone (O₃), hydrogen peroxide (H₂O₂), and ultraviolet radiation (UV) (Kusic et al. 2006; Benitez et al. 2011; Gogate and Pandit 2004; Chidambara-Raj and Quen 2005). A greener alternative to the standard COD method is also available based on the use of hydrogen peroxide ($E^0 = 1.78$ V) to achieve the desired oxidation without the need for toxic chromates (Quintero and Cardona 2010; Gogate and Pandit 2004; Carbajal-Palacios et al. 2012).

Hydrogen peroxide has been used for several years for the treatment of industrial effluents and potable

water, primarily with the aim of removing organic matter (USP Technologies 2017). H₂O₂ is a versatile oxidant with an oxidation potential greater than that of chlorine, chlorine dioxide, and potassium permanganate. Furthermore, H₂O₂ is capable of producing hydroxyl radicals via catalysis in either the presence or absence of radiation (Luiz de Mattos et al. 2003). By adjusting key 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 (Vyrides and Stuckey 2009; Nilsun 1999). The generation of highly oxidizing and reactive species in the reaction medium increases such degradation rates; examples include the superoxide anion radical (O₂⁻), the hydroperoxide anion (HOO⁻), and the highly reactive and non-selective hydroxyl radical ($\cdot\text{OH}$). These species typically first attack unsaturated centers (e.g., chromophores) and then the rest of the organic structures (Gogate and Pandit 2004). Since H₂O₂ is known to generate $\cdot\text{OH}$ upon UV irradiation, we set out to test such a system for COD determination in order to eliminate the use of chromates, reduce reaction times, and decrease the required amounts of the harmful Ag₂SO₄ catalyst.

2 Materials and Methods

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

1. Preparation of solutions

- 1.1 Method no. 1 (standardized method). The solutions for the standard COD determination were prepared in accordance with international standards (37) using K₂Cr₂O₇ (Reasol, 99.0%), H₂SO₄ (Fermont, 96.1%), HgSO₄ (Fermont, 98.4%), and Ag₂SO₄ (Fermont, 98.4%).
- 1.2 Method no. 2 (H₂O₂ as the oxidizing agent). Solutions were prepared as reported 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

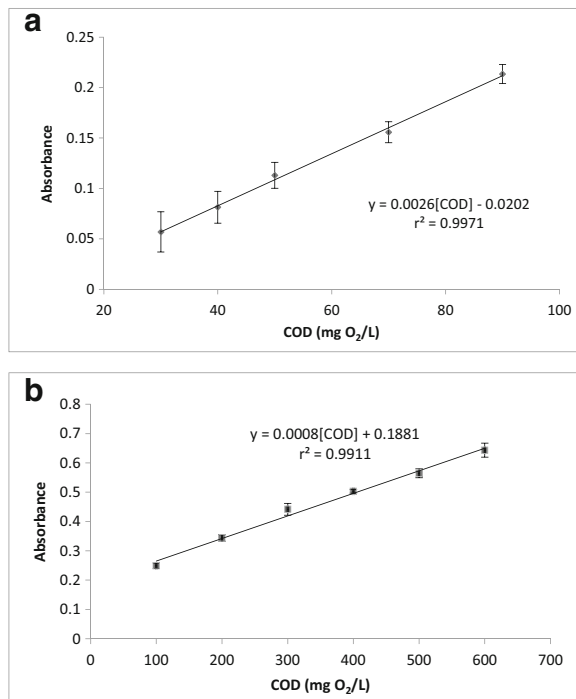


Fig. 1 Calibration curves for two COD ranges: **a** low COD range, 30–90 mg O₂/L, and **b** high COD range, 100–600 mg O₂/L

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 later diluted to 1000 mL with distilled water (Carbajal-Palacios et al. 2012). The acidic catalyst solution was prepared as reported in 1.1.

1.3 Method no. 3 (reduced amount of Ag₂SO₄). The catalytic solution for the experiments aimed at decreasing a silver sulfate was prepared by dissolving 7.5015 g of Ag₂SO₄ in 1.0 L of H₂SO₄. Complete dissolution was achieved after 2 days and the resulting solution was stored in an opaque container to prevent its photodecomposition. The oxidizing solution was prepared as reported in no. 1.2.

1.4 Method no. 4 (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, multi-band UV-254/366 nm, 18 W) was then irradiated onto the sample to decompose H₂O₂ and reduce reaction time. Several exposure times were tested in triplicate: 30, 40, 50, and 60 min.

Table 1 Quintuplicate COD determinations of industrial wastewater samples (method nos. 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)			
Test 1	1093	1234	1035
Test 2	1283	1178	1321
Test 3	950	1235	1173
Test 4	1132	1089	1245
Test 5	1265	1157	1087
Average	1144	1179	1172
Standard deviation	136.5	60.8	115.5
(c) Municipal wastewater plant (Cerro de la Estrella)			
Test 1	1616	1734	2135
Test 2	2023	1823	2046
Test 3	1784	1935	1939
Test 4	1801	2021	2178
Test 5	1698	1690	1724
Average	1784	1841	2004
Standard deviation	152.3	137.3	181.5
(d) Chocolate production wastewater			
Test 1	3303	3358	3548
Test 2	3440	3194	3465
Test 3	3270	3254	3239
Test 4	3281	3246	3294
Test 5	3343	3134	3198
Average	3327	3237	3349
Standard deviation	68.8	82.8	151.0
(e) Wastewater combined from diverse industries			
Test 1	2126	2135	2235
Test 2	2116	2198	1944
Test 3	1906	2045	2176
Test 4	1973	1987	2198
Test 5	2054	2233	2231
Average	2035	2120	2157
Standard deviation	94.5	102.9	121.4

Table 2 Fisher's test for method nos. 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

2. COD determination: decrease of reaction time with UV light.

Samples were prepared and treated as follows.

- 2.1 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. In order to closely match the ISO 6060 applicability range (ISO 1989), standard dilutions were prepared from such stock solutions as follows: 30, 40, 50, 70, 90, 100, 200, 300, 400, 500, and 600 mg of COD/L.
- 2.2 The final digestion solutions were 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.

- 2.3 For the standard COD determinations, a calibration curve was obtained, as described in the international standard method (APHA 1998) using a UV-vis spectrophotometer (Perkin Elmer, Lambda 25) as follows:
 - 2.3.1 Method no. 1: The solutions were digested for 2 h, and their absorbances were read at 620 nm.
 - 2.3.2 Methods nos. 2 and 3: The solutions were digested for 2 h at ambient temperature, and their absorbances were read at 420 nm.
 - 2.3.3 Method no. 4: The solutions were digested for 1 h at ambient temperature under UV radiation (at 30, 40, 50, or 60 min) and their absorbances were read at 420 nm.
 - 2.3.4 A calibration curve was created 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.

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

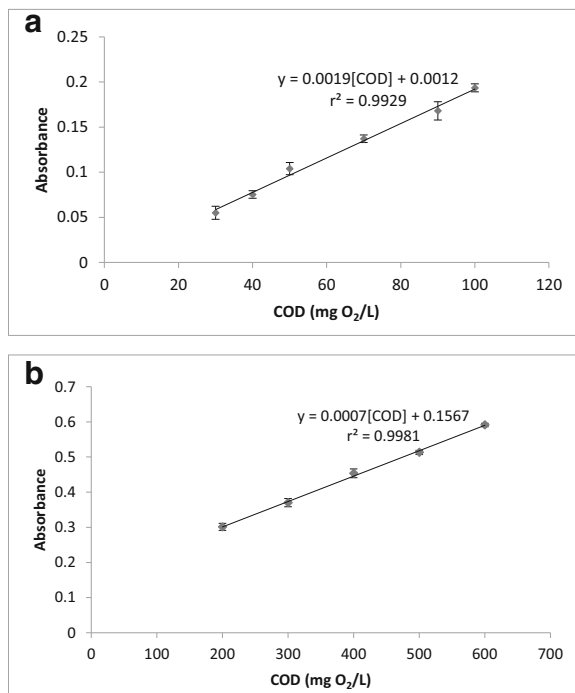


Fig. 2 Calibration curves for the UV-irradiated samples (60 min) for two ranges: **a** low COD range (30–100 mg O₂/L) and **b** high COD range (from 200 to 600 mg O₂/L)

3 Results and Discussion

3.1 Decrease of the Ag₂SO₄ Concentration

As stated earlier, the concentration of Ag₂SO₄ was halved in an attempt to produce a less expensive method and generate less hazardous waste. To this end, quintuplicate tests were performed with two different Ag₂SO₄ concentrations. Halving the original concentration to 0.024 M yielded a good linear correlation, as shown in Fig. 1a (low COD range, 30–90 mg O₂/L) and Fig. 1b (high COD range, 100–600 mg O₂/L). It is noteworthy

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				
Test 1	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)				
Test 1	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)				
Test 1	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				
Test 1	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				
Test 1	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

Table 4 Fisher's test for method nos. 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

that the standard deviations are larger in the low range determinations; nonetheless, these values are still within acceptable limits, as can be observed in the figure. The results with industrial wastewater are also highly reproducible, as shown below in Table 1. Attempts at reducing the concentration of HgSO_4 in the analytical determinations unfortunately did not yield linear results, possibly due to an inability to inhibit the entire amount of halides present in the samples, and these efforts were therefore discontinued.

3.2 Industrial Samples

The following industrial wastewater samples were tested from (a) a cattle slaughterhouse, (b) a municipal wastewater plant (Toluca North Plant), (c) a municipal wastewater plant (Cerro de la Estrella), (d) a chocolate production factory, and (e) wastewater combined from diverse industries (undisclosed upon request). Due to the high initial COD values, a 1/10 dilution had to be performed before the COD analysis. The results

(including averages and standard deviations) are shown in Table 1.

The results obtained with method nos. 2 and 3 are compared below to those obtained with the standard method no. 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.

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.

3.3 Decrease of Reaction Time with UV Light

In an attempt to decrease the reaction time required for method no. 3, samples were irradiated with UV light (i.e., method no. 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

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)
$\text{K}_2\text{Cr}_2\text{O}_7$	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 (<i>F</i> -test, see text)	Good	Good	Good	Good
Cost of 10 tests (\$USD)	1.54	1.46	1.02	1.02

COD ranges: (a) low range, 30–100 mg O₂/L and (b) high range, 200–600 mg O₂/L with the corresponding standard solutions. Good linear correlations were obtained, as shown in Fig. 2a, b. Again, it is noteworthy that the standard deviations are larger in the low range determinations; nonetheless, these values are still small, as shown in Fig. 2a.

A new set of quintuplicate tests was subsequently 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.

From Table 3, it is clear that the results are very similar among the four methods. As seen below, the results obtained with method nos. 2, 3, and 4 are compared to those with the standard method no. 1 by means of Fisher's test.

As observed in Table 4, all of the F-values obtained from the experiments (except those of the unusually cloudy North Plant wastewaters) are smaller than the reference value obtained from tables (i.e., $F = 6.388$ at the 95% confidence level), which endorses the adoption of this proposed greener method with UV-irradiated H₂O₂.

A portion of the results in Tables 1 and 3 obtained with different methods are rather similar. This similarity 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 indicate a greater resistance to oxidation.

In order to assess the practicality of the different methods more effectively, a summary is presented outlining the reagents and quantities used in each one, as well as the reaction times and the usage of electrical energy, see Table 5.

4 Conclusions

A greener, faster, and cheaper method for COD determination is proposed that decreases the toxicity of the standard method by replacing the oxidizing agent K₂Cr₂O₇ with H₂O₂ and by halving the concentration of Ag₂SO₄. The reaction time is also decreased with the help of a UV lamp. Quintuplicate tests conformed to the Fischer test at the 95% confidence level.

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