Replacing dichromate with hydrogen peroxide in the chemical oxygen demand (COD) test

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ABSTRACT

The widely used standard method for chemical oxygen demand (COD) involves hazardous chromium species, and its two-hour heating protocol entails a substantial amount of energy expenditure. In the present work we report a proof of concept for a major modification of this method in the range 10–800 mg_{COD}/L, whereby H_2O_2 is proposed as a replacement oxidizer. This modification not only reduces the use of unsafe chromium species but also allows for the use of milder conditions that decrease the total energy outlay. The results are comparable with those obtained either with the standard method or with a commercial Hach® kit.

Key words | chemical oxygen demand, dichromate, green chemistry, hydrogen peroxide, oxidation

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INTRODUCTION

The enormous pressure on the world's water resources has prompted an increase in the application of analytical procedures to verify its quality. Among the multiple parameters analyzed, the amount of oxygen available for respiration and oxidation processes is of paramount importance. The widely used chemical oxygen demand (COD) test yields the equivalent amount of oxygen required to oxidize the organic matter contained in a water sample (in mg O_2/L), and it is applicable to continental waters, wastewaters, and any water containing appreciable amounts of organic matter (Zhang *et al.* 2007; Domini *et al.* 2009; Yao *et al.* 2009).

This method uses a strong oxidizer, $K_2Cr_2O_7$ (E^0=1.36 V) in the presence of a catalyst, Ag_2SO_4, for the oxidation of organics under acidic conditions (H_2SO_4). Certain inorganic substances may interfere as they are susceptible to oxidation, yielding high results. To prevent this, $HgSO_4$ is added as an inhibitor of halides and pseudo halides (e.g., iodide, sulfide, sulfite and the like) (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 subject to thermal treatment in a digester. The low efficiency of this oxidizing step is responsible for the long digestion times required (ca. 120 min) (Boyles 1997; Sousa *et al.* 2007; Su *et al.* 2007; Berenguer 2009; Yao *et al.* 2009).

Alternative methods have been developed, although many pose their own challenges (e.g., higher costs) (Raposo *et al.* 2008; Domini *et al.* 2009; Vyrides & Stuckey 2009; Zhang *et al.* 2009). We have aimed at the development of a greener alternative based on the use of hydrogen peroxide as the oxidizer (E^0=1.8 V) to achieve the desired oxidation without the need for toxic chromates.

EXPERIMENTAL

The purpose of the following experimental series was to verify the feasibility of using peroxide to replace dichromate for COD determination. To this end, an appropriate wavelength for the analysis was firstly sought. As peroxide is known to be thermally unstable, we then tested its use at room temperature after different reaction times for several COD contents. Once an appropriate reaction time was selected, this peroxide method was used with different wastewater samples and the results compared with those obtained with the standard COD method and with the commercial Hach® kit. The procedures are described next:

(a) The solutions required for the standard COD determination were prepared according to an international protocol (APHA 1998) using $K_2Cr_2O_7$ (Reasol, 99.0%),

H_2SO_4 (Fermont, 96.1%), $HgSO_4$ (Fermont, 98.4%), and Ag_2SO_4 (Fermont, 98.4%).

(b) The solutions required for the COD determination with peroxide were prepared in the same manner as in (a), except that $K_2Cr_2O_7$ was replaced with H_2O_2. In order to provide a suitable amount of H_2O_2 for this purpose, we estimated the stoichiometric amount required for the oxidation of the sample with the highest COD in our range of interest and added it to every sample. The oxidizing solution was then prepared as follows: 5.2 mL of H_2O_2 (30%, J. T. Baker) was added to ca. 500 mL of the water sample followed by 167.0 mL of H_2SO_4 (Fermont, 96.1%) and 33.3 g of $HgSO_4$ (Fermont, 98.4%). This oxidizing mixture was then diluted to 1,000 mL with distilled water. The final room temperature digestion solution was prepared by mixing 1.5 mL of this last solution with 3.5 mL of the acidic catalyst solution and 2.5 mL of water. The acidic catalyst solution was prepared by dissolving 15.0 g of Ag_2SO_4 (Fermont, 98.4%) in 1 L of H_2SO_4 (Fermont, 96.1%); complete dissolution was achieved after 2 days and the resulting solution was then stored in an opaque container to prevent photodecomposition.

(c) A 1,000 mg/L COD mother solution was prepared by drying potassium biphthalate (KHP, 100.0%, J.T. Baker) at 110 °C for 2 h and dissolving 0.8514 g in distilled water to a final volume of 1,000 mL. From this mother solution, standard dilutions were prepared as follows: 10, 30, 40, 50, 60, 70, 80, 90, 100, 150, 200, 300, 400, 600, and 800 mg$_{COD}$/L.

(d) For the standard COD determination, a built-in program was used in a Hach DR/4000U spectrophotometer that required a single check point at 620 nm. The digestion time in the digester was 120 min at 150 °C.

(e) For the COD method using hydrogen peroxide, a suitable wavelength was sought by performing UV absorbance scans of the different reaction components from 200 to 300 nm in a Perkin Elmer (model Lambda 25) spectrophotometer. A three-fold purpose was desired here: (i) avoid interferences due to the natural absorbance peaks of all the components in the reaction mixture, (ii) prevent peroxide photodecomposition at high energy wavelengths, and (iii) obtain reasonable absorbance values for the reaction products.

(f) A suitable oxidation time was determined for the H_2O_2 method by monitoring synthetic water samples in two COD ranges of interest: low COD (10–80 mgO$_2$/L) and high COD (100–800 mgO$_2$/L) after 60, 90,100 and 120 min; the results were compared with those obtained

with the standard COD technique (120 min). Due to the highly oxidizing nature of the peroxide, samples treated with H_2O_2 were found not to require heating for the oxidation step.

(g) Once a suitable oxidation time was established for the H_2O_2 method and an appropriate absorption wavelength was located, a calibration curve was built for each COD range by analyzing selected dilutions of the standard KHP solution in the Hach DR/4000U spectrophotometer using a 1 cm optical path quartz cell.

(h) Lastly, the COD values obtained with the following three different methods applied to real wastewater samples were compared: (1) the standard technique, (2) the proposed method using peroxide, and (3) a commercial Hach® kit.

RESULTS AND DISCUSSION

To find a suitable wavelength for COD determination (and to visualize possible self-interferences), scans were first performed in solutions of the separate components of the digestion solution from 200 to 300 nm. Peaks were observed at ca. 209 and 225 nm in the acid catalyst solution (see Figure 1). Such peaks are also present in the digestion solution. In contrast neither the acid solution nor the peroxide absorbed substantially in the entire scan range. A wavelength that fulfills the three-fold purpose stated earlier was selected at 240 nm. Even though the KHP absorbance shown in the figure could interfere in the selected wavelength, this problem is actually minimal as
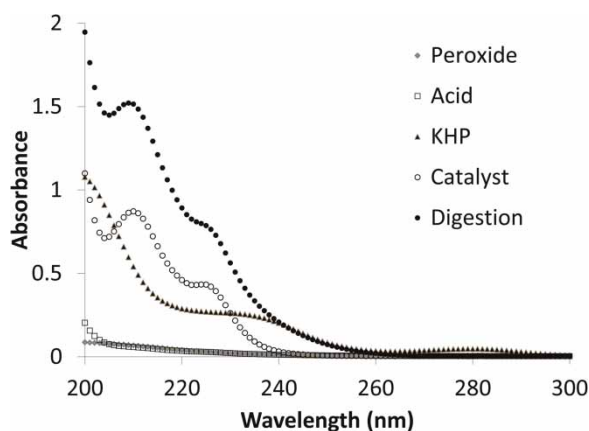

Figure 1 | UV screening scans. Peroxide solution: 0.0505 M H_2O_2. Acid solution: 8.76 M H_2SO_4. KHP solution: 0.2837 g$_{KHP}$/mL. Acidic catalyst solution: 15 g$_{Ag2SO4}$/L$_{H2SO4}$. Digestion solution: as described in (b).

the COD is a destructive test and thus no organics are left after the test so as to affect the method.

Once the appropriate wavelength for the H_2O_2 method was located, the need for a thermal digestion step in KHP solutions was evaluated by subjecting a set of samples to thermal treatment, whereas a spectator set was kept untreated. The solutions not subject to digestion yielded better results (i.e., closer to the values obtained using the standard method). This outcome facilitates the procedure and provides substantial energy savings.

Next, in order to find an appropriate oxidation reaction time to produce a linear absorbance plot, various KHP solutions were subjected to the H_2O_2 treatment described above for different reaction times: 60, 90, 100 and 120 min for the low (10–80 mgO_2/L, Figure 2) and high (100–800 mgO_2/L, Figure 3) COD ranges. The best linear responses were obtained at 120 min in both cases (see the trend lines); their different slopes required the two ranges to be treated separately. The variation of the results is rather small as can be seen in the error bars of Figures 2(b) and 3(b).
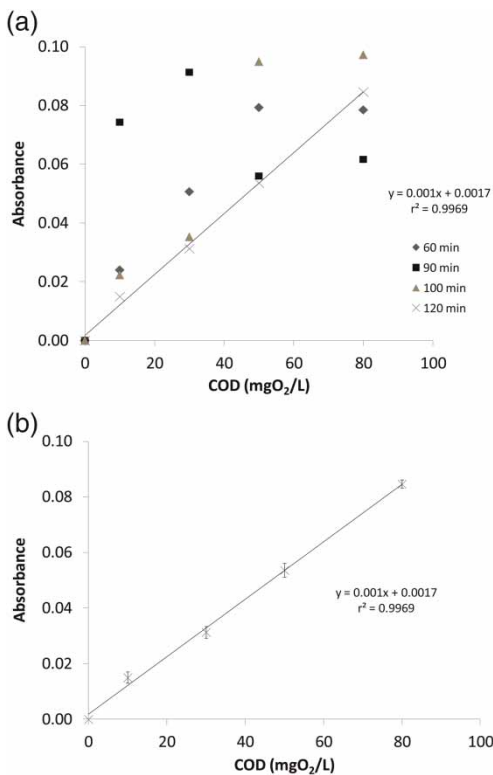
Figure 2 | (a) Absorbance as a function of concentration and reaction time for the low-COD range using the H_2O_2 method. Each data point represents the average of triplicate experiments. (b) The linear fit corresponds to data at 120 min, and the error bars are shown for each point.
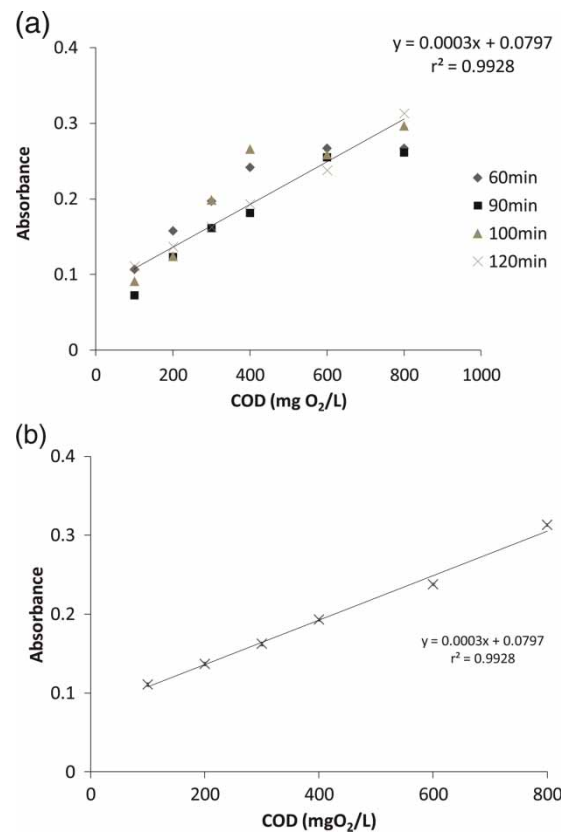
Figure 3 | (a) Absorbance as a function of concentration at different reaction times for the high-COD range using the H_2O_2 method. Each data point represents the average of triplicate experiments. (b) The linear fit corresponds to data at 120 min, and the error bars are shown in each point.

These findings were then used for the COD analysis (using peroxide) of several real samples as follows: (a) municipal wastewater, (b) household residual water, (c) industrial wastewater (from a local soda water company), (d) industrial wastewater (from a chocolate production company), and (e) industrial wastewater from a common collection point of ca. 200 industries (a 1/10 dilution was performed here previous to analysis). These results are compared with those obtained with the standard method as well as with a commercial Hach® kit. The findings using the three methods (standard, peroxide, and Hach® kit), including averages and standard deviations, are shown in Table 1.

Lastly a comparison is made of the three methods regarding the reagents and other requirements. Table 2 shows that the cost per sample with the proposed peroxide method is comparable with that with the standard method, and both are much lower than that with the Hach® kit. No heating is required in the first method, the goodness of the test is rather acceptable, and the need for dichromate is obviated.

Table 1 │ Comparison of the standard, peroxide and Hach® kit methods for the COD determination of several real wastewater samples. All experiments were performed in triplicate

Method:	Standard	Peroxide	Hach® kit
(a) Municipal wastewater			
TEST 1	400.0	405.6	420.0
TEST 2	433.3	433.3	411.0
TEST 3	496.5	443.3	398.0
Average	443.3	427.4	409.7
Std. dev.	49.0	19.5	11.1
(b) Household wastewater			
TEST 1	452.1	422.1	420.0
TEST 2	433.3	416.3	400.0
TEST 3	433.3	411.5	420.0
Average	439.6	416.6	413.3
Std. dev.	10.9	5.3	11.6
(c) Industrial wastewater (from a local soda water company)			
TEST 1	112.3	115.7	110.0
TEST 2	111.9	116.6	112.0
TEST 3	112.4	113.0	113.0
Average	112.2	115.2	111.7
Std. dev.	0.3	1.8	1.5
(d) Industrial wastewater (from a chocolate production company)			
TEST 1	276.9	297.1	270.0
TEST 2	246.1	280.0	270.0
TEST 3	276.9	294.3	290.0
Average	266.6	290.5	276.7
Std. dev.	17.8	9.2	11.6
(e) Industrial wastewater from a common collection point of ca. 200 industries			
TEST 1	2,491.3	2,551.4	2,376.0
TEST 2	2,387.5	2,536.1	2,510.0
TEST 3	2,352.9	2,523.1	2,480.0
Average	2,410.6	2,536.9	2,455.3
Std. dev.	72.0	14.2	70.3

Table 2 │ Comparison of reagents, energy and costs for the three methods used for the COD determination

Reagents and parameters	Standard	Peroxide	Hach® kit
$K_2Cr_2O_7$	Yes	No	Not specified in the commercial product
$HgSO_4$	Yes	Yes	
H_2SO_4	Yes	Yes	
H_2O_2	No	Yes	
Ag_2SO_4	Yes	Yes	
Waste (mL)	75	75	75
Electric power needed	Yes	No	Yes
Heating time (min)	120	0	120
Goodness of the test	Very good, the results are statistically comparable with the Hach® kit	Very good, the results are statistically comparable with the Hach® kit	Very good
Economic cost per 10 determinations (US dollars)	1.80	1.78	12.31

reducing energy expenditure through avoiding the need for a long heating step for thermal digestion.

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CONCLUSIONS

A proof of concept for the substitution of the oxidizer $K_2Cr_2O_7$ by H_2O_2 in COD tests for synthetic and industrial wastewaters is given. Appropriate conditions were found for its application in the 10–800 mg_{COD}/L concentration range. This aspect is an effort towards greening the standard COD test by replacing toxic dichromate with the more environmentally friendly hydrogen peroxide, and by drastically

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