Relationship between theoretical oxygen demand and photocatalytic chemical oxygen demand for specific classes of organic chemicals

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The oxidation behavior of twenty organic chemicals from four different classes (sugars, benzene derivatives, alcohols and carboxyl acids) were investigated using the official chemical oxygen demand (COD) methods (*i.e.*, permanganate and dichromate methods) and their oxidation levels compared with the theoretical oxygen demand (ThOD) values. In addition, the correlation between the official COD and ThOD values was also examined using the $COD_{Mn, Cr}$ method and their relative merits were considered. With the same set of samples, this study also examined the relationship between ThOD values and the response values of a photocatalytic COD sensor which has been developed to overcome several of the problems associated with the official COD methods. The relationship of the response values determined by the photocatalytic COD sensor to those ThOD values was obtained: $r = 0.96$ for the 20 organic chemicals from each different chemical class.

Introduction

The chemical oxygen demand (COD) test is widely used to determine the organic content of wastewater. COD refers to the oxygen required for the complete chemical oxidation of a water sample.[1,2] This is as an arbitrary empirical measurement evaluated by subjecting the sample to oxidation either by potassium permanganate or potassium dichromate in acid solution under working conditions well established in the official method.[1–3] Despite its widespread use, the official methods for COD have several disadvantages and, therefore, the development of automated methods improving the efficiency of pollution control is necessary. The principal disadvantages are as follows: (i) the analysis time is too long, 2–4 h being required for digestion plus additional time for the titration;[2,4,5] (ii) handling is also considerable, thus increasing the probability of errors;[2,4–6] (iii) there is quite a high consumption of expensive (Ag_2SO_4) and toxic ($HgSO_4$, $K_2Cr_2O_7$) chemicals;[4,5] (iv) straight chain carboxy acids are not oxidized in the absence of a catalyst (Ag_2SO_4) and may not be completely oxidized even in the presence of silver sulfate;[7,8] (v) volatile compounds are only oxidized to the extent with which they stay in contact with the liquid media[9] and the heat generated from adding sulfuric acid to the flask may drive volatile compounds out of the solution.[7,10] Finally, a number of methods has been reported in the literature, referring to the determination of COD using different compounds as COD standards: potassium hydrogenphthalate, D-glucose, sodium oxalate, sodium salicylate and sodium acetate, L-glutamic acid and lactose have been mostly employed.[11] It is, however, difficult to obtain correct values for COD in a real sample using these standard substances, because we do not know if the standard substances exist in the real sample.

In our former work,[12] a novel photocatalytic sensor was developed for the determination of COD using oxygen electrode. The measuring principle is based on the direct determination of the oxygen concentration change resulting from photocatalytic oxidation of organic compounds by titanium dioxide (TiO_2). The photocatalytic COD sensor, combined with TiO_2 and the oxygen electrode was found to be an excellent alternative to official COD methods. Additionally, the widespread disadvantages of official COD methods, including long analysis time, handling operations, and use of expensive and toxic reagents, could be overcome.

This paper mainly describes the oxidation behavior of twenty organic compounds, as determined by official COD methods, and the relationship between theoretical oxygen demand (ThOD) values and the response values of the photocatalytic COD sensor for twenty chemicals.

Experimental

Reagents

Experimental COD values for 20 organic chemicals from 4 distinct chemical classes (sugars, benzene derivatives, alcohols and carboxy acids) were used for this analysis. D(+)-glucose, sucrose, D(+)-lactose, ethanol, propan-1-ol, butan-1-ol , butan-2-ol, formic acid, acetic acid, propionic acid, *n*-butyric acid, isobutyric acid, phenol, aniline, and *m*-cresol were purchased from Kishida Chemicals & Co., Ltd. (Osaka, Japan). Methanol, propan-2-ol, *o*-cresol, *p*-cresol, and benzoic acid were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). The *n*-valeric acid and isovaleric acid were obtained from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan). These reagents were without further purification.

In the photocatalytic COD sensor, titanium dioxide beads (Type, ST-B11) used as the photocatalyst were obtained from Ishihara Sangyo, Ltd. (Japan). The carrier solution used in the photocatalytic COD sensor was deionized water. The deionized water used was purified in a Millipore-MilliQ system.

Apparatus and instruments for the photocatalytic COD sensor

The setup of the FIA system for COD determination is shown in Fig. 1. The flow carrier, deionized water in a reservoir, was propelled by a peristaltic pump (Minipuls3, Gilson, France) through an injector (7125NS, Rheodyne, USA), a reference oxygen electrode, a photochemical TiO_2 beads column and an air damper, then transported to a working oxygen electrode, and finally to a waste tank. The reference and working oxygen electrodes were prepared as commercial oxygen electrodes (BO-G, Able, Japan). The photocatalytic column was made

from a quartz tube (id 0.2 cm, od 0.4 cm) filled with TiO_2 beads of particle diameter 0.6 mm held in position with Teflon wool plugs. A UV irradiator together with a 15 W UV lamp (XX-15, Funakoshi, Japan) and a built-in reflector were located 0.5 cm from the side of the photocatalytic column in the UV illumination experiment. The temperature of the reference and working oxygen electrodes was thermostated with a water jacket and temperature controller (SB-9, Tokyo Rikakikai, Japan).

Measuring principle

Theoretical oxygen demand (ThOD) is the stoichiometric amount of oxygen required to oxidize a compound to end products such as CO_2, NH_3, $H_2PO_4^-$, SO_4^{2-}, and H_2O. COD_{Cr} can be estimated from ThOD using the following equation:[7]

$$COD_{Cr} = a \times ThOD, \qquad (1)$$

where a is an empirical constant.

The ThOD for each of the chemicals in this study was determined assuming that organic nitrogen was converted to NH_3 and stoichiometric oxidation of the chemical's carbon, phosphorus, and sulfur occurred according to the following equation:[7]

$$C_nH_mO_e\,X_kN_jS_iP_h + bO_2 \rightarrow nCO_2 + [(m-k-3j-2i-3h)/2]\,H_2O + kHX + jNH_3 + iH_2SO_4 + hH_3PO_4, \qquad (2)$$
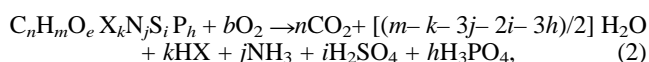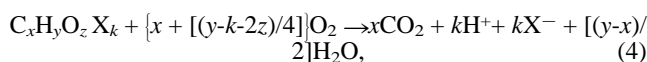
where X represents the sum of all halogens and

$$b = n + [(m-k-3j-2i-3h)/4] - (e/2) + 2i + 2h. \qquad (3)$$

Table 1 presents the oxygen moles, b in eqn. (2) and the values of ThOD for the 20 chemicals used in this study.

It is well known that titanium dioxide photocatalysis leads to stoichiometric photomineralization of organic compounds, as follows:[13]

$$C_xH_yO_z\,X_k + \{x + [(y-k-2z)/4]\}O_2 \rightarrow xCO_2 + kH^+ + kX^- + [(y-x)/2]H_2O, \qquad (4)$$

where X represents a halogen atom.

When the reference oxygen electrode is in contact with the sample solution, dissolved oxygen changes in the sample can be monitored by diffusion across the gas-permeable membrane until the oxygen partial pressures of the sample solution and the internal electrolyte solution in the oxygen electrode finally reach equilibrium. The dissolved oxygen changes, due to the photooxidation of TiO_2 with the samples, were monitored at the working oxygen electrode. Any variation of the concentration of the organic compounds in the sample solution will change the amount of organic compounds in the deionized water, thereby causing a current change of this solution. In all cases, the working oxygen electrode gives a current decrease in response to an increase of organic compounds in the sample solution. Fig.
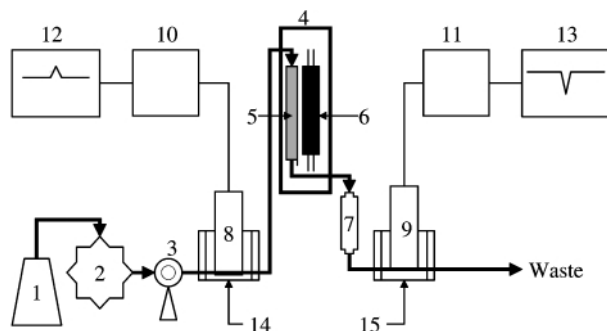
2 shows the current response to the injection of carboxy acids. The response values of this COD sensor using a pair of oxygen electrodes were calculated with the currents at the reference and working oxygen electrodes, respectively. The response values can be calculated as follows:

$$I = \alpha_r \times I_r - \beta_w \times I_w, \qquad (5)$$

where I_r and I_w are the peak heights of the responses from the reference and working oxygen electrodes, respectively. The α_r and β_w are factors for the relative sensitivity against the working and reference oxygen electrodes, respectively.

The measurement was performed as follows. At first, the oxygen electrodes were arranged in a temperature-controlled flow cell, and the responses were recorded. When the UV lamp was turned on, the current in the working oxygen electrode began to decrease until after approximately 10 min, and a steady state was reached. The following five processes are considered to account for the decrease of oxygen in an oxygenated TiO_2 aqueous system without organic compounds.[14,15]
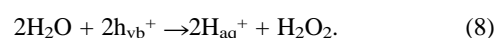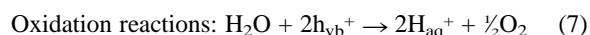
$$\text{Reduction reaction: } O_2 + 2H_{aq}^+ + 2e_{cb}^- \rightarrow H_2O_2 \qquad (6)$$

$$\text{Oxidation reactions: } H_2O + 2h_{vb}^+ \rightarrow 2H_{aq}^+ + \tfrac{1}{2}O_2 \qquad (7)$$

$$2H_2O + 2h_{vb}^+ \rightarrow 2H_{aq}^+ + H_2O_2. \qquad (8)$$

Table 1 ThOD values for substrates used in this study

Chemical class	Substrate	b^a	Concentration/ mg L^{-1}	ThOD^b/ mg L^{-1}
Sugars	D(+)-Glucose	6	10	10.45
	Sucrose	12	10	11.22
	D(+)-Lactose, 1-hydrate	12	10	10.66
Alcohols	Methanol	3/2	5	5.85
	Ethanol	3	5	8.18
	Propan-1-ol	9/2	5	9.56
	Butan-1-ol	6	5	10.44
Carboxy acids	Formic acid	1/2	10	4.16
	Acetic acid	2	10	11.15
	Propionic acid	7/2	10	14.94
	n-Butyric acid	5	10	17.24
	Isobutyric acid	5	10	17.08
	n-Valeric acid	13/2	10	18.74
	Isovaleric acid	13/2	10	18.96
Benzene derivatives	Phenol	7	5	12.62
	Aniline	7	5	12.23
	o-Cresol	17/2	5	13.04
	m-Cresol	17/2	5	12.87
	p-Cresol	17/2	5	12.88
	Benzoic acid	15/2	5	12.92

^{a} The values can be obtained from eqn. (2) for each substrate. ^{b} Calculating equation for the ThOD, (mass in solution $\times$ purity $\times$ density $\times$ 32 $\times b$)/molecular weight

Fig. 1 Schematic diagram of the apparatus: 1, deionized water supply; 2, pump; 3, injection port; 4, reflector; 5, photochemical column consisting of TiO_2 beads; 6, UV lamp (λ_{max} = 365 nm); 7, air damper; 8, reference oxygen electrode; 9, working oxygen electrode; 10, 11, digital multi-meters; 12, 13, chart recorders; 14, 15, thermostatic water baths.
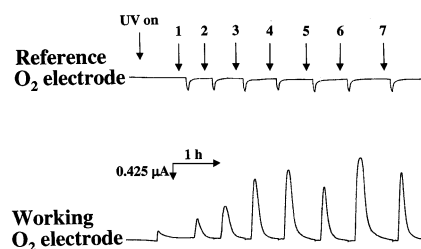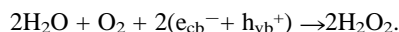

Fig. 2 Responses of the photocatalytic COD sensor. Conditions: substrates, carboxy acids (1, formic acid; 2, acetic acid; 3, propionic acid; 4, n-butyric acid; 5, isobutyric acid; 6, n-valeric acid; 7, isovaleric acid); concentration of substrate, 10 mg L^{-1}; light source, UV lamp (λ_{max} = 365 nm); temperature at oxygen electrodes, 25 °C; amount of TiO_2 beads, 0.9 g; sample volume, 6 ml; flow rate, 2.3 ml min^{-1}.

Overall reactions by combining eqn. (6)and (7):

$$H_2O + \tfrac{1}{2}O_2 + 2(e_{cb}^- + h_{vb}^+) \rightarrow H_2O_2.$$
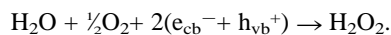
And by combining eqn. (6) and (8) we obtain:

$$2H_2O + O_2 + 2(e_{cb}^- + h_{vb}^+) \rightarrow 2H_2O_2.$$

Here, e_{cb}^- and h_{vb}^+ are the photogenerated electron in the conduction band and the hole in the valence band, respectively.

Once these reference checks had been completed, a sample was injected into the carrier stream. The reference oxygen electrode determined the quantity of oxygen in the sample, whilst the working oxygen electrode monitored the oxygen concentration change resulting from photocatalytic oxidation of organic compounds in the sample. Peak-shaped currents were recorded as a function of time.

Results and discussion

Relationship between ThOD and COD$_{Mn}$[16]

Samples were oxidized by digestion for 30 min with 1 g silver sulfate, 10 ml sulfuric acid (concentrated acid : distilled water = 1:2) and 10 ml aliquot 5 mM potassium permanganate (KMnO$_4$). After digestion, 10 ml aliquot of 12.5 mM sodium oxalate (Na$_2$C$_2$O$_4$) is added and well mixed to react with the remaining MnO$_4^-$ species. With the temperature being kept constant at 60 °C, the concentration of the remaining C$_2$O$_4^{2-}$ is determined by titration with the standard solution of potassium permanganate.

The main weakness of this method is that oxidation of organic substances by the potassium permanganate is not carried out under reflux conditions, and losses of volatile species cannot be avoided. Additionally, it is known that the silver, as a catalyst, is added to enhance oxidation of carboxy acids, but the carboxy acids may not be completely oxidized through the presence of the silver.

The results for the samples measured with the permanganate method were compared with their ThOD values, as indicated in Fig. 3. For sugars and benzene derivatives (with the exception of benzoic acid), the correlation coefficient (r) between the results obtained with the permanganate method (y in mg O$_2$ L^{-1}) and those with the ThOD (x in mg O$_2$ L^{-1}) was found to be 0.82. The linear equation was as follows:

COD (permanganate method) $= 0.68 \times$ ThOD

$$(r = 0.82, n = 8). \quad (9)$$

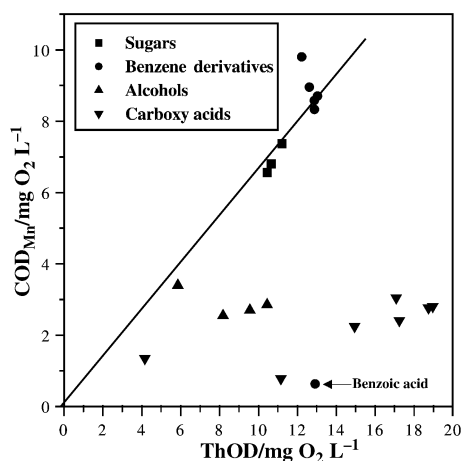The COD values for carboxy acids, however, were found to lie under the straight line [eqn. (9)] that indicated the oxidation ratios in the permanganate method. This implies that these carboxy acids are not oxidized completely with the permanganate method. The COD values for the alcohol group, a typical volatile organic compound, were also found to lie below the straight line.

Relationship between ThOD and COD$_{Cr}$[16]

The COD$_{Cr}$ value is determined by the amount of potassium dichromate reduced by the sample during 2 h of refluxing in a medium of sulfuric acid and silver sulfate catalyst. Chloride interferences are removed by the addition of mercuric sulfate which complexes as muric chloride. After digestion, the residual dichromate is determined by titration with ferrous ammonium sulfate to the ferroin indicator end point. Complete oxidation of all organic compounds, except for straight chain carboxy acids, is achieved. On the other hand, in the first step of the COD$_{Cr}$ procedure, concentrated sulfuric acid is added to the sample to make an acidic medium. This takes several minutes, during which time an increase in temperature—at least locally in the mixture—cannot be avoided and volatile organic components may escape from the open conic flask.

The same set of samples that were used in the permanganate method was also examined here. Fig. 4 shows the correlation between the COD values obtained by the dichromate method and their corresponding ThOD values: a linear relationship was observed in sugars and benzene derivatives (with the exception of benzoic acid), and a better correlation ($r = 0.96$ for 8 samples) compared with the permanganate method was obtained. The linear equation for the dichromate method was as follows:

COD (dichromate method) $= 0.99 \times$ ThOD

$$(r = 0.96, n = 8). \quad (10)$$

When the two correlation equations (9) and (10) are considered, this agrees with the fact that the permanganate method gives oxidation ratios of about 50–70, while the dichromate method achieves 80–100% oxidation ratios.[17] It also shows the problem in attempting to apply the official COD methods to carboxy acids and alcohols.

Relationship between ThOD and the response values of the photocatalytic COD sensor

The same set of samples that were used in the permanganate or dichromate methods was also investigated with the photocatalytic COD sensor. As shown in Fig. 5, all compounds from each different chemical class (sugars, benzene derivatives,
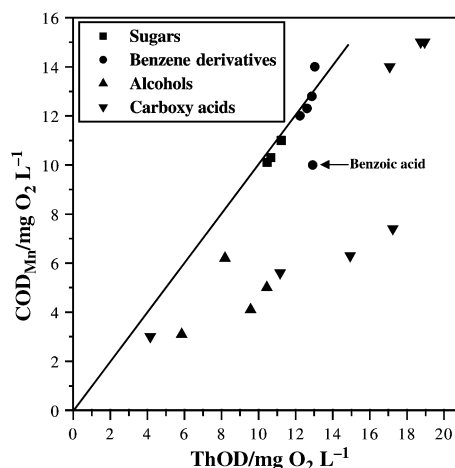

Fig. 3 Relationship between ThOD and COD$_{Mn}$. Substrates were sugars, benzene derivatives, alcohols and carboxy acids.

Fig. 4 Relationship between ThOD and COD$_{Cr}$. Substrates were sugars, benzene derivatives, alcohols and carboxy acids.
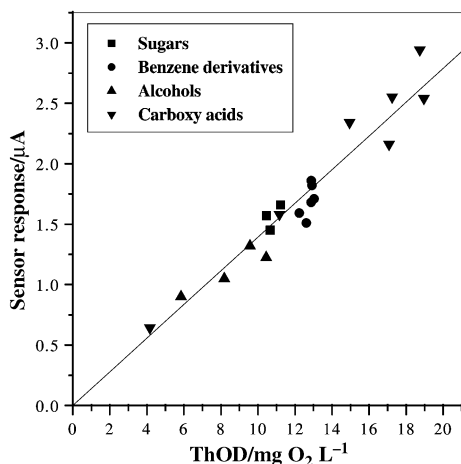
Fig. 5 Relationship between ThOD and the response value of the photocatalytic COD sensor. Experimental conditions are the same as described in Fig. 2 and substrates were sugars, benzene derivatives, alcohols and carboxy acids.

alcohols and carboxy acids) show good agreement with their theoretical values ($r = 0.96$, $n = 20$) using the photocatalytic COD sensor, in marked contrast with the results obtained by official methods.

Conclusions

Statistical analysis has shown that the COD_{Cr} values of chemicals in the sugar and benzene derivative groups (with the exception of benzoic acid) can be estimated simply from $COD_{Cr} \cong ThOD$. The $COD_{Mn, Cr}$ values of chemicals from the carboxy acid and alcohol groups can also be estimated by the ThOD. However, for the carboxy acid and alcohol groups, the COD values are much smaller than those of the sugar and benzene derivative groups (with the exception of benzoic acid). A modification of the official COD methods may be required for individual chemicals from the chemical classes (*e.g.*, carboxy acids and volatile chemicals) that show poor correlation with their ThOD values.

On the other hand, the correlation between ThOD and the response values of the photocatalytic COD sensor were found to be extremely good for all 20 organic chemicals from the 4 different classes, suggesting that the photocatalytic COD sensor is a highly promising candidate for a new COD sensor method.

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