2.1.1 The COD test

In both the COD and BOD tests, the organic material concentration is calculated from the oxidant consumption necessary for the oxidation of the organic material. The main differences are the oxidant that is used and the operational conditions during the tests. In the case of COD, a sample of waste water containing organic material is placed in contact with a very strong inorganic oxidant, a mixture of dichromate and sulphuric acid with silver sulphate as a catalyst. The temperature is increased to the point of ebullition of the mixture, resulting in an increase of the oxidation rate. After two hours (the standard duration of the test) oxidation of the organic compounds is virtually complete. The resulting COD value can be determined by means of titration or with the aid of a spectrophotometer by reading the concentration of formed chromium (Cr^{3+}) concentration. The theoretical COD value of a specific compound can be calculated from stoichiometric considerations. If this theoretical value corresponds to the experimental value, it is concluded that the oxidation of the organic material is complete. The theoretical COD of a compound with a structural formula $C_xH_yO_z$ can be determined from the two redox equations that describe the overall oxidation reaction.

(a) Oxidation reaction:

$$C_xH_yO_z + (2x-z)\cdot H_2O \rightarrow x\cdot CO_2 + (4x+y-2z)\cdot H^+ + (4x+y-2z)\cdot e^- \text{ or}$$

$$1/(4x+y-2z)\cdot C_xH_yO_z + (2x-z)/(4x+y-2z)\cdot H_2O \rightarrow x/(4x+y-2z)\cdot CO_2 + H^+ + e^- \quad (2.1a)$$

(b) Reduction reaction:

$$e^- + H^+ + \tfrac{1}{4}\, O_2 \rightarrow \tfrac{1}{2}\, H_2O \quad (2.1b)$$

After combining Eqs. (2.1a and 2.1b) and rearranging one finds:

$$C_xH_yO_z + \tfrac{1}{4}\cdot(4x+y-2z)\cdot O_2 \rightarrow x\cdot CO_2 + y/2\cdot H_2O \quad (2.1)$$

From Eq. (2.1) it can be noted that the theoretical COD (or theoretical oxygen demand) of 1 mole of a compound $C_xH_yO_z$ amounts to $\tfrac{1}{4}\cdot(4x+y-2z)$ moles of O_2. Knowing that the molar mass of $C_xH_yO_z$ can be expressed as (12x+y+16z) $g.mol^{-1}$ and the molar mass for oxygen is 32 grams, it is concluded that the COD of (12x+y+16z) grams of the compound $C_xH_yO_z$ is equal to $\tfrac{1}{4}\cdot(4x+y-2z)\cdot 32 = 8\cdot(4x+y-2z)$ gram O_2. Hence the theoretical COD per unit mass of $C_xH_yO_z$ is given by:

$$COD_t = 8\cdot(4x+y-2z)/(12x+y+16z) \text{ g COD.g}^{-1}\ C_xH_yO_z \quad (2.2)$$

When the procedure for the COD test is strictly followed, for almost all compounds the experimental result will not differ more than a few percent from the theoretical value. This leads to the conclusion that (l) during the COD test the organic material is completely oxidized and (2) the precision and reproducibility of the test are good.

Eq. (2.2) can be used to calculate the theoretical COD per unit mass for different structural formulas $C_xH_yO_z$. Table 2.1 shows the COD values for some selected compounds. It can be observed that the COD_t value varies considerably, with a minimum value of 0.18 g $COD.g^{-1}$ $C_xH_yO_z$ in the case of oxalic acid $(COOH)_2$ and a maximum of 4.0 g $COD.g^{-1}$ for methane (CH_4).

These figures indicate very clearly, that the mass of an organic compound is not a *priori* indicative for its COD. Hence, the expression "mass of organic material" in the case of COD does not really reflect the mass of the organic compounds, but rather the mass of oxygen required for their complete oxidation.

It can also be concluded that if oxygen is consumed for the oxidation of organic material in a biological treatment plant, by definition the mass of consumed oxygen will always be equal to the mass of oxidised COD. The oxidation of organic material results it its transformation into stable, inorganic compounds like carbon dioxide and water. Hence the mass of oxidised organic material (expressed as COD) can be measured directly by the consumption of oxygen required for this oxidation. This is a very important conclusion and the basis for respirometry, the study of biological processes by measuring the rate of oxygen consumption.

Table 2.1 Theoretical values of COD and TOC per unit mass for selected compounds (I = COD content; II = TOC content and III = COD/TOC ratio)

Component	X	Y	Z	I	II	III
				mg COD. mg^{-1} $C_xH_yO_z$	mg $TOC.mg^{-1}$ $C_xH_yO_z$	mg COD. mg^{-1} TOC
Oxalic acid	2	2	4	0.18	0.27	0.67
Formic acid	1	2	2	0.35	0.26	1.33
Citric acid	2	4	3	0.64	0.32	2.00
Glucose	6	12	6	1.07	0.40	2.67
Lactic acid	3	6	3	1.07	0.40	2.67
Acetic acid	2	4	2	1.07	0.40	2.67
Glycerine	3	8	3	1.22	0.39	3.11
Phenol	6	6	1	2.38	0.77	3.11
Ethyl. glycol	2	6	2	1.29	0.39	3.33
Benzene	6	6	0	3.08	0.92	3.33
Acetone	3	6	1	2.21	0.62	3.56
Palmitic acid	16	32	2	3.43	0.75	3.83
Cyclohexane	6	12	0	3.43	0.86	4.00
Ethylene	2	4	0	3.43	0.86	4.00
Ethanol	2	6	1	2.09	0.52	4.00
Methanol	1	4	1	1.50	0.38	4.00
Ethane	2	6	0	3.73	0.80	4.67
Methane	1	4	0	4.00	0.75	5.33

Example 2.1

What is the theoretical COD value of a solution of 1 $g.l^{-1}$ of glucose ($C_6H_{12}O_6$) ?

Solution:

From Equation (2.2) and knowing that x=6; y=12 and z=6, one has: COD_t = 8·(4·6 + 12 - 2·6)/(12·6 + 12 + 16·6) =192/180 = 1.067 mg $COD.mg^{-1}$ $C_6H_{12}O_6$. Hence the solution with 1 $g.l^{-1}$ of glucose has a theoretical COD of 1067 $mg.l^{-1}$.

Example 2.2

In the traditional COD test (open reflux), a mixture of 10 ml of waste water sample, 5 ml of 0.25 N potassium dichromate and 15 ml of sulphuric acid is utilised. What is the highest value of the COD concentration that can be determined?

Solution:

In the initial mixture the available quantity of dichromate = 5·0.25 = 1.25 meq. If the oxidant is entirely used during the COD test, this would mean that 1.25 meq of organic material is utilised, equivalent to 1.25·8 = 10 mg O_2 as the equivalent weight of oxygen is 32/4 = 8 $gram.eq^{-1}$, see Eq. (2.1b). As the 10 mg of organic material (expressed as COD) were present in a 10 ml waste water sample, its concentration was 10 mg per 10 ml or 1000 $mg.l^{-1}$. It is concluded it is impossible to determine a COD concentration higher than 1000 $mg.l^{-1}$, because there would be no residual dichromate left. In practice it will be attempted to dilute the sample so that the expected COD concentration is about equal to 500 $mg.l^{-1}$.