CVEN 5534 Wastewater Treatment

Supplemental COD and Redox Stoichiometry Information

1. COD mass equivalents of compounds important in wastewater treatment (Table 3.1)
2. REDOX half reactions useful for wastewater treatment process stoichiometry (Table 3.2)
   Source: Biological Wastewater Treatment, Grady, Daigger, and Lim, Marcel-Dekker, NY, 1999.

In using REDOX reactions from Table 3.2, use dimensionless factors:

f_s = fraction of electrons (e.g., substrate) that goes to cell synthesis
≈ Y when units of Y are g-cells as COD/g-substrate as COD
f_e = fraction of electrons (e.g., substrate) that goes to energy
≈ (1 – Y) when units of Y are g-cells as COD/g-substrate as COD

and $\mathbf{f_s + f_e = 1}$

For combining half-reactions in Table 3.2 **when there is both substrate oxidation for energy production and cell ($C_5H_7NO_2$) growth**:

1. Note that all reactions are written in direction of oxidation (left to right)
2. Write cell synthesis and electron acceptor reactions, R_c and R_a, respectively in reverse order, i.e. in reduction direction which become $-R_c$ and $-R_a$.
3. Combine R_c and R_a with electron donor reactions (R_d) for the overall R as:

$$\mathbf{R_d + f_s * (-R_c) + f_e * (-R_a) = R}$$

When cell growth is not included or negligible combine electron donor and electron acceptor reactions:

$$\mathbf{R_d + (-R_a) = R}$$

Table 3.1 COD Mass Equivalents of Some Common Constituents

Constituent[a]	Change of oxidation state	COD equivalent[b]
Biomass, $C_5H_7O_2N$	C to +IV	1.42 g COD/g $C_5H_7O_2N$, 1.42 g COD/g VSS, 1.20 g COD/g TSS
Oxygen (as e^- acceptor)	O(0) to O(−II)	−1.00 g COD/gO_2[c]
Nitrate (as e^- acceptor)	N(+V) to N(0)	−0.646 g COD/g NO_3^-, −2.86 g COD/g N
Nitrate (as N source)	N(+V) to N(−III)	−1.03 g COD/g NO_3^-, −4.57 g COD/g N
Sulfate (as e^- acceptor)	S(+VI) to S(−II)	−0.667 g COD/g $SO_4^=$, −2.00 g COD/g S
Carbon dioxide (as e^- acceptor)	C(+IV) to C(−IV)	−1.45 g COD/g CO_2, −5.33 g COD/g C
CO_2, HCO_3^-, $H_2CO_3^=$	No change in an oxidizing environment	0.00
Organic matter in domestic wastewater, $C_{10}H_{19}O_3N$	C to +IV	1.99 g COD/g organic matter
Protein, $C_{16}H_{24}O_5N_4$	C to +IV	1.50 g COD/g protein
Carbohydrate, CH_2O	C to +IV	1.07 g COD/g carbohydrate
Grease, $C_8H_{16}O$	C to +IV	2.88 g COD/g grease
Acetate, CH_3COO^-	C to +IV	1.08 g COD/g acetate
Propionate, $C_2H_5COO^-$	C to +IV	1.53 g COD/g propionate
Benzoate, $C_6H_5COO^-$	C to +IV	1.98 g COD/g benzoate
Ethanol, C_2H_5OH	C to +IV	2.09 g COD/g ethanol
Lactate, $C_2H_4OHCOO^-$	C to +IV	1.08 g COD/g lactate
Pyruvate, CH_3COCOO^-	C to +IV	0.92 g COD/g pyruvate
Methanol, CH_3OH	C to +IV	1.50 g COD/g methanol
$NH_4^+ \rightarrow NO_3^-$	N(−III) to N(+V)	3.55 g COD/g NH_4^+, 4.57 g COD/g N
$NH_4^+ \rightarrow NO_2^-$	N(−III) to N(+III)	2.67 g COD/g NH_4^+, 3.43 g COD/g N
$NO_2^- \rightarrow NO_3^-$	N(+III) to N(+V)	0.36 g COD/g NO_2^-, 1.14 g COD/g N
$S \rightarrow SO_4^=$	S(0) to S(+VI)	1.50 g COD/g S
$H_2S \rightarrow SO_4^=$	S(−II) to S(+VI)	1.88 g COD/g H_2S, 2.00 g COD/g S
$S_2O_3^= \rightarrow SO_4^=$	S(+II) to S(+VI)	0.57 g COD/g $S_2O_3^=$, 1.00 g COD/g S
$SO_3^= \rightarrow SO_4^=$	S(+IV) to S(+VI)	0.20 g COD/g $SO_3^=$, 0.50 g COD/g S
H_2	H(0) to H(+I)	8.00 g COD/g H

[a]Listed in the same order as the reactants in Table 3.2.
[b]A negative sign implies that the constitutent is receiving electrons.
[c]By definition, oxygen demand is negative oxygen.

Table 3.2 Oxidation Half-Reactions[a]

Reaction number	Half-reactions
Reactions for bacterial cell synthesis (R_c)	
Ammonia as nitrogen source:	
1. $\frac{1}{20} C_5H_7O_2N + \frac{9}{20} H_2O$	$= \frac{1}{5} CO_2 + \frac{1}{20} HCO_3^- + \frac{1}{20} NH_4^+ + H^+ + e^-$
Nitrate as nitrogen source:	
2. $\frac{1}{28} C_5H_7O_2N + \frac{11}{28} H_2O$	$= \frac{1}{28} NO_3^- + \frac{5}{28} CO_2 + \frac{29}{28} H^+ + e^-$
Reactions for electron acceptors (R_a)	
Oxygen:	
3. $\frac{1}{2} H_2O$	$= \frac{1}{4} O_2 + H^+ + e^-$
Nitrate:	
4. $\frac{1}{10} N_2 + \frac{3}{5} H_2O$	$= \frac{1}{5} NO_3^- + \frac{6}{5} H^+ + e^-$
Sulfate:	
5. $\frac{1}{16} H_2S + \frac{1}{16} HS^- + \frac{1}{2} H_2O$	$= \frac{1}{8} SO_4^{=} + \frac{19}{16} H^+ + e^-$
Carbon dioxide (methanogenesis):	
6. $\frac{1}{8} CH_4 + \frac{1}{4} H_2O$	$= \frac{1}{8} CO_2 + H^+ + e^-$
Reactions for electron donors (R_d)	
Organic donors (heterotrophic reactions):	
Domestic wastewater:	
7. $\frac{1}{50} C_{10}H_{19}O_3N + \frac{9}{25} H_2O$	$= \frac{9}{50} CO_2 + \frac{1}{50} NH_4^+ + \frac{1}{50} HCO_3^- + H^+ + e^-$
Protein (amino acids, proteins, nitrogenous organics):	
8. $\frac{1}{66} C_{16}H_{24}O_5N_4 + \frac{27}{66} H_2O$	$= \frac{8}{33} CO_2 + \frac{2}{33} NH_4^+ + \frac{31}{33} H^+ + e^-$
Carbohydrate (cellulose, starch, sugars):	
9. $\frac{1}{4} CH_2O + \frac{1}{4} H_2O$	$= \frac{1}{4} CO_2 + H^+ + e^-$
Grease (fats and oils):	
10. $\frac{1}{46} C_8H_{16}O + \frac{15}{46} H_2O$	$= \frac{4}{23} CO_2 + H^+ + e^-$
Acetate:	
11. $\frac{1}{8} CH_3COO^- + \frac{3}{8} H_2O$	$= \frac{1}{8} CO_2 + \frac{1}{8} HCO_3^- + H^+ + e^-$
Propionate:	
12. $\frac{1}{14} CH_3CH_2COO^- + \frac{5}{14} H_2O$	$= \frac{1}{7} CO_2 + \frac{1}{14} HCO_3^- + H^+ + e^-$
Benzoate:	
13. $\frac{1}{30} C_6H_5COO^- + \frac{13}{30} H_2O$	$= \frac{1}{5} CO_2 + \frac{1}{30} HCO_3^- + H^+ + e^-$

Table 3.2 Continued

Reaction number	Half-reactions
Ethanol:	
14. $\frac{1}{12} CH_3CH_2OH + \frac{1}{4} H_2O$	$= \frac{1}{6} CO_2 + H^+ + e^-$
Lactate:	
15. $\frac{1}{12} CH_3CHOHCOO^- + \frac{1}{3} H_2O$	$= \frac{1}{6} CO_2 + \frac{1}{12} HCO_3^- + H^+ + e^-$
Pyruvate:	
16. $\frac{1}{10} CH_3COCOO^- + \frac{2}{5} H_2O$	$= \frac{1}{5} CO_2 + \frac{1}{10} HCO_3^- + H^+ + e^-$
Methanol:	
17. $\frac{1}{6} CH_3OH + \frac{1}{6} H_2O$	$= \frac{1}{6} CO_2 + H^+ + e^-$
Inorganic donors (autotrophic reactions):	
18. Fe^{++}	$= Fe^{+3} + e^-$
19. $\frac{1}{8} NH_4^+ + \frac{3}{8} H_2O$	$= \frac{1}{8} NO_3^- + \frac{5}{4} H^+ + e^-$
20. $\frac{1}{6} NH_4^+ + \frac{1}{3} H_2O$	$= \frac{1}{6} NO_2^- + \frac{4}{3} H^+ + e^-$
21. $\frac{1}{2} NO_2^- + \frac{1}{2} H_2O$	$= \frac{1}{2} NO_3^- + H^+ + e^-$
22. $\frac{1}{6} S + \frac{2}{3} H_2O$	$= \frac{1}{6} SO_4^= + \frac{4}{3} H^+ + e^-$
23. $\frac{1}{16} H_2S + \frac{1}{16} HS^- + \frac{1}{2} H_2O$	$= \frac{1}{8} SO_4^= + \frac{19}{16} H^+ + e^-$
24. $\frac{1}{8} S_2O_3^= + \frac{5}{8} H_2O$	$= \frac{1}{4} SO_4^= + \frac{5}{4} H^+ + e^-$
25. $\frac{1}{2} SO_3^= + \frac{1}{2} H_2O$	$= \frac{1}{2} SO_4^= + H^+ + e^-$
26. $\frac{1}{2} H_2$	$= H^+ + e^-$

[a]Adapted from McCarty.[77]

of wastewater treatment is the one introduced in Section 2.4.1 and used in Example 3.1.1.1, $C_5H_7O_2N$.[61] Other formulas consisting of the same elements have been used, but they all result in about the same COD per unit of biomass.[75] Another formula has been proposed that includes phosphorus, $C_{60}H_{87}O_{23}N_{12}P$.[76] While awareness of the need for phosphorus by biomass is essential, it is not necessary to include phosphorus in the empirical formula because the mass required is generally about one-fifth of the mass of nitrogen required. This allows the phosphorus requirement to be calculated even when the simpler empirical formula is used.

All empirical formulas for biomass seek to represent in a simple way material composed of a highly complex and integrated mixture of organic molecules. Fur-

Example

substrate consumption, energy and cell production combined (half rxns normalized to 1 e^-)

$$R_d = \frac{1}{4} CH_2O + \frac{1}{4} H_2O \rightarrow \frac{1}{4} CO_2 + H^+ + e^-$$

$$-R_a = \frac{1}{4} O_2 + H^+ + e^- \rightarrow \frac{1}{2} H_2O$$

$$-R_c = \frac{1}{5} CO_2 + \frac{1}{20} HCO_3^- + \frac{1}{20} NH_4^+ + H^+ + e^- \rightarrow \frac{1}{20} C_5H_7NO_2 + \frac{9}{20} H_2O$$

let COD yield, $f_s = 0.4 \frac{g\ COD_{cells}}{g\ COD_{CH_2O}}$ and $f_e = 1 - Y = 0.6 \frac{g\ COD_e}{g\ COD_{CH_2O}}$

$$R_d + f_s(-R_c) + f_e(-R_a) = R$$

R_d $\quad 0.25\,CH_2O + 0.25\,H_2O \rightarrow 0.25\,CO_2 + H^+ + e^-$

$0.6(-R_a)$ $\quad 0.15\,O_2 + 0.6H^+ + 0.6e^- \rightarrow 0.3\,H_2O$

$0.4(-R_c)$ $\quad 0.08\,CO_2 + 0.02\,HCO_3^- + 0.02\,NH_4^+ + 0.4H^+ + 0.4e^- \rightarrow 0.02\,C_5H_7NO_2 + 0.18\,H_2O$

R $\quad 0.25\,CH_2O + 0.15\,O_2 + 0.02\,HCO_3^- + 0.02\,NH_4^+ \rightarrow 0.02\,C_5H_7NO_2 + 0.23\,H_2O + 0.17\,CO_2$

normalize so $a_1 = 1$

$$1\,CH_2O + 0.6\,O_2 + 0.08\,HCO_3^- + 0.08\,NH_4^+ \rightarrow 0.08\,C_5H_7NO_2 + 0.92\,H_2O + 0.68\,CO_2$$

Check C: 1.08 = 1.08 ✓ $\quad$ O: 2.44 = 2.44 ✓ $\quad$ charge: 0 = 0 ✓

N: 0.08 = 0.08 ✓ $\quad$ H: 2.40 = 2.40 ✓

Mass stoichiometry

$$\Psi_i = \frac{a_i \, MW_i}{1\,(MW_1)}$$

$$1\,CH_2O + 0.64\,O_2 + 0.163\,HCO_3^- + 0.048\,NH_4^+ \rightarrow 0.301\,C_5H_7NO_2 + 0.552\,H_2O + 0.997\,CO_2$$

check $\sum_{i=1}^{k} \Psi_i = \sum_{i=k+1}^{m} \Psi_i$ $\quad 1.851 = 1.850$ ✓ (close enuff)

COD stoichiometry

$$Y_i = \frac{\Psi_i \, COD_i}{COD_1}$$

$Y_1 = 1, \quad Y_2 = \frac{0.64(-1)}{1.07} = -0.598$

$Y_3 = \frac{0.301(1.42)}{1.07} = 0.400$

$$1\,COD_{CH_2O} + (-0.598)\,COD_{O_2} \rightarrow 0.4\,COD_{cells}$$

check $\quad -1 + 0.598 + 0.400 = 0$ ✓

Uses:

Suppose you wanted to calculate supplemental substrate? O_2? excess NH_4^+?

Compare consumption of various $\frac{e\ donor}{e\ acceptor}$ ratios

etc, etc.