

Solutions Manual

Resource Recovery from Water: Principles and Application

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CHAPTER 1

Exercise 1.1. A wastewater treatment plant services a community of 50,000 people residing in a catchment of 30 km². Assume that 90% of the inhabitants is connected to the combined sewer network and that 10% of the people are living too remotely to be connected to the centralized sewer network and have household based septic tanks. In order to improve the sustainability of urban wastewater management of the community, resource recovery of nitrogen (in the form of ammonium) has been raised as a potential priority by the city council. In this context, recent developments aimed to recover nitrogen from urine (urine has a high N content, see table 1.1) have gained special interest in recent years. Let us assume that indeed ammonium recovery from urine at a household level can be achieved, and based on this assumption, calculate the following:

- Calculate the amount of nitrogen that can be recovered on a daily and annual basis per household (assuming an average of 4 people per household) and an N recovery efficiency of 90%.
- Calculate the amount of nitrogen that can be recovered at the WWTP assuming a recovery potential of 25% of the incoming N load at the WWTP.
- Considering the values found in a) and b) describe the practical limitations of resource recovery at a household level.
- In addition to the practical issues raised in c), it is important to realize that ammonium is considered a bulk product produced at low cost and at very large industrial scale through the Haber-Bosch process. Explain why this could further reduce the economic potential of decentralized N recovery.

Solution:

- Daily recovery of N per household = $0.9 * 4 \text{ people} * 1.2 \text{ L/capita/d} * 8661 \text{ mg/L} = 37.4 \text{ g/d}$; Yearly recovery of N per household = 13.7 Kg/yr*
- Amount of N recoverable at the WWTP = $0.25 * (0.9 * 50000 \text{ people}) * 1.2 \text{ L/capita/d} * 8661 \text{ mg/L} = 116.9 \text{ Kg/d}$ or 42.7 ton/yr*
- it is clear from a) and b) that the recovery potential on a household level is very small. Next step would be to compare the recovery potential with the market demands of the recovered N. What are volumes, product strengths and quality of the recovered N required by the market?*
- the price of Haber Bosch Nitrogen is less than a dollar per kg. hence, the amount of recovered N per household equals to about \$ dollars per year only.*

Exercise 1.2. A community in Indonesia must build a centralised wastewater treatment system. The system is to service the 60,000 people of the district. An anaerobic pond is selected as a low cost treatment system in order to treat the water to achieve a safe discharge level of BOD₅ of 50 mg/L and capture the biogas for powering gas burning stoves in the community, or burning it to provide a local and renewable source of power for the community. The typical per capita wastewater characteristics highlighted in Table 1.1 apply.

- Estimate the following influent parameters for the sewage stream (mg/L): BOD₅, COD, TN, TP.
- Calculate how much methane (m³/d and GJ/d) could be recovered from the anaerobic pond (Assume $0.18 \text{ m}^3_{\text{methane produced}}/\text{kgBOD5}_{\text{removed}}$ and that the energy content of methane is approximately 37MJ/m³) and determine the number of households that would be supported through the use of this gas for the case of:
 - Cooking gas: where an average household of 5-6 uses 70 MJ/d of methane to power their cooking stoves, or
 - Electricity: assume the energy conversion from methane to electricity is 0.3 and a typical family uses 10 kWh of electricity per day (1 kWh = 3.6 MJ). Comment on the advantages/disadvantages of each proposed plan for methane recovery

Solution:

- a. The COD is calculated as follows: $COD(mg/L) \times \text{Contribution to overall flowrate } (\%/100)$ for each stream (grey water, urine and feces)
 $= 620 \times 0.99 + 10236 \times 0.009 + 155000 \times 0.001 = 860.9 \text{ mgCOD/L}$
Similarly, $BOD_5 = 377.3 \text{ mg/L}$, $TN = 108.2 \text{ mg/L}$, $TP = 18 \text{ mg/L}$
- b. BOD_5 to be removed = Influent – Effluent = $377.3 - 50 = 327.3 \text{ mg/L}$
Flow per capita = 108 L/capita/d
60,000 inhabitants
 BOD_5 removed = 2121 kg/d
Methane produced = $2121 \times 0.18 = 382 \text{ m}^3/\text{d}$
Energy produced = $382 \times 37 = 14,100 \text{ MJ/d} = 14.1 \text{ GJ/d}$
 - i. $14,100/70 = 201.8$ households could use the methane to power their cooking stoves
 - ii. Since $1 \text{ kWh} = 3.6 \text{ MJ}$ and with an efficiency of 0.3, $14,100 \text{ MJ/d} \times 0.3/3.6 \text{ MJ} = 1177 \text{ kWh/d}$
A typical family uses 10 kWh/d , thus $1177/10 = 117.7$ households could use the methane to meet their electricity demand.
More households could make use of the energy in the cooking stove solution, increasing its reach, though distribution might be easier in the case of electricity and the end-use would not be as restricted.

Exercise 1.3. The Canadian city of Halifax is building an activated sludge system at its main wastewater treatment plant that services 170,000 people. Two resource recovery strategies are considered for the sludge produced from this treatment facility, the first consists of one-stage anaerobic digestion for methane recovery from biogas and the other is polyhydroxyalkanoate (PHA) recovery through a 3-stage process. The 3-stage PHA process consists of 1) anaerobic sludge fermentation to volatile fatty acids (VFA), 2) aerobic culture selection through a feast/famine process fed with the effluent of 1), and 3) PHA accumulation from the selected culture in 2) using the effluent of 1). Assume standard (i.e. Table 1.1) wastewater flows and characteristics and that 80 gVSS of sludge are produced per m^3 of wastewater treated by the facility. Considering that the value of PHA is $\$3.5/\text{kg}$ and that the value of methane is $\$0.4/\text{m}^3$, where 1 m^3 of biogas (with a methane content of 65%) is produced per kg of VSS, while 0.1 kg of PHA are produced per kg of VSS in the 3-stage process:

- a. Determine the relative value of the sludge stream using either the PHA recovery or biogas recovery strategy
- b. Discuss the key factors impacting the capital and operational expenditures associated with biogas or PHA production. Which process is likely to incur higher production costs? Why? What would you consider to be the key points impacting your decision on the process to be implemented?

Solution:

- a. The flow of wastewater will be $108 \text{ L/capita/d} \times 170,000 \text{ people} = 18360 \text{ m}^3/\text{d}$
Sludge production is 80 g VSS/m^3 , so 1469 kg VSS/d of sludge is produced
Methane: $0.65 \times 1469 = 955 \text{ m}^3/\text{d}$ produced, with a value of $\$0.4/\text{m}^3$, therefore $\$382/\text{d}$ are generated
PHA: $0.1 \times 1469 = 147 \text{ kg PHA/d}$, with a value of $\$3.5/\text{kg}$, therefore $\$514/\text{d}$ are generated
- b. PHA production is more lucrative, but will likely have higher capital costs (more complex process) and higher operational costs (aeration demand) that must be considered in the economic balance. Moreover, in the case of biogas it is directly beneficially reused, while for PHA an end-user/client will need to be found.

Exercise 1.4. A utility is required to establish wastewater treatment strategies for remote communities at the household level (average of 4 inhabitants per household) and is considering source separation of the urine from the influent wastewater for nitrogen recovery as a fertiliser to be applied agriculturally. Considering the N loading per

capita of Table 1.1 and that the N load per hectare required for fertilisation is 14 kg N/ha, how many households would be required to meet the fertiliser demand for 12 ha in 30 days?

Solution:

*N load from urine = 8661 mg/L (TN in urine) * 109 L/capita/d (total flow) * 0.009 (fraction of urine flow) = 8500 mg N/capita/d*

Household of 4 for 30 d = 1.02 kg N/household

*14 kg N load per ha * 12 ha = 168 kg N, thus 168/1.02 = 165 households needed to meet the fertilizer demand.*

Exercise 1.5. An apartment building in Beijing houses approximately 2,500 inhabitants, where source separation of urine is considered to be implemented for both nitrogen and phosphorus recovery that will be transported to a neighbouring region for fertilisation purposes. Consider that the N and P loading per capita of Table 1.1 applies and that the N and P loads per hectare required for fertilisation are 21 kg N/ha and 9 kg P/ha, respectively. How many hectares could be fertilised from this building per year? What would be the limiting nutrient?

Solution:

*N load from urine = 8500 mg N/capita/d (see above solution). Similarly, 732 mg/L (TP in urine) * 109 L/capita/d (total flow) * 0.009 (fraction of urine flow) = P load from urine = 718 mg P/capita/d.*

2500 inhabitants for 365 d = 7750 kg N/yr and 655 kg P/yr

7750 kg N / 21 kg N/ha = 369 ha, 655 kg P / 9 kg P/ha = 73 ha. Thus, P is the limiting nutrient and 73 ha/yr could be fertilized by this building.

Exercise 1.6. A music festival in Lisbon will have approximately 12,000 people in attendance during the event. The water utility of the region plans to institute source separation of urine from the wastewater at the event to provide a fertiliser for a nearby agricultural region where nitrogen is the limiting nutrient. Considering the N loading per capita of Table 1.1 and that the N load per hectare required for fertilisation is 18 kg N/ha, how many hectares could be fertilised per day?

Solution:

N load from urine = 8500 mg N/capita/d (see above solution).

12,000 people = 102 kg N/d

102 kg N / 18 kg N/ha = 5.66 ha/d could be fertilized

Exercise 1.7. The Singapore airport services approximately 227,000 passengers per day, where source separation of urine will be implemented for both nitrogen and phosphorus recovery for fertilisation. Considering the N and P loading per capita of Table 1.1 and that the N and P loads per hectare required for fertilisation are 31 kg N/ha and 2.5 kg P/ha, respectively, how many hectares could be fertilised from the airport per day? What N or P be the limiting nutrient?

Solution:

N load from urine = 8500 mg N/capita/d. P load from urine = 718 mg P/capita/d. (see above solutions)

227,000 passengers = 1929 kg N/d and 163 kg P/d

1929 kg N / 31 kg N/ha = 62 ha, 163 kg P / 2.5 kg P/ha = 65 ha. Thus, N is the limiting nutrient and 62 ha/d could be fertilized by this airport.

Exercise 1.8. Titanium dioxide nanoparticles are increasingly used in a variety of commercial products such as textiles, paints and personal care products, and the fate of a great part of this titanium is wastewater. Indeed, up to 4% of the TiO₂ applied onto textiles can wash off in a

single wash [39], and they are part of numerous daily life products such as sunscreen and toothpaste, resulting in relevant concentrations of TiO_2 nanoparticles being washed into municipal wastewater systems (Figure 3). TiO_2 must be removed in WWTP since it has been demonstrated that, if left untreated, can be harmful to aquatic life. Up to 85% of titanium typically ends up in the biosolids due to the low solubility of TiO_2 . The state of Arizona conducted a feasibility study regarding viability of recovering TiO_2 in WWTP. It was found that the titanium concentrations in raw wastewater ranged from 181 to 1233 $\mu\text{g/L}$ (median of 26 samples was 321 $\mu\text{g/L}$) [40]. Consider for this study the WWTP of Phoenix 91st Avenue, which serves a population of 2.5 million people, treating a flow rate of approx. 870 ML/day. Two processes of TiO_2 recovery are proposed, one from liquid influent, and another from the biosolids, which are produced at a rate of 100KgDW/ML of influent wastewater treated. Estimate the minimum concentration of TiO_2 in the influent or in the biosolids to make recovery economically viable for either scenario, assuming recovery efficiencies of 95% and 90% for the liquid effluent and the biosolids, respectively. Assume process costs of \$30/ML of influent wastewater and \$58/tonDW of sludge produced, and a value of TiO_2 of \$60 per Kg.

Solution:

Recovery from the liquid influent:

$$\text{TiO}_2 \text{ recovered (Kg/d)} = 0.95 * C \text{ (Kg/ML)} * Q_{\text{treated}} \text{ (ML/d)}$$

$$\text{Cost of recovery} = \$30/\text{ML} * Q_{\text{treated}} \text{ (ML/d)}$$

*For economic viability, the cost of recovery has to be lower than TiO_2 recovered (Kg/d) *\$60/Kg, thus:*

$$C_{\text{min}} \text{ (Kg/L)} = 30/(60*0.95) = 526 \mu\text{g/L}$$

Recovery from the biosolids

$$\text{TiO}_2 \text{ recovered (Kg/d)} = 0.9 * 0.85 * C \text{ (Kg/ML)} * Q_{\text{treated}} \text{ (ML/d)}$$

$$\text{Cost of recovery} = ((\$20/\text{tonDW}) * (\text{ton DW}/1000 \text{ Kg DW})) * 100\text{KgDW/ML} * Q_{\text{treated}} \text{ (ML/d)}$$

*For economic viability, the cost of recovery has to be lower than TiO_2 recovered (Kg/d) *\$60/Kg, thus:*

$$C_{\text{min}} \text{ (Kg/L)} = (58/1000) * 100 / (60*0.9*0.85) = 126 \mu\text{g/L}$$

The concentrations of TiO_2 typically found in the wastewater may not be sufficient to make the recovery of TiO_2 economically viable when recovered directly from wastewater. However, recovery from the biosolids seems to be viable for the whole range of concentrations observed in the plant.

Exercise 1.9. Given that a small town with 3,000 inhabitants is interested in investing in the implementation of an anaerobic digester at their centralized WWTP.

- Calculate the practical calorific biogas production potential of the small town using the data provided in table 1.3.
- In a) you have calculated the potential biogas production. How does this compare to natural gas given that the annual per capita natural gas consumption equals to 2,361 Nm^3 (average consumption in the US? Assume that 1 Nm^3 of natural gas has a caloric value of 40 MJ/m^3).

Solution:

a) Table 1.3 shows that the practical biogas production is in the order of 33 MJ/capita/year (practical). As such, the calorific biogas production potential (maximum) = 3000 inhabitants * 33 MJ/capita/year = 99,000 MJ/yr.

b) The natural gas consumption in the US equals to 2361 Nm^3 /capita * 3000 inhabitants * 40 MJ/m^3 = 283320000 MJ/yr.

Hence, the biogas potential of the anaerobic digester would only represent 0.035% of the total natural gas consumption of the small city!

Exercise 1.10. In this chapter, the different waste streams comprising municipal wastewater have been discussed, without the help of the information provided in this chapter, fill in the table below.

	Grey water (%)	Urine (%)	Feces (%)
Flow rate			
COD			
Nitrogen			
Phosphorus			
Potassium			

Solution: The answer is provided in Table 1.1 of this chapter.

Exercise 1.11. Considering (i) the metal concentrations depicted in Figure 3, (ii) typical coagulant dosing rates in the form of either alum or iron based coagulants and (iii) sludge production rates of 8,000,000 and 9,253,000 ton DM sludge/year for the US and EU, respectively, estimate the total mass flows by filling in the table below.

Metal	Concentration in sludge (mg/kg dry weight)	Total estimated amount in the E.U.-27 (ton/year)	Total estimated amount in the U.S.A. (ton/year)
Fe			
Al			
Ti			
Zn			
Cu			
Ag			
Yt			
Nd			
Au			
Pd			

Solution:

Metal	Concentration in sludge (mg/kg dry weight)	Total estimated amount in the E.U.-27 (ton/year)	Total estimated amount in the U.S.A. (ton/year)
Fe	50,000	462,650	400,000
Al	50,000	462,650	400,000
Ti	1,000	9253	8,000
Zn	620	5,737	4,960
Cu	400	3,701	3,200
Ag	15	139	120
Yt	2	19	16
Nd	1.9	18	15
Au	0.3	2.8	2.4
Pd	0.3	2.8	2.4

CHAPTER 2

Question 2.1. A dairy producing industry fabricating 2,000 L of milk per week (no cheese) is looking for ways to improve its wastewater management. How much wastewater is produced on average by the company over a year? Assuming that half of this wastewater flow comes from fluid milk processing, how much BOD, COD, and TSS is generated at this site over a year?

Solution:

Step 1: Annual generation

Using Table 2, we can calculate the amount of wastewater produced annually:

$$\frac{5 \text{ m}^3 \text{ wastewater (average)}}{1000 \text{ L milk}} \times \frac{2000 \text{ L milk}}{\text{week}} \times \frac{52 \text{ weeks}}{\text{year}} = 520 \frac{\text{m}^3 \text{ wastewater}}{\text{year}}$$

Step 2: BOD, COD, and TSS generation

Using Table 3, we can take the average for the various concentrations and determine annual generation:

$$\begin{aligned} \frac{520 \text{ m}^3 \text{ wastewater}}{\text{year}} \times 0.5 \times \frac{900 \text{ mg BOD}}{\text{L}} \times \frac{1000 \text{ L}}{\text{m}^3} \times \frac{\text{kg}}{10^6 \text{ mg}} &= 234 \frac{\text{kg BOD}}{\text{year}} \\ \frac{520 \text{ m}^3 \text{ wastewater}}{\text{year}} \times 0.5 \times \frac{1675 \text{ mg COD}}{\text{L}} \times \frac{1000 \text{ L}}{\text{m}^3} \times \frac{\text{kg}}{10^6 \text{ mg}} &= 436 \frac{\text{kg COD}}{\text{year}} \\ \frac{520 \text{ m}^3 \text{ wastewater}}{\text{year}} \times 0.5 \times \frac{270 \text{ mg TSS}}{\text{L}} \times \frac{1000 \text{ L}}{\text{m}^3} \times \frac{\text{kg}}{10^6 \text{ mg}} &= 113 \frac{\text{kg TSS}}{\text{year}} \end{aligned}$$

Question 2.2. Compare and discuss the mass loads of BOD, COD, TN, TP, TS, and pH across the following industries:

1. Dairy industry
2. Wood-related industries
3. Textile and leather
4. Oil and gas production and refining

Solution:

We can build the following table with the information found throughout this chapter. Note that numbers in between parentheses are higher ranges found in one or two particular wastewater streams (cheese and whey for dairy, wool scouring for textile), and not an industry standard.

Regarding organic matter, all wastewaters, with the exception of most oil and gas flows, tend to be rich in BOD. COD is also elevated in all evaluated flows, including oil and gas wastes, given the presence of a variety of organic compounds (hydrocarbons). Total suspended solids are also elevated throughout all industries, though highly variable.

For nutrients, nitrogen contents in dairy and wood industries can be elevated and of interest for recovery, either through direct nutrient recovery or through recovery of organic biosolids. For phosphorus, dairy and textile can be good targets for nutrient recovery, while wood and oil and gas have low, and currently uninteresting, recovery potentials. Of the three nutrients (N,P,S), sulfur can be high in three of these industries, with dairy being the exception.

In all cases, pH is extremely variable, ranging from acidic to alkaline.

Industry	BOD (mg/L)	COD (mg/L)	TSS (mg/L)	TN (mg/L)	TP (mg/L)	TS (mg/L)	pH
<i>Dairy</i>	<i>200-6000 (60000)</i>	<i>1000-10000 (50000)</i>	<i>50-6000 (22 000)</i>	<i>10-2000</i>	<i>0-600</i>	<i>-</i>	<i>3-12</i>
<i>Wood</i>	<i>100-27000</i>	<i>600-40000</i>	<i>40-23000</i>	<i>0-600</i>	<i>0-40</i>	<i>10-1300</i>	<i>4-11.5</i>
<i>Textile</i>	<i>200-5000 (60000)</i>	<i>300-20000 (90000)</i>	<i>200-30000</i>	<i>70-80</i>	<i>0-300</i>	<i>0-2250</i>	<i>4-13.5</i>
<i>Oil and gas</i>	<i>80-2000</i>	<i>150-9000</i>	<i>50-47000</i>	<i>0-40</i>	<i>-</i>	<i>10-3500</i>	<i>-</i>

Questions 2.3. What resources could be recovered from pulp and paper industrial sludge? What conventional technologies could be applied that would allow to recover these resources, all while treating the sludge? What compounds could hinder recovery?

Solution:

Energy and nutrients could be recovered from the sludge, for example through anaerobic digestion. The latter produces both biogas and nutrient-rich digestate. Toxic compounds such as chlorinated organics and heavy metals could be present and could hinder valorisation of the resulting end-products.

Question 2.4 Which of the following steps involved in the manufacturing of bleached pulp are responsible for the highest and lowest generation of BOD and TSS: assuming that wood preparation generates 300 L/s of wastewater, pulping produces 150 L/s of wastewater, and bleaching produces 550 L/s (assuming average values for BOD and TSS concentrations).

Solution:

Table 5 provides the data necessary to answer the question. The following values are used for the calculations, in which they are multiplied by the respective flowrates to obtain the amount of each compound per unit of time:

	<i>Flowrate (L/s)</i>	<i>BOD (mg/L)</i>	<i>TSS (mg/L)</i>
<i>Preparation</i>	<i>300</i>	<i>250</i>	<i>600</i>
<i>Pulping</i>	<i>150</i>	<i>245</i>	<i>256</i>
<i>Bleaching</i>	<i>550</i>	<i>140</i>	<i>216</i>

	<i>BOD (g/s)</i>	<i>TSS (g/s)</i>
<i>Preparation</i>	<i>75</i>	<i>180</i>
<i>Pulping</i>	<i>36.75</i>	<i>38.4</i>
<i>Bleaching</i>	<i>77</i>	<i>118.8</i>

Therefore, in this case, bleaching is responsible for the highest BOD generation, while preparation generates the most TSS; pulping producing the least of both.

Question 2.5 A citrus processing plant processes 10 tons of citrus per day, how much wastewater would this process generate annually? What would the yearly BOD production be? How much nitrogen could be expected (low and high, yearly, estimates)? Is this process of interest for energy and/or nutrient recovery?

Solution:

Using the information found in Table 2:

Wastewater generation:

$$\frac{10 \text{ t produced}}{\text{day}} \times \frac{365 \text{ days}}{\text{year}} \times \frac{9 \text{ m}^3 \text{ wastewater}}{\text{t processed}} = 32\,850 \text{ m}^3 \text{ wastewater/year}$$

BOD generation:

$$\frac{32\,850 \text{ m}^3 \text{ wastewater}}{\text{year}} \times \frac{0.320 \text{ kg}}{\text{m}^3 \text{ wastewater}} = 10\,512 \frac{\text{kg BOD}}{\text{year}}$$

TN generation:

$$\text{High estimate: } BOD/TN = 27; 10\,512 \frac{\text{kg BOD}}{\text{year}} \times \frac{\text{kg TN}}{27 \text{ kg BOD}} = 389 \frac{\text{kg TN}}{\text{year}}$$

$$\text{Low estimate: } BOD/TN = 37; 10\,512 \frac{\text{kg BOD}}{\text{year}} \times \frac{\text{kg TN}}{37 \text{ kg BOD}} = 284 \frac{\text{kg TN}}{\text{year}}$$

Though the process generates over 10,000 kg of BOD per year, the concentration of the wastewater is relatively low, making it less likely to be suitable for conventional energy recovery processes such as anaerobic digestion. Concentration of the degradable compounds would likely be necessary. For nitrogen, the concentration is around:

$$300 \frac{\text{kg TN}}{\text{year}} \times \frac{\text{year}}{32\,850 \text{ m}^3} \times \frac{10^6 \text{ mg}}{\text{kg}} \times \frac{1 \text{ m}^3}{1000 \text{ L}} = 9 \text{ mg TN/L}$$

9 mg TN/L may be recoverable, though rather dilute, making its recovery more complicated. Furthermore, wastewaters from citrus processing tend to be acidic, with a low pH (<3). This can make recovery using traditional processes such as stripping difficult or costly, given ammonia volatilization is favored by alkaline conditions.

Question 2.6: Maximum sulfate levels for discharge of wastewaters vary, ranging up to 1000 mg/L, while the standard for drinking water recommended by the World Health Organization is 250 mg/L. Treatment and recovery processes for sulfate include both chemical and biological pathways, such as precipitation and reduction by sulfate-reducing bacteria. Of the industrial wastewaters presented throughout this chapter, which ones would require consideration of sulfates during their treatment?

Solution:

Sulfate concentration	Wastewater	Concentration range (mg/L)
<1000 mg/L	Produced water	nd-3350
	Drilling wastewater	nd-1568
	Textile and leather	0-2250
	Pickling wastewater	200-2000
	Sulfite mill	800-1270
<500 mg/L	Cooling of pig iron	20-650
	Pulping and Kraft mills	5-375
<250 mg/L	Pharmaceutical	80-360

Question 2.7: Wastewater from an industrial process is characterized by a BOD and COD in the orders of 10² and 10³ mg/L, with a pH ranging from low acidic to slightly alkaline. This wastewater is also noted as having a significant load in sodium, chloride and heavy metals,

notably copper and chromium, while nutrient content (TKN and TP) is low. What process does this water stem from?

Solution:

Textile dyeing (wool specifically): The reactive dyeing process is characterized by high sodium and chloride contents, alongside heavy metals used in many dyes. When looking at Table 4, wood dyeing presents a range of BOD of 400-5000 mg/L, 620-7920 mg/L for COD, and pH between 4.6 and 8.

Question 2.8: The major macronutrients recovered from wastewaters for reuse in agriculture are nitrogen, phosphorus, and potassium. What are three other macronutrients that can be recovered from industrial wastewaters and which of the industrial sources and processes presented throughout this chapter could prove interesting for recovery of some of these nutrients?

Solution:

As described in section 2.5, sulfur, magnesium and calcium are also frequently present in industrial wastewaters and are valuable plant macronutrients. Of the characterized flows presented in this chapter, the following wastewaters can be rich in these nutrients:

Sulfur: Cooling of pig iron (20-650 mg sulfate/L) and pickling wastewater (200-2000 mg of sulfate/L), textile and leather wastewaters (0-2250 mg sulfate/L), pulp and paper wastewaters (10-1300 mg sulfate/L), drilling wastewater (<1600 mg sulfate/L), produced water (<3350 mg sulfate/L)

Calcium: Pickling wastewater (50-200 mg/L)

Question 2.9: What compounds, if any, could be of interest to recover in produced water emanating from oil and gas wastewater?

Solution:

Characterization for produced wastewater is provided in Table 8:

Compound	Produced water
TSS (mg/L)	57-353
TDS (mg/L)	2861-226733
BOD (mg/L)	244-2120
COD (mg/L)	1360-3070
Aluminium (mg/L)	-
Ammonia (mg/L)	-
Barium (mg/L)	0.963-787
Benzene (mg/L)	0.0015-1.7
Bromide (mg/L)	270-798
Chloride (mg/L)	698-141200
Mercury (mg/L)	-
Potassium (mg/L)	0-2190
Selenium (mg/L)	-
Sodium (mg/L)	733-63284
Strontium (mg/L)	nd-4370
Sulfate (mg/L)	nd-3350

Following the list of resources of interest presented in section 2.5, we can identify:

Nutrients: Potassium, Sulfate: both valuable macronutrients for agriculture and present in potentially very high concentrations in these waters.

Water: As mentioned in section 2.3, the ratio of produced water to oil can range up to 100:1, meaning that a substantial amount of wastewater is generated. Treatment and recovery of this water is extremely important from an environmental perspective, while also offering a rich source of process water.

Energy: COD and BOD can be recovered from produced wastewater through processes such as anaerobic digestion, though pre-treatment is necessary; sodium at such high concentrations being a strong inhibitor.

Salts: The high concentrations of salts (Na, Cl) allows for potential salt recovery, for example, through reversed osmosis and subsequent selective recovery from the reject (brine).

Question 2.10: What type(s) (mechanical, physical, chemical, biological, thermal) and process(es) do the following descriptions relate to:

1. Conversion of COD into energy by microorganisms in conditions without oxygen.
2. Recovery of water and removal of contaminants by vaporization at ambient temperatures.
3. Conversion of COD into energy at high temperatures and in the presence of oxygen.
4. Recovery of particulate matter, such as organic solids, based on size using membranes.
5. Immobilization of contaminants onto a surface based on their ionic charge.
6. Separation of compounds based on differences in freezing/boiling points.
7. Recovery of phosphate and ammonium by addition of magnesium to form struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$).
8. Recovery of energy, biosolids and biooil at high temperatures without oxygen.
9. Agglomeration of particles into flocs and separation based on size or density.
10. Recovery of stripped ammonia (gas) using sulfuric acid (H_2SO_4) to form ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$.

Solution:

1. *Biological process; anaerobic digestion*
2. *Physical process; evaporation*
3. *Thermal process; either gasification or incineration.*
4. *Mechanical process; filtration*
5. *Physical process; adsorption OR Chemical process; ion-exchange. The difference between the two depends on whether chemical (ionic) bonds are formed.*
6. *Physical process; evaporation, distillation and freeze concentration.*
7. *Chemical process; precipitation.*
8. *Thermal process; pyrolysis.*
9. *Physical process; flocculation AND mechanical process; filtration or sedimentation.*
10. *Chemical process; scrubbing.*

CHAPTER 3

Exercise 3.1. In the Netherlands, some 0.17 ton (wet) residual per mega liter (ML) drinking water produced is generated. Calculate the amount of residuals produced per year in the Netherlands assuming a water usage per capita per day of 130 liters.

Solution:

In 2017, the population of the Netherlands was approximately 17 million people. Therefore, the total amount of residuals produced during the production of drinking water equals to 17,000,000 [person equivalents] × 130 [liter/person equivalent] × 365 [days] / 1,000,000 = 806,650 ML per year. This equals to 0.17 × 806,650 = 137,131 tons of residuals on an annual basis.

Exercise 3.2. Use the same residual production rate as in Exercise 1, but now calculate for the total amount of residuals produced on a yearly basis for the USA. Note that the average water consumption in the USA is over 400 liters per capita per day.

Solution:

In 2017, the population of the USA was approximately 326 million people. Therefore, the total amount of residuals produced during the production of drinking water equals to 326,000,000 [person equivalents] × 400 [liter/person equivalent] × 365 [days] / 1,000,000 = 47,596,000 ML per year. This equals to about 0.17 × 47,596,000 = 8,091,320 tons (~8 million tons) of residuals on an annual basis.

Exercise 3.3. Assuming an average coagulant dosing of either aluminum sulfate or iron chloride, what would the yearly production of coagulation sludge (in dry matter) be for the Netherlands, Australia, USA, India and China?

Solution:

As discussed in this chapter on page 3, typical coagulant dosing rates range from 10 to 150 mg/L for aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$), 10 to 250 mg/L for ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$) and 5 to 150 mg/L for ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$). These coagulant dosing rates already consider the product quality used on site. For example, $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ generally is delivered in solutions of around 49%. In order to calculate the amount of sludge produced you need to make some assumptions in terms of purity of the produced sludge. Despite the fact that aluminum and iron chemistry is quite complex, assuming that the majority of the iron and aluminum added to the water ultimately ends up in the sludge in the form of $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$, respectively, is justifiable and will provide a fairly accurate estimation. Furthermore, the quality of the produced sludge differs with a product quality in terms of Fe ranging from very low to very high (almost all sludge is present as coagulant). The latter is highly related to the quality of the source water. For this exercise, assume a $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ content of 80%, which is a representable value found in practice (personal communication, Aquaminerals).

The calculations that need to be done in order to answer this question are as follows: (1) Look for the population size of the Netherlands, Australia, USA, India and China, (2) Look for the average drinking water consumption per person per day, (3) calculate the average coagulant dosing (expressed in mg Fe/L or mg Al/L), (4) convert the value found in step 3 to amount of sludge produced [molar weight $\text{Fe}(\text{OH})_3$ / Fe × value found in step 3], (5) divide the value found in 4 by the $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ content of the produced sludge (i.e. assumed at 80%).

Example calculation for the Netherlands:

- 1. Inhabitants: 17,000,000 persons*

2. *Water consumption: 130 L per person per day*
3. *average concentration of Al or Fe dosed:*

$$\frac{80 \text{ mg Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O/L}}{54 \text{ mg Al}^{3+}/\text{mM Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}} \times \frac{\text{mM Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}}{594 \text{ mg Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}} \times 54 \text{ mg Al}^{3+}/\text{L} = 7 \text{ mg Al}^{3+}/\text{L}$$

$$\frac{75 \text{ mg FeCl}_3 \cdot 6\text{H}_2\text{O/L}}{56 \text{ mg Fe}^{3+}/\text{mM FeCl}_3 \cdot 6\text{H}_2\text{O}} \times \frac{\text{mM FeCl}_3 \cdot 6\text{H}_2\text{O}}{270 \text{ mg FeCl}_3 \cdot 6\text{H}_2\text{O}} \times 56 \text{ mg Fe}^{3+}/\text{L} = 16 \text{ mg Fe}^{3+}/\text{L}$$

4. *Fe(OH)₃ and Al(OH)₃ content of the produced sludge:*

$$7 \text{ mg Al}^{3+}/\text{L} \times 105 \text{ mg Al(OH)}_3/\text{mM Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O} \times \frac{\text{mM Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}}{54 \text{ mg Al}^{3+}} = 14 \text{ mg Al(OH)}_3/\text{L}$$

$$16 \text{ mg Fe}^{3+}/\text{L} \times 107 \text{ mg Fe(OH)}_3/\text{mM FeCl}_3 \cdot 6\text{H}_2\text{O} \times \frac{\text{mM FeCl}_3 \cdot 6\text{H}_2\text{O}}{56 \text{ mg Fe}^{3+}} = 30 \text{ mg Fe(OH)}_3/\text{L}$$

5. *Actual Fe(OH)₃ and Al(OH)₃ content of the produced sludge:*

$$14 \text{ mg Al(OH)}_3/\text{L} \times 0.8 = 11 \text{ mg Al(OH)}_3/\text{L}$$

$$30 \text{ mg Fe(OH)}_3/\text{L} \times 0.8 = 24 \text{ mg Fe(OH)}_3/\text{L}$$

$$11 \text{ mg Al(OH)}_3/\text{L} \times 17,000,000 \text{ person} \times 130 \text{ liter/person per day} / 10^9 = 25 \text{ tons of Al(OH)}_3 \text{ produced per day.}$$

$$24 \text{ mg Fe(OH)}_3/\text{L} \times 17,000,000 \text{ person} \times 130 \text{ liter/person per day} / 10^9 = 53 \text{ tons of Fe(OH)}_3 \text{ produced per day.}$$

Note that in this exercise we calculate the amount produced on a dry matter basis. In practice, often limited dewaterability is achieved with moisture contents as high as 80-85%, even after dewatering. The above calculations should leave you with the appreciation of the order of scale of potential resources that can be recovered during the production of drinking water.

Exercise 3.4. Assuming an average coagulant dosing of either aluminum sulfate or iron chloride (i.e. $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), what would the yearly production of coagulation sludge similarly to Q 3.3 (in dry matter) be for two typical water treatment plant (WTP), e.g. 30,000 m³/day (small to medium city) and 300,000 m³/day (typical large plant).

Solution:

1. *Small to medium WTP*

*The plant produces 30 000 m³/day which equals to 30 ML/day × 365 days = 10,950 ML/year.
11 mg Al(OH)₃/L × 10,950,000,000 liter/year / 10⁹ = 120 tons of Al(OH)₃ produced per year.*

$$24 \text{ mg Fe(OH)}_3/\text{L} \times 10,950,000,000 \text{ [liter/year]} / 10^9 = 263 \text{ tons of Fe(OH)}_3 \text{ produced per year.}$$

2. *Large WTP*

The plant produces 300 000 m³/day which equals to 300 ML/day × 365 days = 109,500 ML/year.

$$11 \text{ mg Al(OH)}_3/\text{L} \times 10,950,000,000 \text{ [liter/year]} / 10^9 = 1205 \text{ tons of Al(OH)}_3 \text{ produced per year.}$$

24 mg Fe(OH)₃/L × 109,500,000,000 [liter/year] / 10⁹ = 2628 tons of Fe(OH)₃ produced per year.

Access to logistics and current market needs with subsequent product uptake greatly depends on the amount of local production capacity of the sludge. Do you think the amount of coagulant sludge produced warrants successful recovery and commercialization for both WTP sizes?

Exercise 3.5. What are the key resources that can be recovered at drinking water treatment plants that are either naturally present in the various sources (i.e. ground water, surface and sea water) used for the production of drinking water as well as the resources added to the drinking water production process? More specifically, what are the major resources that can be recovered from the following processes?

- a. Aeration of ground water;
- b. Coagulation-flocculation-sedimentation;
- c. Low-pressure membrane filtration;
- d. High-pressure membrane filtration;
- e. Ion-exchange.

Solution:

In Table 1, the commonly applied treatment processes during the production of drinking water using different water sources and the potential resources that can be recovered are summarized.

Exercise 3.6. What are the most critical impurities in relation to the major resources that can be recovered identified in Exercise 3.4.?

Solution:

In both Table 1 and 2, some of the impurities are listed. Note that this list is not complete. Depending on the quality of the source water there can be a plethora of impurities present in the recovered product. This is well known for heavy metals, but organic contaminants such as pesticides and persistent organic chemicals (albeit present in very low concentrations, i.e. often ng/L range) are under increasing scrutiny. Depending on the type of resource recovered and its end-use, this needs to be taken into consideration.

Exercise 3.7. Provide a qualitative overview of the major resources identified in Exercise 3.4 that can be recovered from:

- a. Aeration of ground water;
- a. Coagulation-flocculation-sedimentation;
- b. Low-pressure membrane filtration;
- c. High-pressure membrane filtration;
- d. Ion-exchange.

Solution:

Please refer to Table 3.1.

Exercise 3.8. As discussed in this chapter, there is a clear distinction between the resources naturally present in the water sources and the resources added during the treatment processes. Design a scheme that provides an overview of resources added in the treatment processes and naturally present in different water sources used.

Solution:

Please refer to the Sankey diagram (Figure 3.3).

Exercise 3.9. A clay brick manufacturer produces 25 million bricks per year, each of them weighing about 2 kg. The manufacturer uses 10% m/m coagulation sludge from drinking water

production in the brick production process. Let us assume that an average drinking water production site produces 7.500 tonnes of sludge with a dry weight of 33,3% annually. How many drinking water production locations need to work together to meet the demand of this manufacturer?

Solution:

Demand is $25 \text{ M} \times 2 \text{ kg} \times 10\% = 5 \text{ M kg} = 5.000 \text{ tonnes}$. Supply per site is $7.500 \times 33,3\% = 2.500 \text{ tonnes}$. So two sites have to work together. Note: that is at least 2 sites, because of imbalances of production (over the year, production stops) it is strongly advised to over some oversupply to avoid the clay brick manufacturer to run out of supply. You can see that logistics and supply chain robustness often is an important aspect in resource recovery.

CHAPTER 4

Multiple choice test

Instructions: Please read each question carefully and then select the letter of the correct answer! Only one answer is correct!

1. Water reuse could be the most competitive option to mitigate water stress in the following conditions:
 - a. Existence of water reuse regulations
 - b. Needs for water transfers for neighboring river basins
 - c. Avoiding water conservation measures
 - d. Expansion of agricultural lands and food production

Solution: b

2. What are the most important factors/components for the success of water reuse projects?
 - a. Water conservation policies, water reuse regulations and standards
 - b. Availability of wastewater treatment technologies
 - c. Financial and political incentives
 - d. Public acceptance and education

Solution: d

3. Which water reuse application requires the least treatment for reuse?
 - a. Toilet flushing
 - b. Aquifer recharge
 - c. Agricultural irrigation
 - d. Industrial reuse

Solution: c

4. Which of the following contaminants are not critical for water reuse safety in terms of health, environmental, agronomic and technical risks?
 - a. Suspended solids
 - b. Nitrates
 - c. Salinity
 - d. Redox potential

Solution: d

5. Which of the following contaminants cannot be removed by conventional tertiary treatment?
 - a. Turbidity
 - b. Dissolved solids
 - c. Viruses
 - d. Bacteria

Solution: b

6. Why do membrane technologies have a key role in high-quality water recycling around the world?
 - a. Affordable costs and easier operation
 - b. Possibility for easy to verify virus log removal
 - c. Physical barrier to microorganisms (viruses, bacteria and protozoa) and dissolved matter
 - d. High public acceptance and trust in reliability

Solution: c

Exercise 4.1: Estimate the UV dose needed to disinfect filtered secondary effluent according to the regulatory requirements of 4 log removal of MS2 phages (an indicator of the most resistant viruses and microorganisms) on the basis of the bench (collimated beam tests) and pilot scale shown on **Figure 4.9**.

What are the main factors influencing the difference between bench (collimated beam tests) and pilot scale results? What UV technology will you recommend for this application?

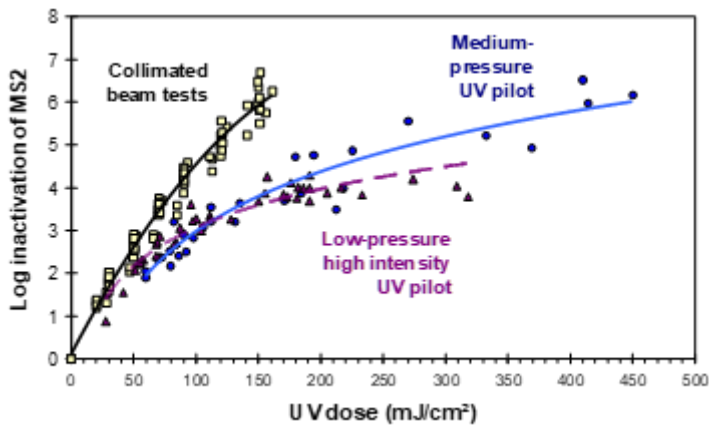


Figure 4.9. Bench and pilot-scale results of inactivation of MS2 phages

Solution:

On the basis of this pilot plant study, the required UV dose to achieve 4 log virus removal seems to be quite high, 200 mJ/cm² compared to 80 mJ/cm² defined by means of bench-scale collimated beam tests. The two main factors influencing UV dose at full scale are hydraulic loads, variations of which could lead to short circuiting, and suspended solids content. Both UV technologies have a similar UV dose requirement, and the final choice will be made on the basis of the analysis of Capex, O&M costs, potential constraints for operation and feedback from existing UV facilities.

Exercise 4.2. Define the transferred ozone dose needed to disinfect secondary effluents to comply with the Spanish standards for non-restricted irrigation with recycled water of <200 *E. coli*/100 mL, in the case when the inlet coliform concentration is 6 logs (10⁶ *E. coli*/100 mL). The results of the pilot plant study are shown in **Table 4.3**. What should the full-scale ozone dose be, assuming an ozone transfer efficiency of 85%?

Table 4.3. Pilot plant results of ozonation of filtered secondary effluents.

Ozone transferred dose, mg/L	Concentration of <i>E.coli</i> /100 mL		Log removal -log ₁₀ (N/N ₀)
	Secondary effluents	Inlet of the ozone bubble column	
1	32,000	500	1.81
2	360,000	900	2.60
3	530,000	300	3.25
4	1,500,000	410	3.56
5	280,000	50	3.75
10	250,000	2	5.10

Solution:

On the basis of this pilot plant study, the required UV dose can be defined by plotting the log-log plot of pilot plant results. The required transferred ozone dose to achieve 4 log coliform removal is 4 mg/L, with an applied dose of 5 mg/L to take into account the ozone transfer efficiency.

Exercise 4.3: The withdrawal permit for irrigation of the agricultural area in the Green Valley will expire in 3 years. Local authorities informed the irrigation consortium that the permit for irrigation will be not renewed due to the severe overexploitation of the local aquifer. The irrigation areas and the main categories of cultivated crops are shown in **Figure 4.10**.

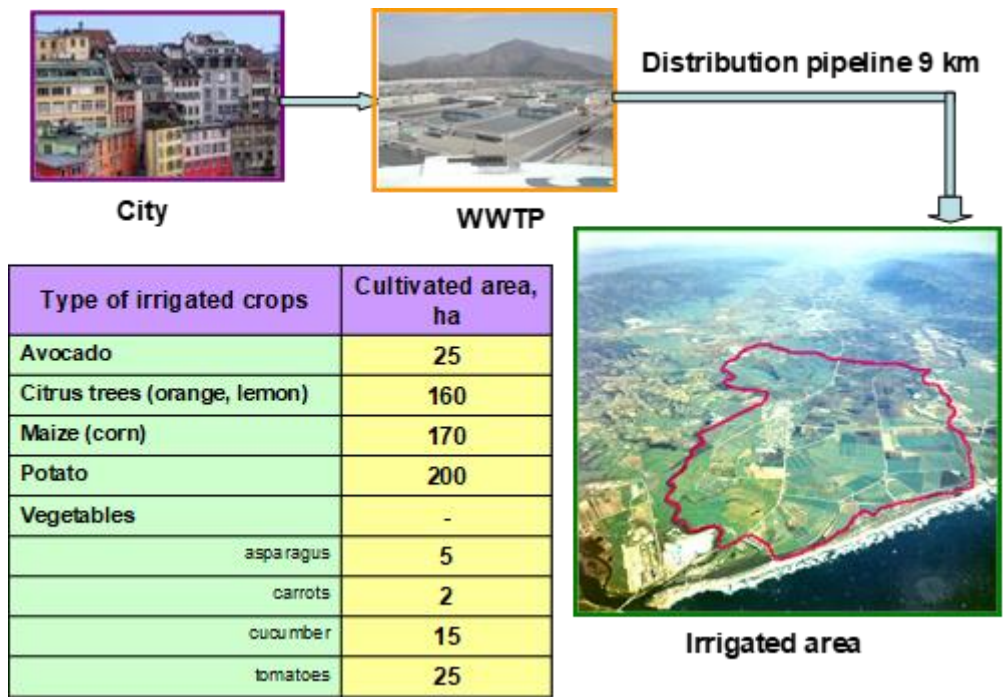


Figure 4.10. Scheme of the water recycling project and the cultivated areas (total irrigated area of 602 ha)

Two kinds of irrigation systems are implemented (recent rehabilitation): (1) sprinkler irrigation for the maize and potatoes, and (2) drip irrigation for the other crops (fruit trees and vegetables). Irrigated fields are located at a distance of 9 km from an existent wastewater treatment plant with conventional activated sludge treatment. The plant's average daily capacity is 100,000 m³/d and the discharge consent (95%ile) is 30 mg/L suspended solids and 25 mg/L BOD₅. The water quality requirements for the use of recycled water for agricultural irrigation are as follows:

- Crops eaten raw: <0.1 helminth/L, <100 *E. coli*/100 mL, turbidity <10 NTU, suspended solids <20 mg SS/L
- No contact, cooking, pasture: <0.1 helminth/L, 1000 *E. coli*/100 mL, <35 mg SS/L
- Drip irrigation, fodder, nurseries: <0.1 helminth/L, 10⁴ *E. coli*/100 mL, <35 mg SS/L

The main task of the exercise is to evaluate the costs and benefits of the water reuse option by means of a multi-criteria analysis and select the most cost competitive and easy to operate tertiary treatment for the production of recycled water for irrigation. The sub-tasks are as follows:

- a. Calculate the **hydraulic loading rate** for irrigation and the associated daily water demand
 1. Calculate the net irrigation requirements (depending on the type of crops and leaching requirements)

2. Calculate the irrigation hydraulic loading rate, taking into account water efficiency of irrigation methods
 3. Calculate the daily water volume required for irrigation on the basis of the area of the irrigated fields
- b. Define the **level of disinfection** of recycled water for irrigation of cultivated crops and propose the appropriate tertiary treatment
1. Analyse water reuse regulations
 2. Identify the required level of disinfection for each type of cultivated crop
 3. Define the recycled water quality to be provided for irrigation, and explain the main criteria for the choice and why only one treatment should be applied
 4. Select an appropriate tertiary treatment scheme (one-two alternative options)
- c. Evaluate **economic and social dimensions of water reuse** (multi-criteria analysis)
1. Identify the potential benefits of the use of recycled water for irrigation, including avoided direct and indirect costs and environmental impacts
 2. Discuss the economic viability of the project
 3. Discuss social dimensions of water reuse, including public acceptance, public education, market strategies, etc.; When should public communication start?

The characteristics of the irrigated fields are given in **Table 4.4**. The growth period is assumed to be the same for all crops (6 months), and the agronomic parameters of wastewater are in an acceptable range. Irrigation efficiency is 65% for sprinkler irrigation and 85% for drip irrigation.

Table 4.4. List of crops grown by the farmers and their water requirements.

Type of crop	Water requirements, mm/growing period (ET _c -P)	Sensitivity to water supply	Leaching fraction, %
Avocado	1000	Medium high	40
Citrus trees (orange, lemon)	1200	Low to medium-high	
Maize (corn)	800	High	
Potato	700	Medium high	
Vegetables			
asparagus	*1000	*High	0
carrots			80
cucumber			20
tomatoes			20

*To facilitate the exercise, the water requirements are assumed to be the same during the irrigation period

The hydraulic loading rate for irrigation L_w is the water that is consumed through evapotranspiration (ET_c), leaching and water losses in distribution systems. Evapotranspiration (ET_c) depends on the type of crops and is calculated from the reference evapotranspiration (mm/unit of time), which is influenced by climate conditions and the crop coefficient K_c . K_c varies from 0.04 to 1.27 as a function of crops.

Hydraulic loading rate is calculated using the following equation:

$$L_w = NR/(E_i/100) = (ET_c - P)(1 + LF/100) (100/E_i) \text{ (eq. 4.1)}$$

Where NR is net irrigation requirement (mm/unit of time) $NR = (ET_c - P) (1 + LF/100)$

ET_c – crop evapotranspiration, mm/unit time

P – precipitation, mm/unit time

E_i – irrigation efficiency, %

LF – leaching fraction defined previously, %

To simplify the calculation, it is recommended to use the water requirements (ET_c-P) from **Table 4.4**, which take into account crop requirements, precipitation and evapotranspiration. The repartition of water demand is assumed to be uniform during the growth period. In fact, water demand increases with plant growth to reach its maximum at mid-season. On the basis of the calculated hydraulic loading rates in mm/day, the quantity of irrigation water must be calculated in m^3/d in order to design the hydraulic capacity of tertiary treatment.

The most common treatment schemes enabling the achievement of various levels of disinfection of secondary effluents are illustrated by **Figure 4.11**.

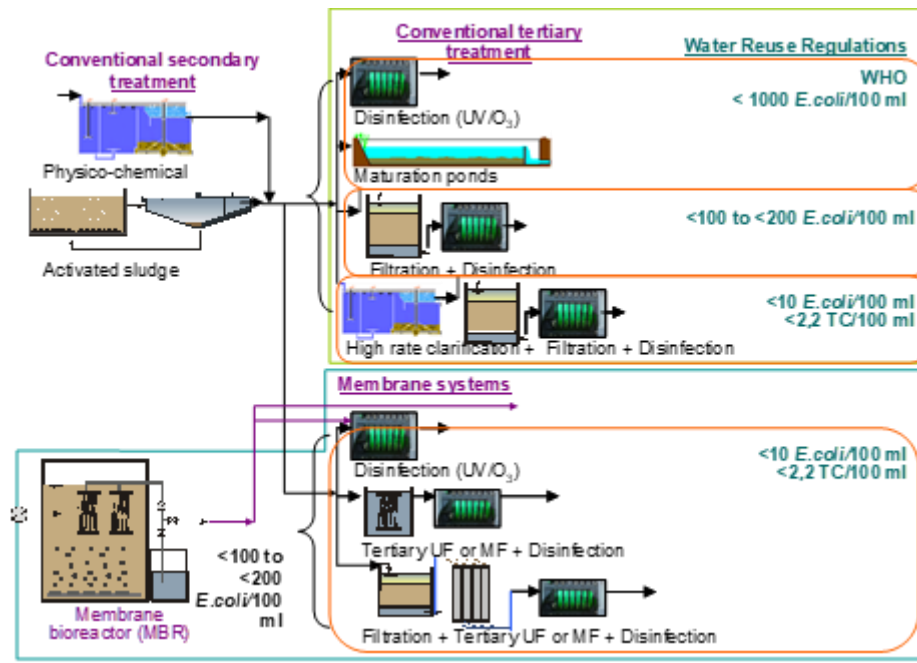


Figure 4.11. Selected tertiary treatment trains enabling to achieve various disinfection levels.

Direct cost comparison of wastewater treatment capital and operations costs is characterized by great uncertainty and imprecision due to the strong influence of technical and local conditions, various patterns of fund granting, different treatment targets and large variations of plant size. The most important consideration regarding wastewater treatment costs is that over the operational lifetime of the given sewage treatment plant, the operation and maintenance costs (O&M costs) may be as important as or even higher than constructions costs, in particular for advanced tertiary treatment.

For this exercise, it is proposed to evaluate the economic viability on the basis of the life cycle costs of additional treatment and pipelines from the treatment plant to the irrigated areas. It can be assumed that the Capex of the tertiary treatment by filtration and UV for such a high treatment capacity is 3.7 million €, plus the Capex of the distribution system of 7.2 million € (at the basis of the cost of pipelines in a rural area of 800 €/ml, linear meter). Life cycle costs were estimated at 0.05 €/m³. The costs of pumping stations and storage reservoirs are not included. As a rule, the cost of pumping stations is negligible compared to the cost of the distribution network and the most common storage reservoirs for agricultural irrigation are constructed using only soil excavation and impermeabilisation (open reservoirs similar to lagoons, in many cases receiving also rain and surface water).

One of the most important parts of this exercise is to evaluate the potential benefits of the use of recycled water for irrigation, including avoided direct and indirect costs and environmental impacts. It would also be relevant to discuss the pricing strategy of the project, assuming that

farmers did not pay for irrigation water or had fresh water fees of 0.02 €/m³. The economic benefits could be related to the revenue effects on agriculture of water shortage and/or water supply cut that can occur during the next years. In several cases, only water reuse can provide a drought proof alternative resource for irrigation, enabling farmers to maintain agricultural activities. For example, each crop is characterised by a given income multiplier from 1.2 to 2.5, meaning that a 1€ change in farm-gate revenue results in a 1.2 to 2.5€ revenue change in the overall regional economy. As a rule, fruits have the highest multiplier among all crop categories.

Solution:

The hydraulic loading rate for irrigation of each crop is calculated by means of eq.1 (1 ha = 10,000 m²). For example, for avocado the calculation for 6-month irrigation is as follows:

- 1. Net irrigation rate: $NR = (ET_c - P) (1 + LF/100) = 1000/6 \times (1 + 0.4/100) = 233 \text{ mm/month}$*
- 2. Hydraulic loading rate: $L_w = NR/(E_i/100) = 233 / (85/100) = 274 \text{ mm/month} = 9.13 \text{ mm/d}$*
- 3. Required flow rate: $Q = L_w \times \text{irrigated area} \times 10,000/1000 = 9.13 \times 25 \times 10,000/1000 = 2283 \text{ m}^3/\text{d}$.*
- 4. Repeating the steps 1-3 for the other crops, the total daily irrigation flow rate which must be supplied by the recycling plant to meet the demand of the 8 crops would equal to 56,580 m³/d.*

When comparing this flow rate with the average hydraulic capacity of the wastewater treatment plant, it should be noticed that a significant part of the secondary effluents, 60%, are needed for irrigation. To further discuss the project feasibility, it is very important to check the daily wastewater flow variations, in particular during the irrigation period, as a rule during summer, when the inlet flow can be lower. In this case, the existence or the construction of a storage reservoir could be needed. Moreover, if the wastewater discharge is in a river, it is necessary to take into account also the minimal discharge flow which be required to maintain the river flow.

The next part is the selection of the best option of tertiary treatment. The analysis of the background data indicates also that the requirements for the quality of the secondary effluents are quite low, which indicate that the discharge could take place in a large river or sea, with a high dilution rate and the effluents quality may be quite poor for direct water reuse.

*On the basis of the analysis of the local water reuse regulations, it can be concluded that all crops need filtration or polishing in maturation ponds, lagoons (to achieve <0,1 helminth egg and 10³-10⁴ E. coli/100 mL). Irrigation of vegetables requires advanced disinfection (UV or ozone, because chlorination could be not allowed in some countries due to potential by-product generation) in order to achieve <0,1 helminth egg and <100 E. coli/100 mL. Drip irrigation also requires good filtration to avoid clogging. Consequently, on the basis of the **Figure 12**, the possible tertiary treatment options could be (1) natural treatment by maturation ponds that can ensure also the storage of recycled water plus satellite treatment only for the irrigation of vegetables or filtration plus UV for the entire irrigation schemes to avoid clogging, enhance public acceptance and product quality and marketing.*

Finally, the cost/benefits should be discussed. Taking in view the high value of the cultivated crops and their importance to local economy and food safety, the benefits of this water reuse project could overweight the costs. Moreover, this project has also the potential to cover O&M costs. For the construction of distribution pipelines, subsidies and grants could be necessary. The economic viability of the project can be increased if local authorities decides to refurbish the existing wastewater treatment plant integrating tertiary treatment in the new project or replacing activated sludge treatment by a MBR system, at least for a part of the flow.

Exercise 4.4. Two methods of tertiary treatment are being considered for golf course irrigation using conventional high load activated sludge and activated sludge with nitrogen removal, filtration and disinfection. Nutrient level ranges are 25 ± 10 mg N_{tot}/L and 7 ± 5 mg N_{tot}/L for the 1st and the 2nd option, respectively. In general, turf grass requires up to 16 nutrients, from which nine are needed in much larger quantities (macronutrients, including carbon, hydrogen, oxygen, nitrogen, phosphorus, potassium, calcium, magnesium, and sulfur). Nitrogen applications occur more frequently and in larger quantities than any other fertilizer-supplied nutrient because plants require more nitrogen and it is typically the most yield-limiting nutrient. Treated wastewater could provide a great part of the needed nitrogen and a part of some of the other macronutrients. For this exercise, it is necessary to estimate the fertilisation capacity of recycled water for the irrigation of 10 ha for each option in kg N/ha, assuming a water requirement for irrigation of 700 mm per year for an irrigation period of 4 months and recommended fertilization rate in the range of 40-50 kg N/ha per month. Evaluate and discuss the feasibility, advantages and disadvantages of each option.

Solution:

The monthly nitrogen loading rate is calculated as follows:

1. *Monthly applied volume per hectare = $700 / (4 \times 1000) \times 1 \times 10,000 = 1750 \text{ m}^3/\text{ha}$ per month.*
2. *The nitrogen load is for the 1st case $43.75 \text{ kg N/ha} = 1750 \times 25 / 1000$ (kg N/m³), and for the 2nd case – $12.25 \text{ kg N/ha} = 1750 \times 7 / 1000$ (kg N/m³).*

The results clearly demonstrate the advantage to use nitrogen from recycled water, which can cover almost all nitrogen requirements when nitrogen removal is not applied during wastewater treatment. In general, the nitrogen available in treated wastewater is in easily assimilable forms of ammonia or nitrate.

Exercise 4.5. The use of disinfected tertiary effluents is planned for a golf course with a total area of 24 ha. One pond on the golf course will be used for the storage and supply of recycled water to alleviate the effect of peak water demand and minimise the cost of the distribution system. Calculate the required volume of operational storage to cover the peak irrigation demand for 3 days without recycled water supply. The allowed timing for irrigation is only during the night, between 22h00 and 4h00. During the peak daily demand, 10 mm of water is applied in a 2 h duration every day for the irrigation of the total area, which is equally divided in three areas. Evaporation and irrigation efficiency will be not taken into account. Discuss the result and feasibility of such storage.

Solution:

The hydraulic loading rate for irrigation is calculated as follows:

1. *Daily irrigation volume: $(10 \text{ mm} \times 24 \text{ ha} \times 2 \text{ h}) \times 10,000 / 1000 = 4800 \text{ m}^3/\text{d}$.*
2. *The total volume of storage is $14,400 \text{ m}^3$.*
3. *Taking into account the relatively low depth of the open storage reservoirs within the golf course (for safety reasons), a 1.5 deep open reservoir will require almost 1 ha area. In this case, the implementation of a standard fiberglass storage reservoir could be considered at the treatment plant, which for the required storage volume will have a diameter of 54 m and water depth of 6 m.*
4. *The most cost competitive solution is to rely on the reliability of water production at the recycling facility and decrease the storage volume to a hydraulic residence time of 0.5 days of the peak demand.*

Exercise 4.6. A large municipality has upgraded its wastewater treatment plant with a conventional activated sludge system for nitrogen removal, followed by sand filtration and UV disinfection to meet a very stringent standard of <10 *E. coli*/100 mL for unrestricted agricultural irrigation. The total capacity of the plant is one million person equivalents (p.e.) and dry weather flow of 350,000 m³/d, with the annual capacity for the production of high-quality recycled water of 124 million m³/yr. The amount of water required for the irrigation of 15,000

ha of rice and corn is 500 mm for 3 months of growing period. The pumping cost of recycled water for 3 months of operation is 30,000 €/yr. The fertilizing value of recycled water can be assumed to be 0.04 €/m³. At the past, farmers were using surface water for irrigation, free of charge. Calculate the right sale price of recycled water for farmers, if the total O&M cost of 0.12 €/m³ of the plant should be covered only by the agricultural use, as well as the recycled water pumping cost. Discuss the willingness and ability of farmers to cover this cost and propose other strategies to ensure the economic viability of this project.

Solution:

The required annual volume for irrigation is:

- 1. Total recycled water delivery, m³/year = (500 x 1) x (15,000 x 10,000/1000) = 75,000,000 m. It should be noticed that 60% of annual volume of treated water is recycled for the production of high-value crops, in particular rice and corn, which are requiring high volumes of irrigation water.*
- 2. On the basis of the known unitary O&M cost of 0.12 €/m³, the annual operation and maintenance costs are 14,880,000 €/yr = 0.12 x 124,000,000. If this annual O&M cost should be covered only by the recycled water delivered to farmer, the minimum recycled water price should be 0.20 €. If the pumping cost (energy consumption for pumping) should be added, the additional price is 0.00004 €/m³.*

The given example is only an approximate calculation, because O&M costs vary from year to year depending on replacement cost, and inflation rate should also be taken into account. Even if the agricultural production includes high-value crops, it is doubtful that farmers will accept to pay such a high recycled water price. It could be judicious to start with a relatively low recycled water price in the range on 0.05-0.07 €/m³, underlining the fertilising value of recycled water estimated at 0.04 €/m³. Additional revenues could be provided by increasing the price of potable water, adding a tax for the preservation of water resources, and/or selling recycled water to industry or for landscape irrigation at higher rate.

Another option could be to switch-off tertiary treatment during a part of the year, but in this case fixed O&M costs will still remain, which could be as high as 40-50% of the cost during full capacity operation.

CHAPTER 5

Exercise 5.1. A wastewater stream contains 5 g.L⁻¹ carbohydrate, 2 g.L⁻¹ protein and 1 g.L⁻¹ fat, oil and grease. If the waste is completely degradable, calculate:

- The maximum theoretical methane that could be produced from this waste stream.
- The total volume and composition of the biogas stream (HINT: consider CH₄ and CO₂ only).
- The potential heat that could be generated from the biogas (HINT 55 MJ.kg⁻¹ CH₄).
- The potential electricity that could be generated from the biogas (HINT: electrical efficiency 0.35).

Solution:

- a. The theoretical methane potential of each component in the wastewater can be determined using data presented in Table 5.1, a summary of calculations is shown in the table below. The maximum theoretical methane production is 4.08 L CH₄ per L of wastewater.

Component	Concentration (g VS.L ⁻¹ WW)	Theoretical CH ₄ (L.kg ⁻¹ VS)	Total Theoretical CH ₄ (L.L ⁻¹ WW)	Biogas composition (% CH ₄)	Total Biogas (L.L ⁻¹ WW)
Carbohydrate (cellulose)	5	415	2.08	50	4.15
Proteins	2	496	0.99	50	1.98
Lipids	1	1007	1.01	71	1.42
Total			4.08		7.55

- b. Based on the calculation table above, total theoretical methane production from the wastewater is 4.08 L CH₄ per L of wastewater, using the biogas composition information in Table 5.1, the total biogas production would be 7.55 L biogas per L of wastewater. This corresponds to a theoretical biogas composition of 54% methane. The actual biogas composition may appear higher or lower as CO₂ solubility is impacted strongly by pH and other environmental factors.
- c. The potential heat that could be generated from the biogas (HINT 55 MJ/kg CH₄)

To solve this problem, first convert the volumetric CH₄ production to a mass of CH₄.

$$4.08 \text{ L CH}_4/\text{L WW} \times 1 \text{ mol CH}_4/22.4 \text{ L CH}_4 \times 16 \text{ g CH}_4/1 \text{ mol CH}_4 = 2.91 \text{ g CH}_4/\text{L WW}$$

The next step is to multiply the theoretical mass of CH₄ produced by the heating energy content of the CH₄:

$$2.91 \text{ g CH}_4/\text{L WW} \times 1 \text{ kg CH}_4/1000 \text{ g CH}_4 \times 55 \text{ MJ}/1 \text{ kg CH}_4 = 0.16 \text{ MJ}/\text{L WW} = 160 \text{ MJ}/\text{m}^3 \text{ WW}$$

The theoretical heat energy that could be produced using anaerobic digestion, followed by combustion of the biogas is 160 MJ per m³ of wastewater. Note at gas energy prices of \$10/GJ, this corresponds to \$1.6 per m³ of the wastewater.

- d. The potential electricity that could be generated from the biogas (HINT: electrical efficiency 0.35)

To solve this problem, multiply the heat energy of the biogas by an electrical efficiency of 0.35:

$$160 \text{ MJ/m}^3 \text{ WW} \times 0.35 \times 1 \text{ kWh/3.6 MJ} = 15.6 \text{ kWh/m}^3 \text{ WW}$$

The wastewater could be used to generate 15.6 kWh of electricity per m³ of wastewater if 100% of the organics are converted to biogas.

Exercise 5.2. A solid phase plug flow digester is loaded with a waste stream that contains tCOD at 120,000 g.kg⁻¹. The waste stream has a degradable fraction of 0.65 and an apparent hydrolysis rate coefficient of 0.08 day⁻¹. If the waste is well inoculated and the SRT in the reactor is 30 days, determine the expected methane yield (per gCOD added) and the fraction of COD removed.

Solution:

The first step in this problem is to determine the methane potential for the waste. In this case the methane potential will be determined using the degradable fraction to determine the degradable COD and then converting this to methane equivalent:

$$120 \text{ g COD/1 kg waste} \times 0.65 \times 0.35 \text{ L CH}_4/\text{1 g COD} = 27.3 \text{ L CH}_4/\text{1 kg waste}$$

Next, Equation 5.5 is used to determine methane production in a plug flow reactor with an SRT of 30 days:

$$\text{CH}_4 = B_0(1 - e^{-kt}) = 27.3 \text{ L CH}_4/\text{1 kg waste} \times (1 - e^{-0.08 \times 30}) = 24.8 \text{ L CH}_4/\text{1 kg waste}$$

Estimated methane production in the plug flow reactor is 24.8 L CH₄. kg⁻¹ waste. Follow the reverse procedure to convert the methane yield into COD equivalent units.

$$24.8 \text{ L CH}_4/\text{1 kg waste} \times 1 \text{ g COD}/0.35 \text{ L CH}_4 = 70.92 \text{ g COD (CH}_4)/\text{1 kg waste}$$

The raw waste contained 120 g COD.kg⁻¹ of waste and estimated methane production accounts for 70.92 g COD.kg⁻¹, therefore COD removed as methane is 59.1%.

Exercise 5.3. Typical wastewater production from an animal processing plant is shown below:

Flow: 2,500 m³.d⁻¹
COD: 6000 mg.L⁻¹
TSS: 1,000 mg.L⁻¹
FOG: 2,500 mg.L⁻¹
TKN: 200 mg.L⁻¹
TP: 65 mg.L⁻¹
pH: 7 - 9
Temp: 36°C

- Using organic loading rate as a critical design parameter, estimate the size of an AnMBR required to treat this wastewater,
- The AnMBR is designed with an external submerged membrane module containing microfiltration membranes. If the membranes operate at a flux of 15 LMH, estimate the required membrane surface area?
- If the external membrane module contains approximately 100m²/m³ tank volume, estimate the additional tank volume required for the membranes.
- Estimate the methane production when COD conversion in the reactor is 80% of the organic load.

Solution:

- a. Table 4 shows that typical design organic loading rates for AnMBR's range from 1 – 15 gCOD.L⁻¹.d¹, in practice this range is too large for confident and efficient plant design and experimental testing would be required. Without access to further information, use a moderate design organic loading rate of 8 gCOD.L⁻¹.d¹. Start by determining the total organic load to the process:

$$2,500 \text{ m}^3 \text{ wastewater/1 day} \times 6 \text{ kg COD/1 m}^3 \text{ wastewater} = 15,000 \text{ kg COD/1 day}$$

Next, the required AnMBR volume is determined by dividing the organic load to the process by the design organic loading rate:

$$15,000 \text{ kg COD/1 day} \times 1 \text{ m}^3 \cdot \text{day} / 8 \text{ kg COD} = 1,875 \text{ m}^3 \text{ reactor volume}$$

Therefore, the required reactor volume is 1,875 m³. To estimate the required membrane area, consider critical flux ranges for the wastewater.

- b. The plant is required to treat 2,500 m³ of water per day (~105 m³.h⁻¹). Microfiltration membranes at a flux of 15 L.m⁻².h⁻¹ (0.015 m³.m⁻².h⁻¹) is used. Therefore, 7,000 m² membrane area would be required.
- c. The plant will require 7,000 m² of microfiltration membranes. If the membranes modules contain 100m²/m³, the volume of the membrane module would be an additional 70 m³.
- d. The first step in this problem is to determine the methane potential for the waste. In this case the methane potential will be determined using the degradable fraction to determine the degradable COD and then converting this to methane equivalent:

$$6 \text{ g COD/1 L waste} \times 2,500,000 \text{ L waste/1 day} \times 0.35 \text{ L CH}_4/1 \text{ g COD} \times 0.8 = 4,200,000 \text{ L CH}_4/1 \text{ day}$$

Estimated methane production is 4,200 m³ per day when the COD conversion is 80%. Next, convert to heating energy using 39 MJ.m⁻³ (at 0°C and 1 atm). The theoretical heat energy that could be produced using anaerobic digestion, followed by combustion of the biogas is 164 GJ per day.

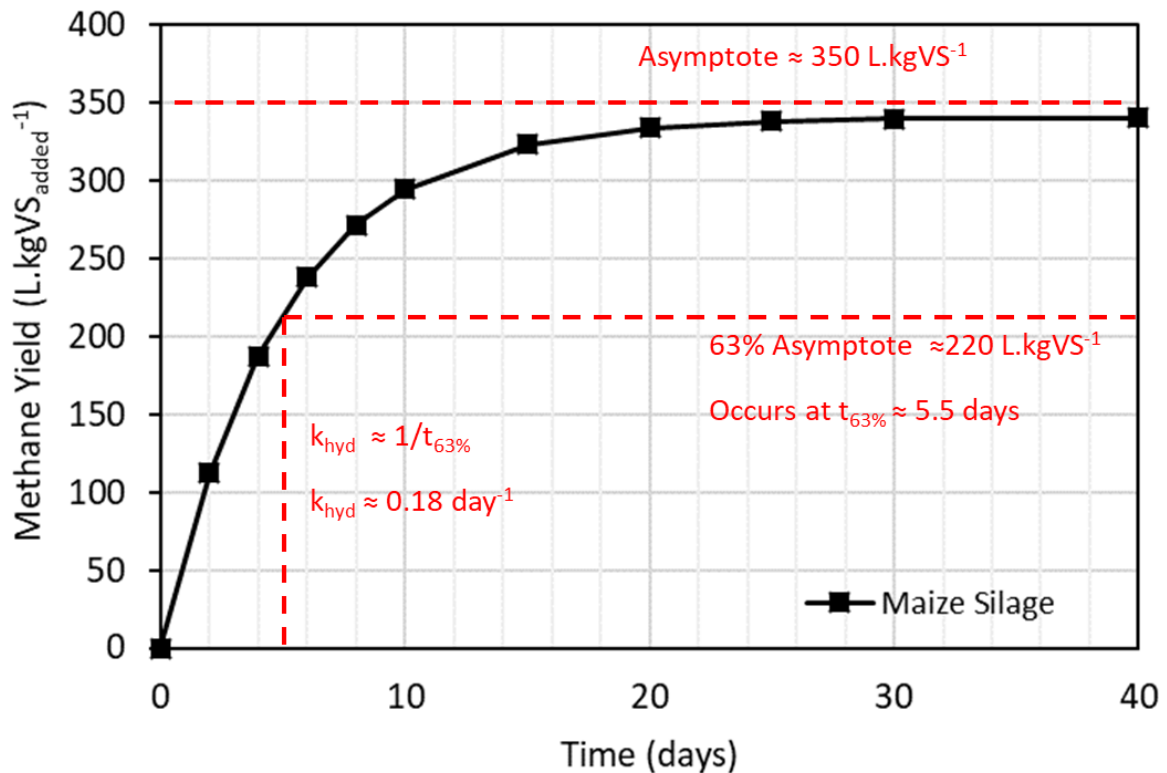
Exercise 5.4. Experimental results from a series of bio-chemical methane potential tests are shown in the table below.

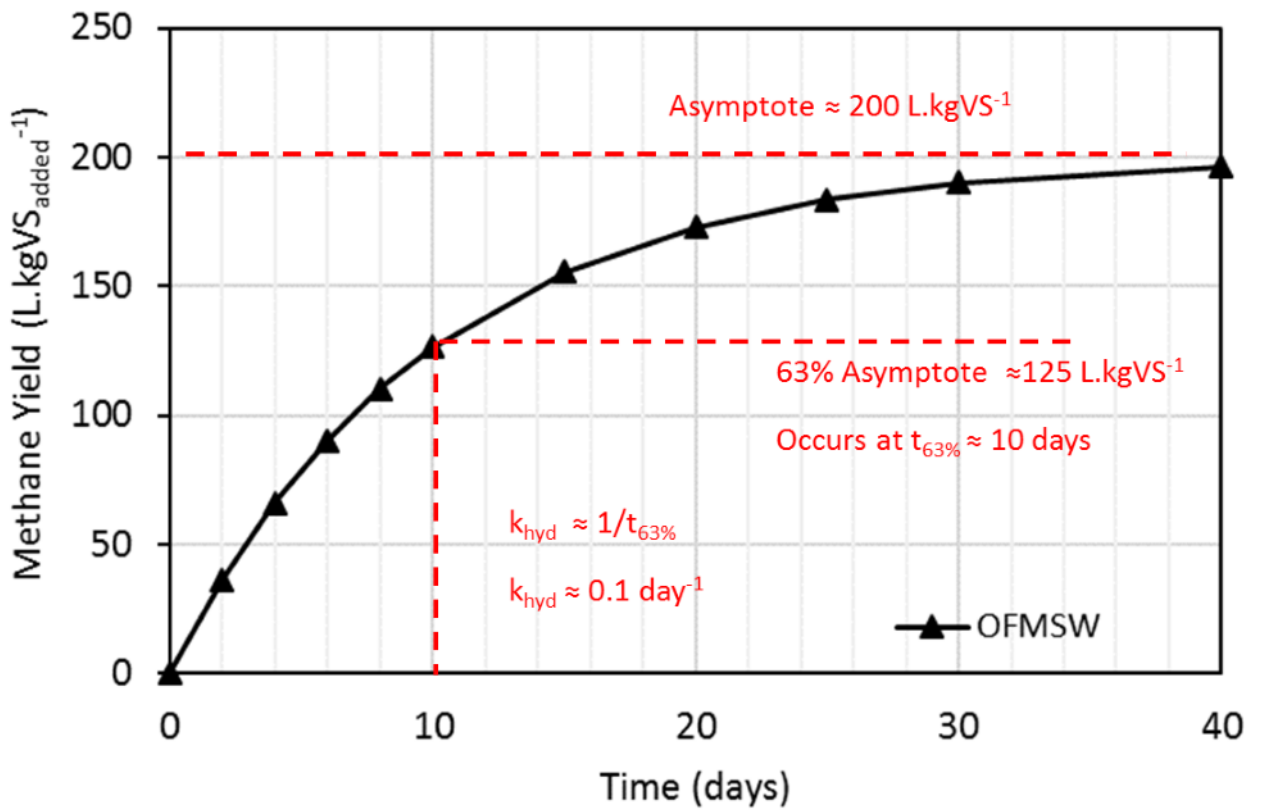
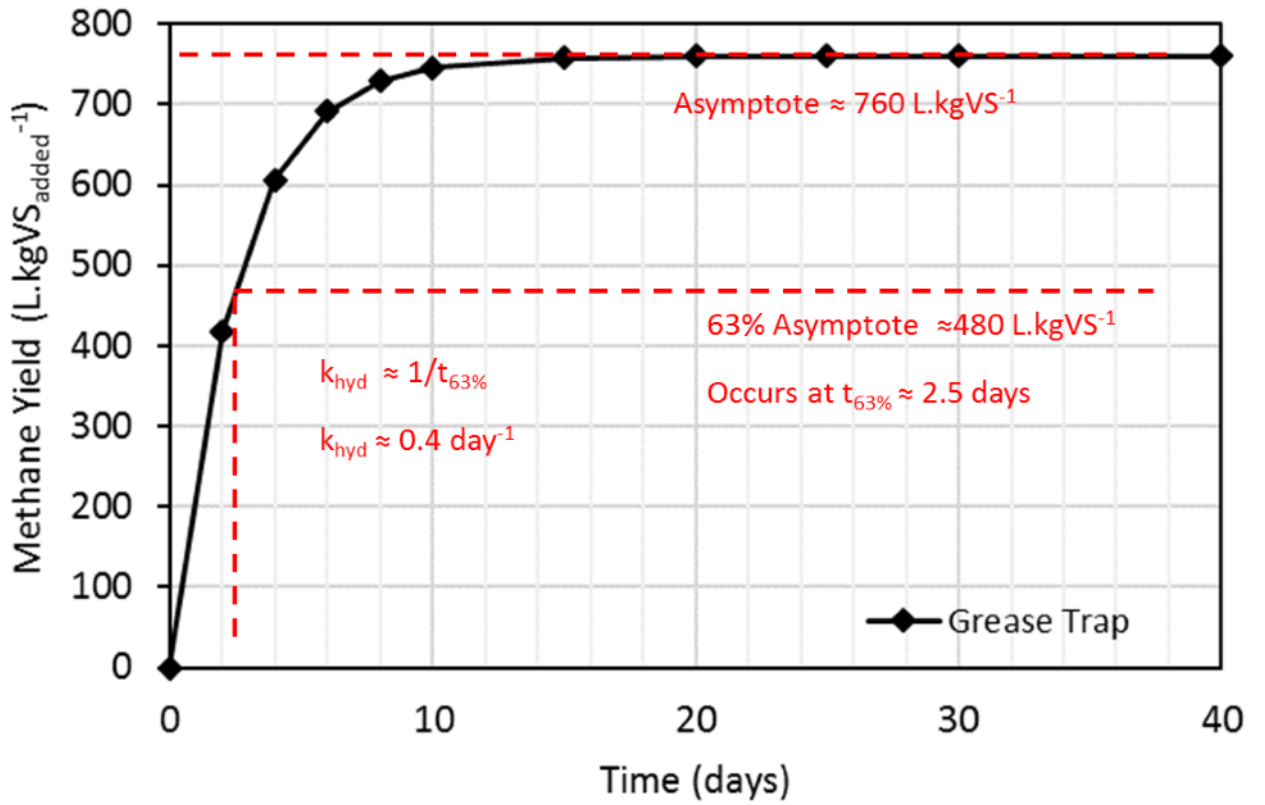
Time (days)	Pig Manure	Grease Waste	Trap	Organic Fraction of MSW
	CH ₄ (L.kgVS ⁻¹)	CH ₄ (L.kgVS ⁻¹)		CH ₄ (L.kgVS ⁻¹)
0	0	0		0
2	112	419		36
4	187	607		66
6	238	691		90
8	271	729		110
10	294	746		126
15	323	758		155
20	334	760		173
25	338	760		184
30	339	760		190

- For each substrate, determine the ultimate methane potential (B_0), and the apparent hydrolysis rate coefficient (k_{hyd}) (HINT: you can use graphical methods to estimate the parameters)
- Do any of the tests show signs of microbial inhibition?

Solution:

- Graphical methods were used to estimate the ultimate methane potential (B_0), and the apparent hydrolysis rate coefficient (k_{hyd}) for each substrate.
 Step 1 is to plot the data provided using graph paper.
 Step 2 is to identify the asymptote of the methane production curve. This represents the limit of methane production.
 Step 3 is to calculate 63% of the methane asymptote and plot this on the graph
 Step 4 is to identify the time required to reach 63% of the asymptote methane production
 Step 5 the hydrolysis rate coefficient is calculated as $1/t_{63\%}$.
 Graphical solutions for each substrate are presented:





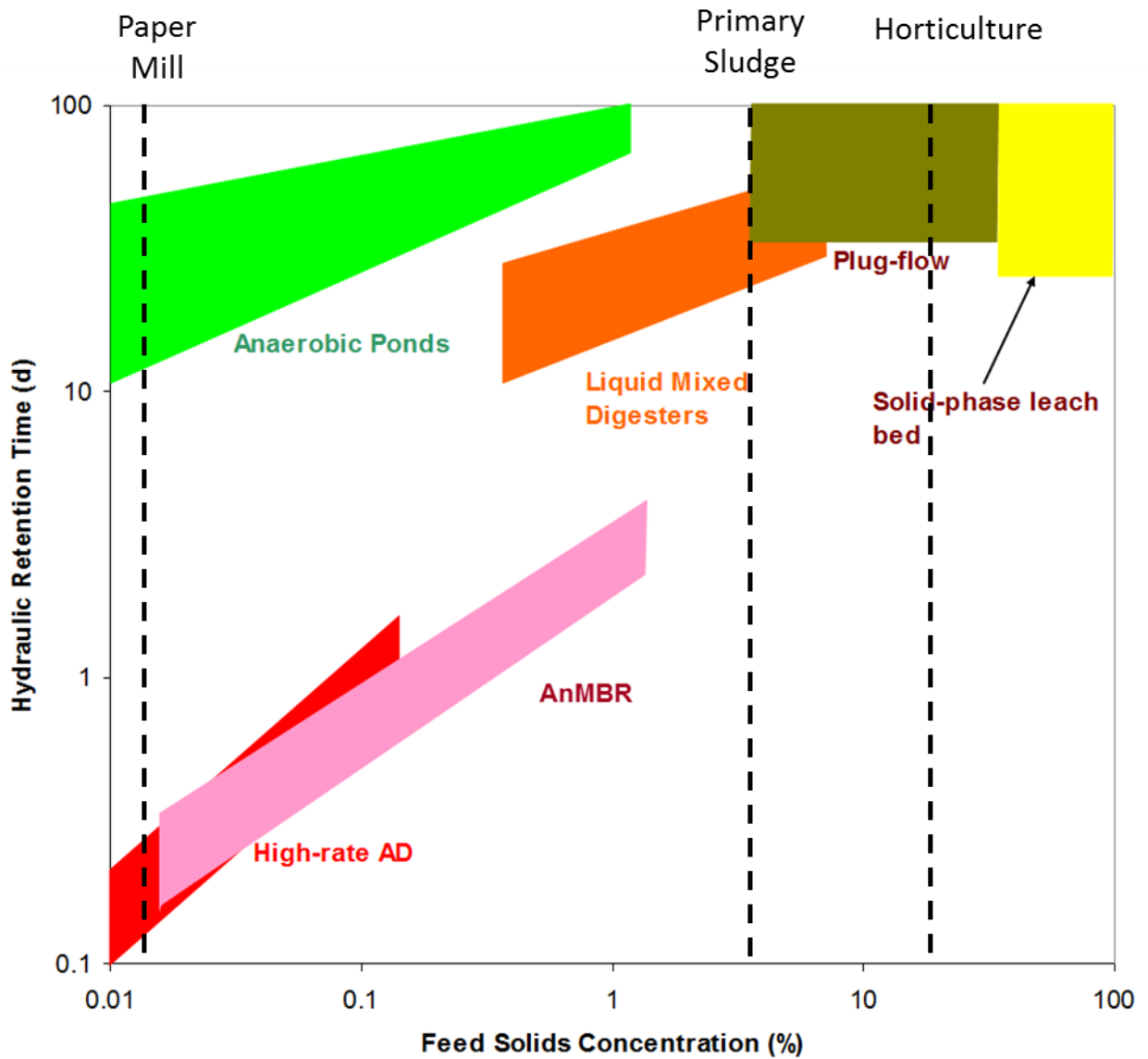
- b. The tests do not show signs of inhibition. All tests appear to follow a standard first order curve – meaning the highest rate of methane production occurs at the start of the test and methane production rates decline as tests progress. There is no delay before the onset of methane production and no unexpected depressions in methane production rate.

Exercise 5.5. For each of the wastewater streams in the table below, suggest a suitable anaerobic digestion technology. Justify your selection:

Industry	Municipal Primary Sludge	Paper Mill Wastewater	Mixed Horticultural Waste
Volumetric flow (m^3d^{-1})	80	1,200	150 (Seasonal)
tCOD (mg.L^{-1})	70,000	10,000	265,000
sCOD (mg.L^{-1})	22,000	6,500	30,000
TSS (mg.L^{-1})	44,000	150	215,000
VSS (mg.L^{-1})	34,000	140	180,000
FOG (mg.L^{-1})	3,000	<1	1,500
TKN (mg.L^{-1})	1,500	30	3,500
TP (mg.L^{-1})	260	<1	520

Solution:

A general first step, compare the composition of each waste against different reactor configurations using Figure 5.11. The problem does not provide any information on the degradation characteristics of each material, therefore the comparison is limited to solids concentration.



Municipal Primary Sludge:

The feed concentration of primary sludge is 4% and is likely too concentrated for lagoons or high rate granular processes. It may be possible to treat the primary sludge in an AnMBR, however the high solids concentration is likely to increase membrane fouling and create some operating difficulties. The primary sludge is too dilute for plug-flow and solid phase technologies.

The primary sludge is well within the typically operating range of mixed liquor digesters. The mixed liquor digesters are very flexible and can be sized to accommodate the degradation rate of the sludge.

Paper Mill Wastewater:

The paper mill wastewater is a dilute stream with very low solids and little to no FOG. This wastewater would be suitable for either lagoon treatment or a high rate granular process. More information is required to assess and site specific constraints such as the available footprint for the treatment plant or seasonal climate (i.e. lagoon temperature). In general, a UASB would be selected in an urban area, while a UASB or lagoon may be utilised in a rural area.

Note: paper mill wastewater could be treated in a mixed liquor digester, however the organic loading rate would be very low and the capital investment would be large. While technically achievable, this would not be an efficient use of economic resources.

Mixed Horticultural Waste:

The feed concentration of mixed horticultural waste is >20% solids. This is too high for lagoon or high rate processes.

The mixed horticultural waste is well within the typically operating range of a plug flow reactor. Plug flow reactors are flexible and can be sized to accommodate the degradation rate of the waste. Solid phase batch reactors could be considered, however more information on the waste production volumes and seasonal variations would be required.

An alternative treatment option would be to dilute the horticultural waste and treat using a mixed liquor digester, but this would require a larger anaerobic digester and a larger treatment footprint.

Exercise 5.6. A food production plant discharges wastewater to sewer after primary treatment. As is typical in food processing plants, the WWTP sees large variations in wastewater quality and flow, with the following characteristics after primary treatment:

Flow: 900 - 1500 m³.d⁻¹
COD: 600 - 1000 mg.L⁻¹
TSS: 250 mg.L⁻¹
pH: 7 - 9
Temp: 32°C

The food processing plant is in a rural location with a warm temperate climate. The plant is considering either a covered anaerobic lagoon or a high rate granular process.

- If a UASB reactor is used to treat this wastewater, recommend an appropriate reactor size.
- If a covered anaerobic lagoon is used to treat this wastewater, recommend an appropriate lagoon size.
- Present advantages and disadvantages of each treatment option and provide a recommendation.
- Discuss design strategies or ancillary equipment that could be added to the process to address the disadvantages mentioned in part (c).

Solution:

Before trying to size equipment, its important to understand the volume of wastewater to be treated and organic load. The flowrate and composition of the waste are provided as a range. We could use the middle of each range to represent an average flowrate and composition, or we could use the maximum flow and concentration to represent an upper limit of the load:

Average:

$$1,300 \text{ m}^3 \text{ wastewater/1 day} \times 0.8 \text{ kg BOD/1 m}^3 \text{ wastewater} = 1,040 \text{ kg COD/1 day}$$

Upper Limit:

$$1,500 \text{ m}^3 \text{ wastewater/1 day} \times 1 \text{ kg BOD/1 m}^3 \text{ wastewater} = 1,500 \text{ kg COD/1 day}$$

When sizing equipment in this problem we use the upper limit calculated for the organic load, however this is a conservative approach and may result in equipment that is oversized.

- a. From Table 2, the design organic loading rate for a UASB reactor is $10 \text{ kgCOD}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$. The required UASB volume is determined by dividing the organic load by the design organic loading rate:

$$1,500 \text{ kg COD}/1 \text{ day} \times 1 \text{ m}^3\cdot\text{day}/10 \text{ kg COD} = 150 \text{ m}^3 \text{ reactor volume}$$

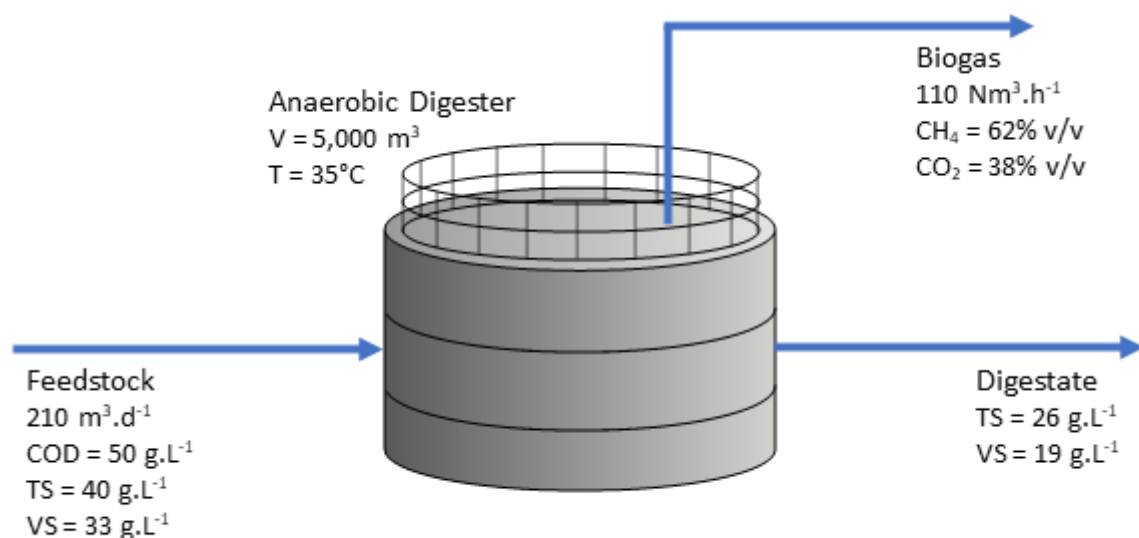
Therefore, the required reactor volume is 150 m^3 .

- b. From Table 2, the range of design organic loading rates covered anaerobic lagoons is $0.1 - 0.5 \text{ kgCOD}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$, an average value of $0.3 \text{ kgCOD}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$ will be used. The required CAL volume is determined by dividing the organic load by the design organic loading rate:

$$1,500 \text{ kg COD}/1 \text{ day} \times 1 \text{ m}^3\cdot\text{day}/0.3 \text{ kg COD} = 5,000 \text{ m}^3 \text{ reactor volume}$$

- c. The UASB will occupy a very small footprint in comparison to the CAL, however the HRT in the UASB is very short, in the range of 2 hours, this provides very little capacity to equalize variations in flow and concentration and presents a significant operating risk to the process. The CAL will occupy a very large footprint in comparison to the UASB, however the HRT is also much larger at several days. This provides a much greater capacity to equalize variations in flow and concentration and should reduce the impact of flow variations on the AD microbiology. However, it will be more difficult to control temperature in the CAL and it will be more difficult to implement other process corrections that may be required.
- d. A pre-fermentation tank could be installed prior to a UASB to equalize flow patterns and minimise the variations in the feed entering the digester, this would increase the footprint of the plant, but would decrease the process risk.

Exercise 5.7. Consider the mixed liquor anaerobic digestion process summarized in the flowsheet below:



- a. Determine the solids retention time in the process
 b. Calculate the organic loading rate for the process

- c. Calculate the volatile solids destruction using: the mass balance equation, the Van Kleeck Equation, gas flow.
- d. Estimate the fraction of COD removed from the waste stream and the expected COD concentration of the digestate.

Solution:

- a. The solids retention time is equal to the reactor volume divided by the volumetric feed rate. In this scenario, the solids retention time is:

$$\text{SRT (days)} = \text{Reactor Volume (m}^3\text{)} / \text{Feed rate (m}^3\text{/d)} = (5,000 \text{ m}^3) / (210 \text{ m}^3\text{/d}) = 23.8 \text{ days}$$

- b. The organic loading to a digester is calculated from the COD concentration in the feed and the volume of feed added to the process. The OLR can then be calculated using the organic load and reactor volume as below:

$$\text{OLR (kgCOD/m}^3\text{.d)} = (\text{Feed Concentration (kgCOD/m}^3\text{)} \times \text{Feed rate (m}^3\text{/d)}) / \text{Reactor Volume (m}^3\text{)}$$

$$\text{OLR} = (50 \text{ kgCOD/m}^3) \times (210 \text{ m}^3\text{/d}) / (5000 \text{ m}^3) = 2.1 \text{ kgCOD/m}^3\text{.d}$$

- c. Volatile solids destruction is calculated based on mass balance, van Kleeck and gas flow using equations presented in Table 5:
Mass balance equation:

$$\text{MB VS destruction (\%)} = 100 \times (\text{VS}_{in} \text{ (g/L)} - \text{VS}_{out} \text{ (g/L)}) / \text{VS}_{in} \text{ (g/L)}$$

$$\text{MB VS destruction} = 100 \times (33 \text{ (g/L)} - 19 \text{ (g/L)}) / 33 \text{ (g/L)} = 42.4\%$$

Van Kleeck Equation:

$$\text{Van Kleeck VS destruction (\%)} = 100 \times ((\text{VS/TS})_{in} - (\text{VS/TS})_{out}) / ((\text{VS/TS})_{in} - ((\text{VS/TS})_{in} \times (\text{VS/TS})_{out}))$$

$$\text{Van Kleeck VS destruction (\%)} = 100 \times ((33/40)_{in} - (19/26)_{out}) / ((33/40)_{in} - ((33/40)_{in} \times (19/26)_{out})) = 42.4\%$$

Therefore, VS destruction is calculated as 42.4% using the mass balance equation and 42.4% using the van Kleeck equation. These results indicate there are no issues with sampling.

Gas Flow Equation:

$$\text{Gas flow VS Destruction (\%)} = 100 \times (\text{COD}_{\text{gas}} \text{ (kg COD}\cdot\text{d}^{-1}\text{)}) / (\text{COD}_{in} \text{ (kg COD}\cdot\text{d}^{-1}\text{)})$$

$$\text{Gas flow VS Destruction (\%)} = 100 \times (2.9 \text{ kg COD/Nm}^3 \times 2640 \text{ Nm}^3\text{/d} \times 62\%) / (50 \text{ kg COD/m}^3 \times 210 \text{ m}^3\text{/d}) = 45.2\%$$

VS destruction is calculated as 45.2% using gas flow data and is marginally higher than mass balance and van Kleeck calculations. VS destruction based on gas flow does not include direct measurement of VS and assumes that the feedstock degrades uniformly. This assumption is not always true and it is not uncommon for the gas flow method to show some difference to other calculation methods.

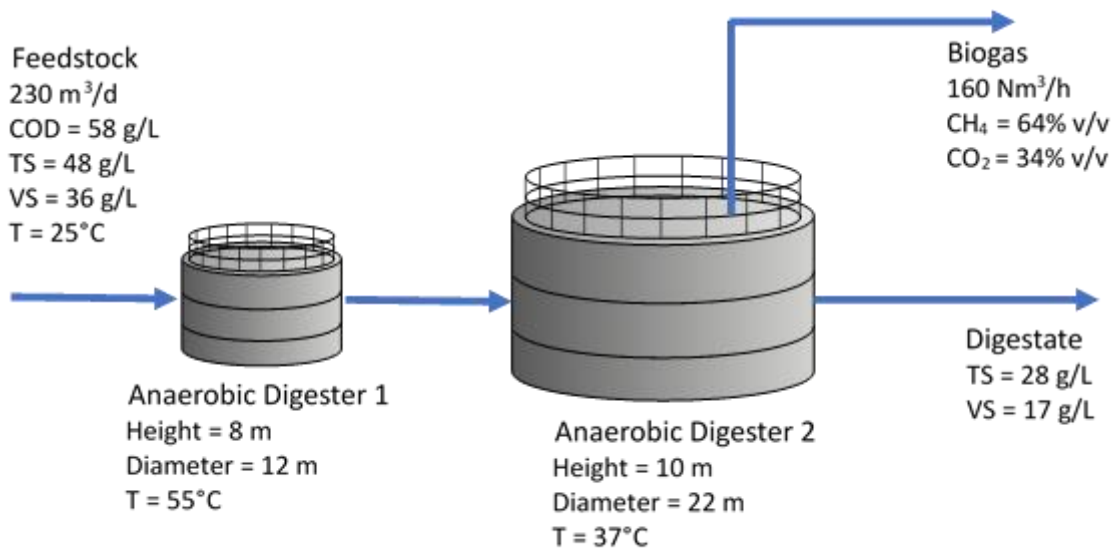
- d. The method for estimating the fraction of COD removed from the waste stream is the same method applied to determine gas flow VS destruction.

$$\text{Gas flow COD (\%)} = 100 \times \text{COD}_{\text{gas}} (\text{kg COD} \cdot \text{d}^{-1}) / \text{COD}_{\text{in}} (\text{kg COD} \cdot \text{d}^{-1})$$

$$\text{Gas flow COD (\%)} = (2.9 \text{ kg COD/Nm}^3 \times 2640 \text{ Nm}^3/\text{d} \times 62\%) / (50 \text{ kg COD/m}^3 \times 210 \text{ m}^3/\text{d}) = 45.2\%$$

Therefore, 45.2% of the COD is removed from the waste in the form of biogas and 54.8% of COD remains in the digestate. The COD concentration of the feed is 50 g.L⁻¹, therefore the COD concentration of the digestate is estimated at 27.4 g.L⁻¹.

Exercise 5.8. You have been asked to evaluate a novel 2-stage anaerobic digestion process shown in the flowsheet below. The digesters have been constructed above the ground using concrete without insulation. The average ambient temperature is 25°C.



- Calculate the solids retention time for each digester and the combined retention time for the process. Is the retention time sufficient?
- Calculate the heating requirement for anaerobic digester 1
- Calculate the heating requirement for anaerobic digester 2
- Calculate the heating energy from combustion of the biogas.
- Is this process net energy-generating or net energy-consuming?

Solutions:

- First calculate the volume of each digester using the dimensions provided in the flowsheet and assuming the geometry is a cylinder.

Digester 1 volume

$$\text{Volume m}^3 = \pi(\text{Diameter}/2)^2 \times \text{height} = \pi(12 \text{ m}/2)^2 \times 8 \text{ m} = 905 \text{ m}^3$$

Digester 2 volume

$$\text{Volume m}^3 = \pi(\text{Diameter}/2)^2 \times \text{height} = \pi(22 \text{ m}/2)^2 \times 10 \text{ m} = 3,800 \text{ m}^3$$

Next, calculate the solids retention time in each reactor. Assume the volumetric feed rate is 230m³.d⁻¹ and is the same for each reactor:

Digester 1 SRT:

$$\text{SRT (days)} = \text{Reactor Volume (m}^3\text{)} / \text{Feed rate (m}^3\text{/d)} = 905 \text{ m}^3 / 230 \text{ m}^3\text{/d} = 3.9 \text{ days}$$

Digester 2 SRT:

$$\text{SRT (days)} = \text{Reactor Volume (m}^3\text{)} / \text{Feed rate (m}^3\text{/d)} = 3,800 \text{ m}^3 / 230 \text{ m}^3\text{/d} = 16.5 \text{ days}$$

The SRT was calculated as 3.9 days for Digester 1 and 16.5 days for Digester 2. This gives a combined SRT of 20.4 days. Digester 1 operates at 55°C and minimum retention times at this temperature are short and therefore the design is likely appropriate (Table 3). Similarly, the SRT of 16.5 days for Digester 2 is above the desired minimum SRT for mesophilic processes (Table 3).

- b. The heating requirements of an anaerobic digestion process consist of the heat required to raise the feedstock from ambient to the digester operating and the heat required to compensate for losses through the reactor surface and process pipelines.

Heat requirements to raise the temperature of the feedstock entering digester 1:

$$Q_{\text{feed}} = m \cdot CP (T_{\text{dig}} - T_{\text{amb}}) = 230 \text{ t/d} \times 4.2 \text{ MJ/t} \cdot ^\circ\text{C} (55^\circ\text{C} - 25^\circ\text{C}) = 28,980 \text{ MJ/d} = 335 \text{ kW}$$

Heat requirements to compensate for heat loss from digester 1:

$$Q_{\text{losses}} = UA (T_{\text{dig}} - T_{\text{amb}})$$

Calculate heat loss from each surface separately:

Roof:

The diameter of the digester is 12m, therefore the surface area of the roof is:

$$\text{Surface Area} = \pi(\text{Diameter}/2)^2 = \pi(12 \text{ m}/2)^2 = 113 \text{ m}^2$$

The heat loss transfer coefficient for a concrete roof is taken from Table 5 as 5.0 W.m⁻².°C⁻¹, therefore heat loss from the roof is:

$$Q_{\text{losses}} = 5.0 \text{ W/m}^2 \cdot ^\circ\text{C} \times 113 \text{ m}^2 (55^\circ\text{C} - 25^\circ\text{C}) = 17 \text{ kW}$$

Walls:

The digester has a circumference of 37.7m and a height of 8m, therefore the wall surface area is 301.6 m². The heat loss transfer coefficient for concrete walls without insulation is taken from Table 5 as 5.1 W.m⁻².°C⁻¹, therefore heat loss from the digester walls is:

$$Q_{\text{losses}} = 5.1 \text{ W/m}^2 \cdot ^\circ\text{C} \times 301 \text{ m}^2 (55^\circ\text{C} - 25^\circ\text{C}) = 46 \text{ kW}$$

Bottom:

The diameter of the digester is 12m, therefore the surface area of the bottom is:

$$\text{Surface Area} = \pi(\text{Diameter}/2)^2 = \pi(12 \text{ m}/2)^2 = 113 \text{ m}^2$$

The heat loss transfer coefficient for the bottom is taken from Table 5 as 2.85 W.m⁻².°C⁻¹, and the ground temperature is assumed equal to ambient, therefore heat loss from the digester bottom is:

$$Q_{\text{losses}} = 2.85 \text{ W/m}^2 \cdot ^\circ\text{C} \times 113 \text{ m}^2 (55^\circ\text{C} - 25^\circ\text{C}) = 9.7 \text{ kW}$$

Therefore total heat loss for digester 1 is 72.7 kW and the total heating requirement for digester 1 is approximately 408 kW.

- c. In the case of digester 2, begin by calculating heat loss from the digester. Again, calculate heat loss from each surface separately:

Roof:

The diameter of the digester is 22m, therefore the surface area of the roof is:

$$\text{Surface Area} = \pi(\text{Diameter}/2)^2 = \pi(22 \text{ m}/2)^2 = 380 \text{ m}^2$$

The heat loss transfer coefficient for a concrete roof is taken from Table 5 as $5.0 \text{ W}\cdot\text{m}^{-2}\cdot\text{C}^{-1}$, therefore heat loss from the roof is:

$$Q_{\text{losses}} = 5.0 \text{ W}/\text{m}^2\cdot\text{C} \times 380 \text{ m}^2 (37\text{C} - 25\text{C}) = 22.8 \text{ kW}$$

Walls:

The digester has a circumference of 69.1m and a height of 12m, therefore the wall surface area is 691.1 m^2 . The heat loss transfer coefficient for concrete walls without insulation is taken from Table 5 as $5.1 \text{ W}\cdot\text{m}^{-2}\cdot\text{C}^{-1}$, therefore heat loss from the digester walls is:

$$Q_{\text{losses}} = 5.1 \text{ W}/\text{m}^2\cdot\text{C} \times 691 \text{ m}^2 (37\text{C} - 25\text{C}) = 42.3 \text{ kW}$$

Bottom:

The surface area of the bottom of digester 2 is 380m^2 . The heat loss transfer coefficient for the bottom is taken from Table 5 as $2.85 \text{ W}\cdot\text{m}^{-2}\cdot\text{C}^{-1}$, and the ground temperature is assumed equal to ambient, therefore heat loss from the digester bottom is:

$$Q_{\text{losses}} = 2.85 \text{ W}/\text{m}^2\cdot\text{C} \times 380 \text{ m}^2 (37\text{C} - 25\text{C}) = 13 \text{ kW}$$

Therefore, total heat loss for digester 2 is 78.1 kW. In the case of digester 2, the feed stream is available at 55C , however the digester operates at 37C . Heat available through cooling of the feedstock entering digester 2:

$$Q_{\text{feed}} = m\cdot\text{CP} (T_d - T_a) = 230 \text{ t}/\text{d} \times 4.2 \text{ MJ}/\text{t}\cdot\text{C} (37\text{C} - 55\text{C}) = -17,388 \text{ MJ}/\text{d} = -201 \text{ kW}$$

Digester 2 is expected to lose 78 kW of heat energy to the environment, however the feed contains 201 kW of excess heat energy due to the thermophilic conditions in digester 1. Therefore, excess heat from the feed exceeds heat loss to the environment and cooling may be required to maintain digester 2 at 37C .

- d. Calculate the heating energy from combustion of the biogas.
Estimated biogas production is $3,840 \text{ m}^3$ per day containing $2,458 \text{ m}^3$ per day methane. Next, convert to heating energy using $39 \text{ MJ}\cdot\text{m}^{-3}$ (at 0C and 1 atm). The theoretical heat energy that could be produced from the biogas produced in digester 2 is 95.6 GJ per day, this corresponds to 1.1 MW of heat energy.
- e. The potential heat energy from the process is 1.1 MW and significantly exceeds the heat energy requirements of the process at 408 kW (note that heat energy is not supplied to digester 2). Mixing energy for the digesters is calculated using Table 4 and by assuming mechanical agitation. Mixing energy is estimated at 7 kW for digester 1 and 30 kW for digester 2. The energy required for heating and mixing is less than

50% of the heating value of the biogas and therefore the process is likely to be net energy-generating.

Exercise 5.9. You have been asked to evaluate the feasibility of single-stage anaerobic digestion applied to Dairy manure. The raw dairy manure has a composition of 210 g.L⁻¹ TS, 185 g.L⁻¹ VS, 295 g.L⁻¹ COD, 4.4 g.L⁻¹ TKN and an average daily production rate of 60 metric ton/day on a fresh weight basis. Your lab has conducted BMP testing and report that the B₀, f_d, and k_{hyd} values for the waste at 35°C are 340 L.kgVS⁻¹, 0.55, and 0.14 day⁻¹ respectively. Consider the 2 options below:

- A continuous mixed liquor reactor with a maximum feed concentration of 5% TS
- A continuous solid phase plug flow reactor with a maximum feed concentration of 15% TS

Determine the size requirement of each option. Discuss how this might impact the footprint and heating requirement (no calculations required). Which option would you recommend, explain your answer?

Solution:

Reactor sizing is based on the SRT required to recover 80% of available methane potential. For a plug flow reactor, a first order batch equation is used (Equation 5.5), for a continuous mixed liquor reactor a first order CSTR equation is used (Equation 5.6).

Plug Flow reactor:

Begin with Equation 5.5, and rearrange the equation to target the SRT (t):

$$CH_4 = B_0(1 - e^{-k_{hyd} \cdot t})$$

Rearrange to:

$$t = \ln(1 - CH_4 / B_0) / (-k) = \ln(1 - 0.8) / (-0.14/d) = 11.5 \text{ days}$$

The initial mass of waste is 60 metric tons per day at a solids concentration of 21% TS, the waste needs to be diluted to 15% TS for the plug flow reactor and this will increase the mass to 84 metric tons per day. Assume this is equal to 84 m³ per day to calculate a required reactor volume of 966 m³.

CSTR reactor:

Begin with Equation 5.6, and rearrange the equation to target the SRT (t):

$$CH_4 = B_0 (1 - 1 / (1 + k_{hyd} \cdot t))$$

Can also be written as:

$$CH_4 / B_0 = (1 - 1 / (1 + k_{hyd} \cdot t))$$

Substitute in known values:

$$0.8 = (1 - 1 / (1 + t \cdot 0.14 \text{ d}^{-1}))$$

Rearrange this equation as solve for SRT (t) to get 28.6 days. The initial mass of waste is 60 metric tons per day at a solids concentration of 21% TS, the waste needs to be diluted to 5% TS for the continuous mixed liquor reactor and this will increase the mass to 252 metric tons per day. Assume this is equal to 252 m³ per day to calculate a required reactor volume of 7207 m³.

Note: in this application, the continuous mixed liquor process would be more than 7 times larger than the plug flow reactor. As a consequence, the plug flow reactor would occupy a smaller footprint and would have lower heat loss to the environment. More information would be required about specific reactor materials and geometry to calculate actual energy savings.

CHAPTER 6

Exercises

Exercise 6.1. If you have an anaerobic digester with an infinite volume, resulting in an infinite residence time for the substrate, would you produce more methane under mesophilic or thermophilic temperatures? Discuss the reason

Solution:

Methane production would be the same under mesophilic or thermophilic temperatures, because faster kinetics of thermophilic temperatures would not make a difference if the residence time of the substrate in the reactor is infinite.

Exercise 6.2. Why is there a thermodynamic advantage of anaerobic digestion as compared to other types of fermentation?

Solution:

Because as opposed to any other type of fermentation, AD produces methane and carbon dioxide as the final products, which have the most reduced and oxidized forms of carbon, respectively. This way, the microbiome is essentially harvesting all the energy that possibly can from the organic substrate, and evidently more than it would if the final products were lactate, ethanol, etc.

Exercise 6.3. A large dairy farm is using anaerobic digestion to produce biogas from cattle manure with a capacity of $6E6 \text{ m}^3 \cdot \text{yr}^{-1}$. The farm is considering adding a PSA system to convert the biogas into biomethane, which qualifies for renewable energy credits. However, their biogas contains 450 ppm(v) of hydrogen sulfide (H_2S), which is detrimental to the adsorption column (e.g., it forms irreversible bonds with the sorbent), and needs to be removed prior to PSA. A local industry produces iron-oxide impregnated wood chips, which could be used as a H_2S scrubbing material. The absorptive capacity of the wood chips is related to its iron oxide content, which is $190 \text{ kg Fe}_2\text{O}_3 \cdot \text{m}^{-3}$. To complete their economic analysis of the proposed system, they need to calculate the amount of wood chips required for H_2S scrubbing. Calculate the annual consumption of wood chips in cubic meters. Assume the wood chips have a 90% capacity factor relative to the theoretical maximum absorption. Note: the molecular weight of $\text{Fe}_2\text{O}_3 = 159.687 \text{ g} \cdot \text{mol}^{-1}$, and $\text{H}_2\text{S} = 34.1 \text{ g} \cdot \text{mol}^{-1}$.

Solution:

Determine the stoichiometric relationship of the solid-state absorption reaction:



Use the stoichiometric relationship to calculate the theoretical maximum absorption capacity of the wood chips:

$$(3 \text{ mol H}_2\text{S} / 1 \text{ mol Fe}_2\text{O}_3) * (34.1 \text{ g} \cdot \text{mol}^{-1} / 159.687 \text{ g} \cdot \text{mol}^{-1}) = 0.64 \text{ g H}_2\text{S} / \text{g Fe}_2\text{O}_3$$

Determine the annual quantity of H_2S contained in the produced biogas:

$$(6E6 \text{ m}^3 \cdot \text{yr}^{-1}) * (4.5E-4 \text{ m}^3 \text{ H}_2\text{S} \cdot \text{m}^{-3} \text{ biogas}) = 2700 \text{ m}^3 \text{ H}_2\text{S} \cdot \text{yr}^{-1}$$

Convert H_2S volume to H_2S mass assuming $22.4 \text{ L} \cdot \text{mol}^{-1}$ for an ideal gas:

$$(2700 \text{ m}^3 \text{ H}_2\text{S} \cdot \text{yr}^{-1}) / (0.0224 \text{ m}^3 \cdot \text{mol}^{-1}) * (34.1 \text{ g} \cdot \text{mol}^{-1}) = 4.11E6 \text{ g H}_2\text{S} \cdot \text{yr}^{-1} = 4110 \text{ kg H}_2\text{S} \cdot \text{yr}^{-1}$$

Calculate the mass of wood chips required per year at a 90% capacity factor:

$$(4110 \text{ kg H}_2\text{S} \cdot \text{yr}^{-1}) / (0.9 * 0.64 \text{ kg H}_2\text{S} / \text{kg Fe}_2\text{O}_3) = 7135 \text{ kg Fe}_2\text{O}_3 \cdot \text{yr}^{-1}$$

Finally, calculate the volume of wood chips:

$$7135 \text{ kg Fe}_2\text{O}_3 \cdot \text{yr}^{-1} / 190 \text{ kg Fe}_2\text{O}_3 \cdot \text{m}^{-3} = 37.6 \text{ m}^3 \cdot \text{yr}^{-1}$$

Exercise 6.4. A dairy farm with 3,000 cows has a manure waste flow of 500 m³/d (10% solids). The total organic carbon (TOC) concentration in manure is 60 g/L. The hydraulic retention time (HRT) in AD is 20 days. The TOC removal efficiency in AD is 80% and for each kg of TOC removed, the digester generates 0.25 m³ of CH₄. The residual TOC is then subjected to hydrothermal liquefaction (HTL), which converts 60% of the carbon into bio-crude oil carbon. Assume manure has the density of water.

- A) What should be the size of the AD?
- B) What is the CH₄ production per unit of digester?
- C) What is the effluent carbon flow from the AD to HTL?
- D) How much carbon (as CH₄ and bio-crude oil) can be recovered per cow per day.
- E) Describe the advantages and disadvantages for each one of the following integration:
 - 1) TH-AD; and 2) AD-HTL.

Solutions:

A. $V (m^3) = Q (m^3/day) \times \theta (day) = 500 \times 20 = 10,000 m^3$

B. $Q_m = QEMS_{in} = 500 m^3/d \times 0.8 \times 0.25 m^3/kg \times 0.06 kg/L \times 1000 L/m^3 = 6000 m^3 CH_4/d$

C. $Q_c = Q (TOC_{in} - TOC_{removed}) = 500 m^3/d \times 12 g/L \times 1000 L/m^3 \times 1 kg/1000 g = 6000 kg TOC/d$

D. $Q_m = 6000 m^3 CH_4/day \div 3000 cows = 2 m^3 CH_4 day/cow$

$Q_{oil} = 0.6 \times 6000 kg TOC/day \div 3000 cows = 1.2 kg TOC/day/cow$

E. (1.1) advantages of TH-AD: a) increasing the loading rates; b) increasing the rate of biogas production; c) improving the dewaterability of the sludge; and d) sterilization of the sludge.

(1.2) disadvantages of TH-AD: a) higher rates of proteins decomposition might increase the free ammonia concentrations; b) higher operation costs (comparing to AD alone).

(2.1) advantages of AD-HTL: a) additional valuable product (bio-oil); b) shorter thermal conversion process; c) higher total conversion of waste carbon.

(2.2) disadvantages of AD-HTL: a) at higher HTL temperatures aqueous phase might be toxic for further reuse; b) higher operation costs (comparing to AD alone).

Exercise 6.5. Calculate the composition of the product gas leaving the P2G bioreactor, if pure carbon dioxide (no biogas) is introduced with hydrogen at a ratio of 1:4 and assuming that (i) 25%, (ii) 50%, (iii) 75%, or (iv) 100% of the carbon dioxide are consumed by biomethanation. All the water generated by methanation can be assumed to remain as liquid.

Solution:

CO ₂ conversion (%)	Product gas composition		
	Hydrogen (%)	Carbon dioxide (%)	Biomethane (%)
25	75.00	18.75	6.25
50	66.66	16.66	16.66
75	50.00	12.50	37.50
100	0.00	0.00	100.00

Exercise 6.6. A) Compare power-to-methane and power-to-hydrogen and name two advantages of each technology; and B) Can you think of reasons, why the hydrogen content in the natural gas grid is restricted?

Solution:**A)**

power-to-methane	<ul style="list-style-type: none"> Methane infrastructure is well-established (storage, natural gas grid, combustion processes and engines for transport and mobility applications) Additional decarbonization possible, due to carbon dioxide conversion.
power-to-hydrogen	<ul style="list-style-type: none"> Higher efficiency for overall conversion from electricity to gas (no losses of second process step methanation). Fewer process steps and components, resulting in lower cost.

B)

- Lower heating value compared to methane Not compatible with all combustion processes and applications designed for natural gas.
- Hydrogen diffusion through many materials due to low molecule size Storage problem.

Exercise 6.7. Performing electrolysis in an electrolyte solution (50 mL) that contains 1 M NaOH by passing 1mmol e⁻,

- Discuss which species will be oxidized at the anode based on the standard reduction potential, OH⁻ ions or water?
- Calculate how much oxygen will be produced at the anode?
- Discuss which species will be reduced at the cathode based on the standard reduction potential, Na⁺ ions or water (assuming H⁺ reduction is negligible)?
- Calculate how much hydrogen will be produced at the cathode?

Solution:

- $O_2(g) + 2H_2O + 4e^- \leftrightarrow 4OH^-(aq) \quad E^0 = +0.401 V$
 $O_2(g) + 4H^+ + 4e^- \leftrightarrow 2H_2O \quad E^0 = +1.229 V$
 Higher reduction potential of oxygen to OH⁻ than that to H₂O indicates higher favourability of OH⁻ oxidation than H₂O, and therefore OH⁻ will be oxidized at the anode to produce O₂.
- The stoichiometric ratio of e⁻ to O₂ is 4 to 1, and therefore passing 1mmol e⁻ yields 0.25 mmol O₂.
- $2H_2O + 2e^- \leftrightarrow H_2(g) + 2OH^-(aq) \quad E^0 = -0.8277 V$
 $Na^+ + e^- \leftrightarrow Na(s) \quad E^0 = -2.71 V$
 Higher reduction potential of H₂O indicates a higher reduction favourability of H₂O at the cathode than that of Na⁺, and therefore H₂O will be reduced to produce H₂.
- The stoichiometric ratio of e⁻ to H₂ is 2 to 1, and therefore passing 1mmol e⁻ yields 0.5 mmol H₂.

Exercise 6.8. Considering the information you have from this chapter and given that $\Delta G = \Delta H - T \cdot \Delta S$, conclude whether the change in Gibb's free energy is more negative at 37°C or at 65°C for hydrogenotrophic methanogenesis? Evaluate what this implies for the maximum biomass yield per methane of thermophilic hydrogenotrophic methanogens compared to mesophilic species?

Solution:

The entropy term is negative and the reaction is exothermic (negative entropy term). At a higher temperature (65°C) the term $T \cdot \Delta S$ will be more negative overall, and thus the Gibb's free energy will be less negative compared to lower temperature (37°C).

The maximum energy that can be „harvested“ per molecule of methane produced is, therefore, smaller, and more methane has to be produced to achieve the same biomass yield. Or, in other words, the biomass yield per methane is lower for thermophilic hydrogenotrophic

methanogens. This seems to be opposing the conclusion that a biomethanation process should be operated under thermophilic conditions. However, biomass yield is not the goal of the biomethanation process, and biological rates are still higher at elevated temperatures. Furthermore, with a lower biomass yield, less carbon is „lost“ to biomass, which is what we really want.

Additional discussion through questions

Question 6.9: Is it possible to avoid the formation of carbon dioxide by biological means? How would you do it?

Solution:

There's no right or wrong answer here, since it's meant for discussion, but the following bullet points could be addressed here by the students:

- Would they operate with biogas or purified CO₂? Where do they see the pros and cons?*
- Integration of process-heat from electrolysis and methanation into anaerobic digester, heating of WWTP buildings, etc.*
- Usage of electrolytic oxygen to improve aerobic processes of WWTP.*
- Injection of biomethane into the gas grid? Or would they build a gas station for cars? Or even something different?*

Question 6.10: In each of the technologies described in this chapter, carbon dioxide was considered a valueless by-product. However, given that many of the off-streams have been enriched in CO₂, should these off-streams really be considered valueless? Can you think of a particular application where this CO₂ maybe be useful? If so, which biogas upgrading technology would be the most advantageous for the proposed application?

Solution:

This question is more open-ended question with several possible answers.

Question 6.11: As the lead engineer of a WWTP, you are in charge to integrate a P2G system to treat the biogas stream (50% carbon dioxide, 50% methane) of the WWTP's anaerobic digester. You are asked to give a presentation to the board of directors in which you provide a concept on how the process will be integrated with all its mass and energy streams into the WWTP's infrastructure. Can you identify synergistic effects?

Solution:

This question is more open-ended question with several possible answers.

Question 6.12: After reading about the thermophilic methanogens,

A) Do you think the thermophilic character of *M. thermautotrophicus* is an advantage or disadvantage for biomethanation applications?

B) Which are the only substrates that *M. thermautotrophicus* can metabolize?

C) Do you need to add a carbon source to the growth medium of *M. thermautotrophicus*? If yes, which one. If no, why not?

Solution:

- A) It is an advantage because of: 1) higher rates of methane production per reactor volume; 2) less change for microbial contamination; 3) better methane degassing; and 4) at room temperature, the culture is dormant and can be stored easily.*
- B) CO₂, H₂, and formate is ok as well.*
- C) The answer is no: M. thermautotrophicus is a chemolithoautotrophic microbe that uses non-organic carbon sources, such as CO₂ or formate, as its sole energy and carbon source.*

Question 6.13: With the biochemical reaction of carbon dioxide and hydrogen gas into methane and water at a high production rate, would you need to heat or cool the reactor if you want to operate at a temperature of 65°C, and why?

Solution:

You would need to cool, because the reaction of H_2 and CO_2 to CH_4 and H_2O is exergonic.

Question 6.14: Can you think of another way to convert a liquid into a gas besides vaporization?

Solution:

Electrolysis.

CHAPTER 7

Exercise 7.1. Hydrolysis is the rate-limiting step in anaerobic conversions, and is usually described using a first order kinetic (see Eq. 7.1). Assuming a substrate with an initial solids concentration of $30 \text{ g COD}\cdot\text{L}^{-1}$ and an anaerobic hydrolysis constant of 0.1 d^{-1} , how long should the HRT of a reactor be to ensure at least 85% substrate conversion?

Solution:

Starting from equation 7.1:

$$dF/dt = -k_h \cdot F$$

1. Rearrange the equation
 $dF/F = -k_h \cdot dt$
2. Integrate this first order derivative.
 - a. $\int dF/F = \int -k_h \cdot dt$
 - b. $\ln F - \ln F_o = -k_h \cdot t$
 - c. $\ln(F/F_o) = -k_h \cdot t$
 - d. $F = F_o \cdot e^{-k_h \cdot t}$
3. From step 2c
 - a. $\ln(F/F_o) = -k_h \cdot t$
 - b. $\ln(30 \cdot 0.85 / 30) = -0.1 \cdot t$
 - c. $\ln(0.85) = -0.1 \cdot t$
 - d. $-0.16 = -0.1 \cdot t$
 - e. $t = 1.6 \text{ d}$

Exercise 7.2. Calculate the ATP yield of a lactic acid fermentation of 1 kg glucose [$\text{mol ATP}\cdot\text{kg glucose}^{-1}$], according to the information provided in Table 3. If a wastewater contains $30 \text{ g glucose}\cdot\text{L}^{-1}$, how much energy can be potentially harvested by microorganisms performing such fermentation [$\text{mol ATP}\cdot\text{L}^{-1}$]?

Solution:

1. Calculate ATP per kg of glucose
 - a. According to Table 2, 2 moles of ATP are produced per mol of glucose
 - b. 1 mole of glucose = 160 g (based on its molecular weight)
 - c. Determine mol ATP per kg = $2 \text{ mol ATP}\cdot\text{mol glucose}^{-1} \cdot 1000 \text{ g}\cdot\text{kg}^{-1} / 160 \text{ g glucose}\cdot\text{mol glucose}^{-1} = 12.5 \text{ mol ATP kg}^{-1} \text{ glucose}$
2. Calculate energy generated per L of wastewater
 - a. Convert kg to g: $12.5 \text{ mol ATP}\cdot\text{kg}^{-1} \text{ glucose} / 1000 \text{ g}\cdot\text{kg}^{-1} \text{ glucose} = 0.0125 \text{ mol ATP}\cdot\text{g}^{-1} \text{ glucose}$
 - b. Calculate for the wastewater: $30 \text{ g glucose}\cdot\text{L}^{-1} \cdot 0.0125 \text{ mol ATP}\cdot\text{g}^{-1} \text{ glucose} = 0.375 \text{ mol ATP}\cdot\text{L}^{-1}$

Exercise 7.3. A continuous stirred tank reactor (CSTR) of 50 m^3 of volume treating industrial wastewater is operated at a hydraulic retention time of 4 days. If the concentration of organic matter in the wastewater is $45 \text{ g COD}\cdot\text{L}^{-1}$, what is the organic loading rate of the system [$\text{g COD}\cdot\text{L}^{-1}\cdot\text{d}^{-1}$]? If the biomass concentration in your reactor is $5 \text{ g VSS}\cdot\text{L}^{-1}$, what is then your F/M ratio [$\text{Kg COD}\cdot\text{Kg VSS}^{-1}\cdot\text{d}^{-1}$]?

Solution:

1. Calculate the organic loading rate
 - a. The organic loading rate (OLR) can be calculated as $\text{OLR} = \text{Concentration} \cdot \text{Q/V}$, which is equivalent to $\text{OLR} = \text{Concentration}/\text{HRT}$

b. $OLR = 45 \text{ g COD}\cdot\text{L}^{-1} / 4 \text{ days} = 11.25 \text{ g COD}\cdot\text{L}^{-1}\cdot\text{d}^{-1}$

2. Calculate the F/M ratio

a. Divide your OLR by the biomass concentration in your reactor

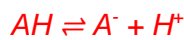
b. $F/M \text{ ratio} = 11.25 \text{ g COD}\cdot\text{L}^{-1}\cdot\text{d}^{-1} / 5 \text{ g VSS}\cdot\text{L}^{-1}$

c. $F/M \text{ ratio} = 2.25 \text{ g COD} / \text{g VSS}\cdot\text{d}^{-1} = 2.25 \text{ kg COD} / \text{kg VSS}\cdot\text{d}^{-1}$

Exercise 7.4. In a given fermentation process, carbohydrate-rich wastewater is fermented to either: i) lactic acid; or ii) propionic acid. Calculate the NaOH requirements as $\text{meq OH}^{-}\cdot\text{mol}^{-1}$ acid produced and $\text{kg NaOH}\cdot\text{kg}^{-1}$ acid produced for each scenario at two operational pHs, 5.5 and 7. The pK_a of lactic acid and propionic acid are 3.85 and 4.87 respectively.

Solution:

1. Lactic acid and propionic acid are weak organic acids that are partially dissociated at mildly acidic pHs.



2. Their speciation can be calculated according to the formula:

$$K_a = [A^{-}][H^{+}] / [AH], \text{ all in mol}\cdot\text{L}^{-1}$$

3. K_a can be obtained from the pK_a according to the formula:

$$K_a = 10^{-(pK_a)}$$

4. For a given pH the concentration of H^{+} can be calculated as:

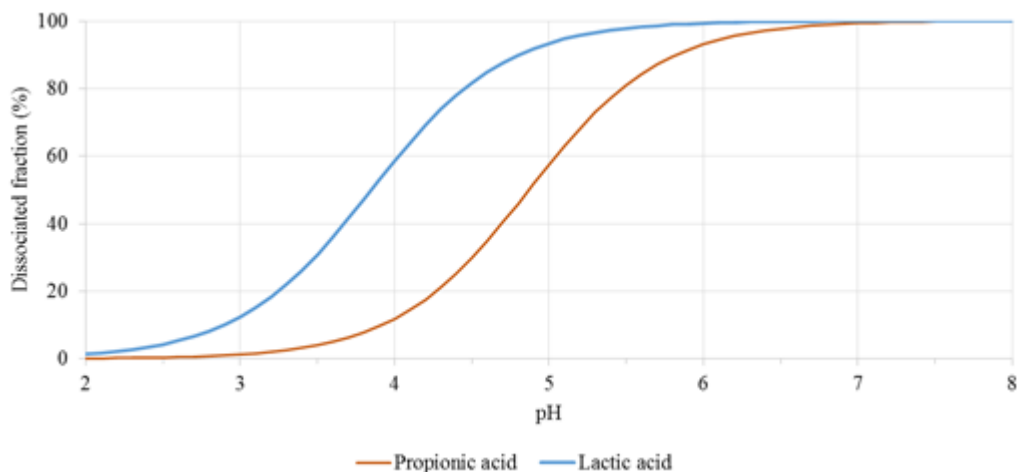
$$[H^{+}] = 10^{-(pH)}$$

5. The concentrations at equilibrium at a given pH can be calculated based on the pK_a and concentration of protons according to the formula given in step 2.

6. Based on the concentrations of each fraction, one can calculate the fraction of the acid that is dissociated (or undissociated). For the dissociated fraction one can use the following formula:

$$\text{fraction that is dissociated (\%)} = ([H^{+}] / ([AH] + [H^{+}])) \times 100$$

7. From this information one can construct the following dissociation curves for propionic and lactic acid.



8. At pH 5.5, the dissociated fractions of propionic and lactic acid are 81% and 98%, respectively. At pH 7, the dissociated fractions of propionic and lactic acid are 99% and 100%, respectively.

9. Calculations at pH 5.5

- a. Propionic acid: out of every mole produced, 81% will dissociate and will require base addition to keep the pH at the same level (ignoring buffering). Therefore 0.81 meq $\text{OH}^- \cdot \text{mol}^{-1}$ acid produced will need to be added.

Considering molar weights of 74 and 40 g/mol for propionic acid and NaOH, respectively:

$$\text{kg NaOH} \cdot \text{kg}^{-1} \text{ propionic acid produced} = 0.81 \text{ meq OH}^- \cdot \text{mol}^{-1} \text{ acid} * 0.04 \text{ kg meq OH}^{-1} / 0.074 \text{ kg propionic acid} \cdot \text{mol}^{-1} \text{ acid} = 0.44 \text{ kg NaOH} \cdot \text{kg}^{-1} \text{ propionic acid produced}$$

- b. Lactic acid: out of every mole produced, 98% will dissociate and will require base addition to keep the pH at the same level (ignoring buffering). Therefore 0.98 meq $\text{OH}^- \cdot \text{mol}^{-1}$ acid produced will need to be added.

Considering molar weights of 90 and 40 g/mol for propionic acid and NaOH, respectively:

$$\text{kg NaOH} \cdot \text{kg}^{-1} \text{ lactic acid produced} = 0.98 \text{ meq OH}^- \cdot \text{mol}^{-1} \text{ acid} * 0.04 \text{ kg meq OH}^{-1} / 0.090 \text{ kg lactic acid} \cdot \text{mol}^{-1} \text{ acid} = 0.44 \text{ kg NaOH} \cdot \text{kg}^{-1} \text{ lactic acid produced}$$

10. Calculations at pH 7

- a. Propionic acid: out of every mole produced, 99% will dissociate and will require base addition to keep the pH at the same level (ignoring buffering). Therefore 0.99 meq $\text{OH}^- \cdot \text{mol}^{-1}$ acid produced will need to be added.

Considering molar weights of 74 and 40 g/mol for propionic acid and NaOH, respectively:

$$\text{kg NaOH} \cdot \text{kg}^{-1} \text{ propionic acid produced} = 0.99 \text{ meq OH}^- \cdot \text{mol}^{-1} \text{ acid} * 0.04 \text{ kg meq OH}^{-1} / 0.074 \text{ kg propionic acid} \cdot \text{mol}^{-1} \text{ acid} = 0.53 \text{ kg NaOH} \cdot \text{kg}^{-1} \text{ propionic acid produced}$$

- b. Lactic acid: out of every mole produced, 100% will dissociate and will require base addition to keep the pH at the same level (ignoring buffering). Therefore 1 meq $\text{OH}^- \cdot \text{mol}^{-1}$ acid produced will need to be added.

Considering molar weights of 90 and 40 g·mol⁻¹ for propionic acid and NaOH, respectively:

$$\text{kg NaOH} \cdot \text{kg}^{-1} \text{ lactic acid produced} = 1 \text{ meq OH}^- \cdot \text{mol}^{-1} \text{ acid} * 0.04 \text{ kg meq OH}^{-1} / 0.090 \text{ kg lactic acid} \cdot \text{mol}^{-1} \text{ acid} = 0.44 \text{ kg NaOH} \cdot \text{kg}^{-1} \text{ lactic acid produced}$$

Exercise 7.5. A food and beverage industry produces daily a wastewater flow of 250 m³, containing 27 g·L⁻¹ COD, of which 87% is biodegradable. Calculate what would be the maximum annual caproic acid production if all organic material can be selectively converted to it. Assume that 5% of the bCOD ends up in biomass.

Solution:

1. Calculate COD flux = flow * concentration = $250 \text{ m}^3 \cdot \text{d}^{-1} * 27 \text{ kg COD} \cdot \text{m}^{-3} = 6750 \text{ kg COD} \cdot \text{d}^{-1}$
2. Convert COD into bCOD = $6750 \text{ kg COD} \cdot \text{m}^{-3} * 0.87 = 5873 \text{ kg bCOD} \cdot \text{d}^{-1}$
3. Calculate the daily MCCA production in bCOD = $5873 \text{ kg bCOD} \cdot \text{d}^{-1} * 0.95 = 5579 \text{ kg bCOD-C6} \cdot \text{d}^{-1}$
4. Determine the bCOD of caproic acid
 - a. Establish the electrons present in caproic acid based on the formula $\text{C}_6\text{H}_{12}\text{O}_2 + 10\text{H}_2\text{O} \rightarrow 6\text{CO}_2 + 32\text{e}^- + 32\text{H}^+$
 - b. Determine the bCOD based on the fact that 4 mole electrons equal 1 mol (b)COD
 - c. 1 mol caproic acid = 8 mol bCOD
5. Convert bCOD-C6 into kg C6 = $5579 \text{ kg bCOD-C6} \cdot \text{d}^{-1} * 1 \text{ mol bCOD} \cdot 0.032 \text{ kg bCOD}^{-1} * 1 \text{ mol C6} \cdot 8 \text{ mol bCOD-C6}^{-1} * 0.116 \text{ kg C6} \cdot \text{mol C6}^{-1} = 2528 \text{ kg C6} \cdot \text{d}^{-1}$
6. Calculate annual production based on 365 days = $2528 \text{ kg C6} \cdot \text{d}^{-1} * 365 = 923 \text{ tonnes C6/year}$

Exercise 7.6. Caproic acid is produced at a rate of $0.7 \text{ g} \cdot \text{L}^{-1} \cdot \text{h}^{-1}$ in a CSTR operated at an HRT of 2 days. What should be the caproic acid extraction rate [$\text{g} \cdot \text{L}^{-1} \cdot \text{h}^{-1}$] to ensure a concentration at the effluent below $1 \text{ g caproic acid} \cdot \text{L}^{-1}$?

Solution:

1. Make a balance of the system
 - a. Concentration in the broth = (rate of production – rate of extraction) * HRT
 - b. Concentration in the broth = $1 \text{ g} \cdot \text{L}^{-1} = (0.7 \text{ g} \cdot \text{L}^{-1} \cdot \text{h}^{-1} - \text{rate of extraction}) * 2 \text{ days} * 24 \text{ h} \cdot \text{d}^{-1}$
 - c. Rate of extraction = $0.68 \text{ g} \cdot \text{L}^{-1} \cdot \text{h}^{-1}$

Exercise 7.7. A fermentation broth contains $10 \text{ g butyric acid} \cdot \text{L}^{-1}$ and $5 \text{ g caproic acid} \cdot \text{L}^{-1}$. Assuming pka of 4.82 and 4.88, respectively, calculate the concentration of their undissociated form at a pH of 5.5 and 7. By which factor should we concentrate this stream to allow their recovery by phase separation?

Solution:

1. We can use the same approach as in Exercise 4 to calculate the concentration of the different dissociated and undissociated compounds. To calculate the undissociated fraction one can use the following formula:

$$\text{fraction that is undissociated (\%)} = \left(\frac{[\text{AH}]}{([\text{AH}] + [\text{H}^+])} \right) \times 100$$

2. At pH 5.5:
 - a. The fractions of undissociated butyric and caproic acid are 17% and 19%, respectively.
 - b. Based on their total concentrations in solution, one can calculate the concentration of the undissociated fractions.
 - c. Butyric acid undissociated concentration = $10 \text{ g butyric acid} \cdot \text{L}^{-1} * 0.17 = 1.7 \text{ g undissociated butyric acid} \cdot \text{L}^{-1}$.
 - d. Caproic acid undissociated concentration = $5 \text{ g butyric acid} \cdot \text{L}^{-1} * 0.19 = 0.95 \text{ g undissociated caproic acid} \cdot \text{L}^{-1}$.
 - e. The maximum solubility in water of butyric and caproic acid(s) can be found in Section 7.4.2.1. Butyric acid is fully miscible in water and therefore cannot be phased separated. Caproic acid has a maximum water solubility of $10.8 \text{ g} \cdot \text{L}^{-1}$. To start recovering caproic acid from our solution by phase separation we would need to up-concentrate it by a factor of 11.4.

3. At pH 7:

- The fractions of undissociated butyric and caproic acid are both 1%. Since we have seen that butyric acid cannot be phased separated in step 2, we will not further discuss it.
- Caproic acid undissociated concentration = $5 \text{ g butyric acid} \cdot \text{L}^{-1} * 0.01 = 0.05 \text{ g undissociated caproic acid} \cdot \text{L}^{-1}$.
- To start recovering caproic acid from our solution by phase separation at pH 7 we would need to upconcentrate it by a factor of 216.

Exercise 7.8. A dairy industry has invested in a process to convert their wastewater streams ($200 \text{ m}^3 \cdot \text{d}^{-1}$) into MCCA, which consists of a continuous stirred bioreactor coupled to an in-line extraction system ($V=100 \text{ m}^3$). Caproic acid is the dominant end product and it is produced at a rate of $0.5 \text{ g} \cdot \text{L}^{-1} \cdot \text{h}^{-1}$. The reactor pH is controlled at 5.5 and extraction is set in a way that the caproic acid concentration in solution is always equal or below $1 \text{ g} \cdot \text{L}^{-1}$. A process issue results in a failure in the extraction system, but does not affect the bioreactor operation. As a result, caproic acid accumulates in the system. If we assume that the impact of caproic acid toxicity can be described using a non-competitive inhibition term and the K_i for this specific microbial community is $0.15 \text{ g} \cdot \text{L}^{-1}$, how would activity be reduced if extraction is stopped for 24 hours. For the sake of simplicity, assume that production rate will remain unaffected during that period.

Solution:

- Make a caproic acid mass balance of the system:

$$C_i n + 1 = C_i n + dC/dt$$

$$dC/dt = -Q_{out}V \cdot C + r$$

Where

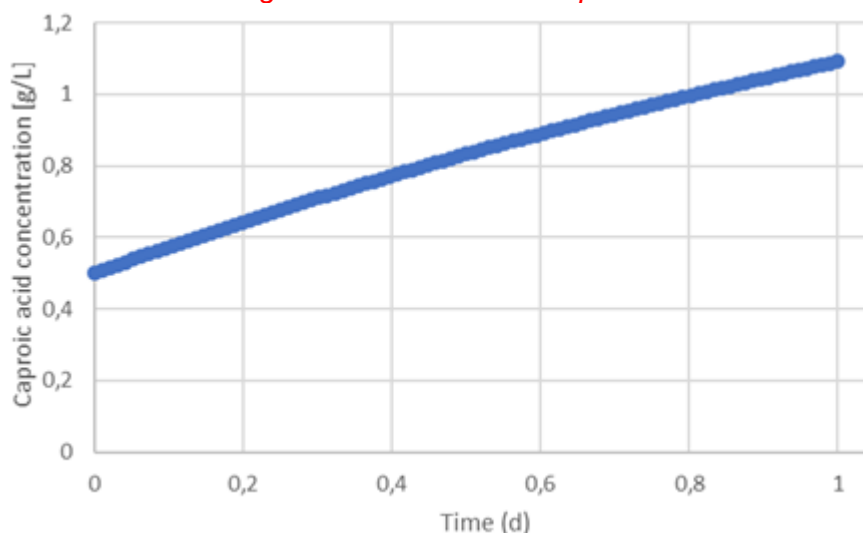
C_t is the concentration of caproic acid at a given time

dC/dt is the change in concentration of caproic acid as a function of time

$-Q_{out}V \cdot C$ is the amount of caproic acid leaving the system via the outflow

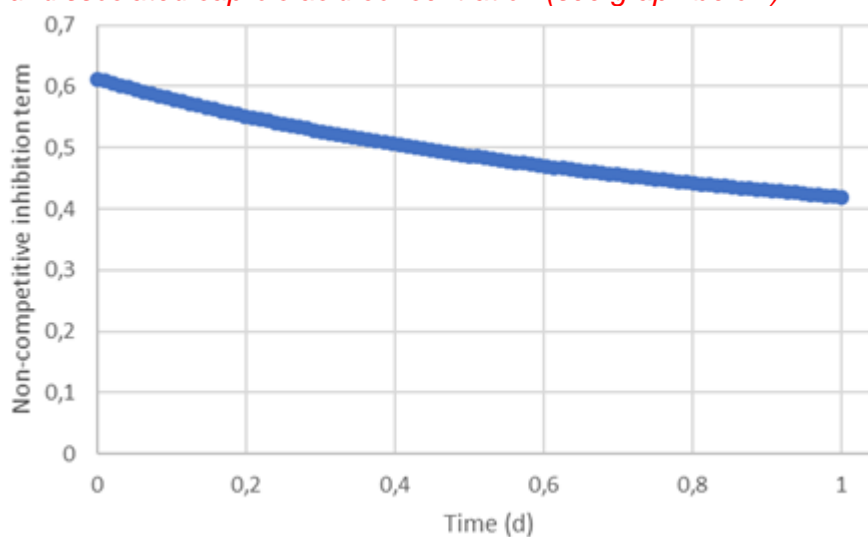
r is the caproic acid production rate

- Determine the change in concentration of caproic acid as a function of time.



- Calculate the concentration of undissociated caproic at pH 5.5. This can be easily determined by using the information of Exercise 7. At pH of 5.5, 19% of the caproic acid is in its undissociated form, therefore you only need to multiply the concentrations obtained in Step 2 by 0.9.

4. Determine the value of the non-competitive inhibition term as a function of the undissociated caproic acid concentration (see graph below).



5. Compare the value of the term at t_0 and t_{24h} . Its initial value is 0.61 and at 24h 0.42. This means that the observed activity would be reduced by approximately 30%. Please bear in mind that here we assumed the production rate was unaffected to avoid overcomplicating the exercise.

Exercise 7.9. A bio-production plant consist of fermentation and downstream processing. The fermentation step has a yield of 4 mmol propionic acid·g COD⁻¹. The propionic acid in the fermentation broth can be recovered with a 75% efficiency. If we want to produce 100 tonne propionic acid·d⁻¹, what should be the substrate loading [tonne COD·d⁻¹]?

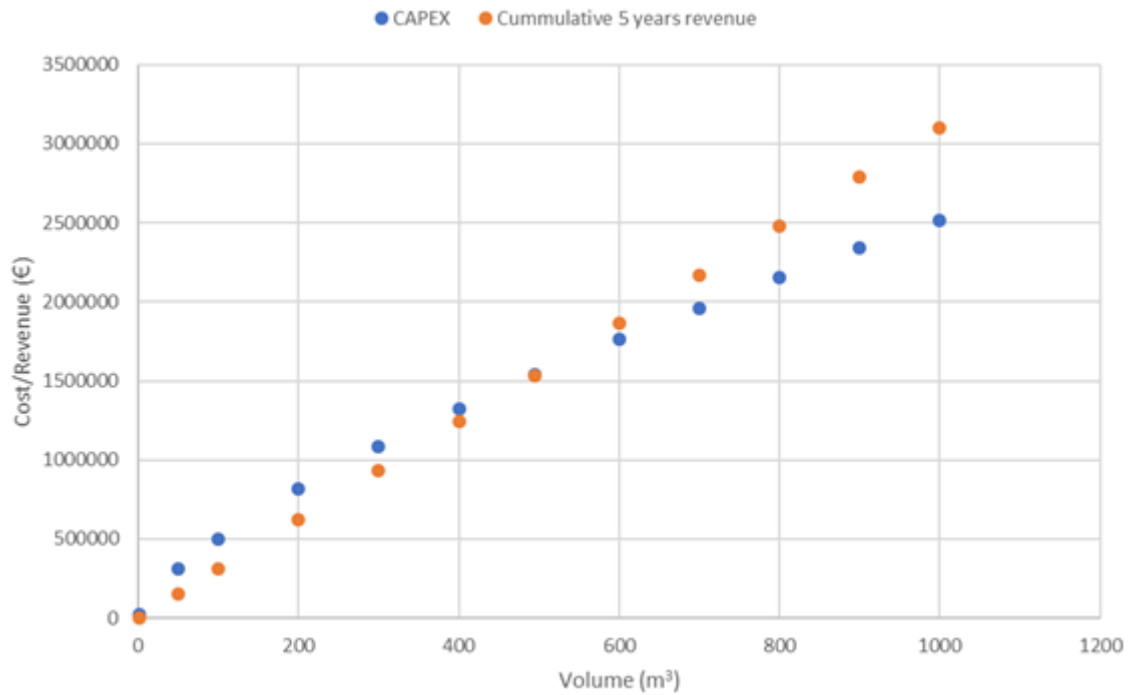
Solution:

1. Taking the target production as starting point we can calculate the substrate loading following the next steps:
 - a. Propionic acid to be produced in the reactor [tonne propionic acid·d⁻¹] = tonne recovered [tonne propionic acid·d⁻¹] / recovery efficiency = 100/0.75 = 133.3 tonne propionic acid·d⁻¹
 - b. Propionic acid produced in the reactor [in mol propionic acid·d⁻¹] = tonne produced * conversion factor from tonne to gram / molar mass of propionic acid = 133.3 * 1,000,000 / 74 = 1,801,801 mol propionic acid·d⁻¹
 - c. Substrate loading = propionic acid produced * conversion factor from mol to mmmol * yield * conversion factor from g COD to tonne COD = 1,801,801 * 1000 / 4 * 1,000,000 = 450.5 tonne COD·d⁻¹

Exercise 7.10. The size of an installation determines the investment needed, although often not in a linear manner. Larger installations are comparatively cheaper than smaller plants when one takes into consideration the cost per unit of volume. This is usually described using a scaling law of the formula: $Cost_2 = Cost_1 \cdot (Size_2/Size_1)^a$, where $Cost_1$ is the cost to build a certain installation of $Size_1$, and $Cost_2$ is the cost to build it at a different scale, $Size_2$. This costs are related by a parameter a , which reflects the linearity in scale-up cost. Imagine that constructing a 1m³ installation to produce and extract a mixture of SCCA (acetic, butyric and propionic acids) costs €20,000. Assuming an a of 0.7, a unit production of 1 tonne SCCA·m⁻³·d⁻¹, a selling price of €1700·tonne⁻¹, what should be the plant size to reach break-even in 5 year.

Solution:

1. Plot the cost and revenue over 5 years period as a function of the plant capacity (m^3)



2. Determine the intersect, which defines the break-even size after 5 years of operation. In this case the volume of the plant (including all pre- and post-processing equipment) is $495 m^3$.

CHAPTER 8

Exercise 8.1. A centralized municipal wastewater treatment plant services a city of 750,000 inhabitant equivalents. In order to improve the sustainability of urban wastewater management of the city, the city council has raised the recovery of cellulose from municipal wastewater through micro-sieves as one of the priority resources. Based on a toilet paper usage of 10 kg toilet paper/person/year (i.e. typical consumption in Western European countries):

- Calculate the amount of cellulose that can be recovered at the WWTP on a daily and annual basis at a practical relevant cellulose recovery efficiency of a micro-sieve unit of 80%. For the sake of simplicity assume that toilet paper is 100% cellulose.
- Calculate the theoretical amount of methane (in m³) that can be generated from the amount of cellulose embedded in the wastewater matrix when not being recovered as cellulose but being fed to an anaerobic digestion. Assume that the COD content of cellulose is equal to 1.1 gram COD/gram cellulose, that the cellulose can be fully degraded during mesophilic anaerobic digestion, and that 0.5 m³ methane are produced per kg of COD converted.
- Assuming that 1 m³ of biogas is equivalent to 6.27 kWh, that the conversion of methane to electricity in a CHP unit is 40% and the electricity consumption of a household of 4 people is 20 kWh/day, how many households can theoretically be powered from the produced electricity from the anaerobic digestion of cellulose.

Solution:

- Assuming that 100% of the toilet paper is flushed into the toilet;
Annual toilet paper production = 7500 ton/y
Daily toilet paper usage is 10 kg/person/year / 365 d/year = 0.0274 kg/person/d
In the WWTP of the city (750,000 PE); the plant receives (7500 ton/365) x 1000 = 20,548 kg toilet paper/d in the influent
Considering the 80% recovery rate of the microsieving unit;
7500 ton/y x 0.8 = 6000 ton cellulose/y
20,548 kg/d x 0.8 = 16,438 kg cellulose/d can be recovered.*
- 6000 ton cellulose/y x 1.1 = 6600 ton COD/y
Based on complete degradation of cellulose in mesophilic anaerobic digestion;
6600 ton COD/y x 1000 kg/ton x 0.5 m³CH₄/kg COD = 3,300,000 m³/y*
- Daily electricity production = 3,300,000 m³ biogas/y * 6.27 kWh/m³ biogas * 40% efficiency / 365 days/year = 22,675 kWh/d
Number of households = 22,675 kWh/d / 20 kWh/d/household = 1,133.7 = 1,133 households*

Exercise 8.2. In various regions in the world existing WWTPs in urban areas are reaching their maximum capacity in terms of solids and COD load due to increase in population growth within the catchment area of the WWTP during the last decade(s). Some of these WWTPs have serious constraints in terms of available land for extension of the WWTP. In this context, beyond the context of the importance of resource recovery, the implementation of micro-sieves can be of particular interest.

- Based on typical surface loading rates for primary settling tanks and micro-sieves of 1.5-2.5 and 100 m³/m²/hour, respectively, calculate the footprint of primary settling and micro-sieve for a WWTP with a capacity of 500,000 PE. Assume a wastewater production of 120 L/PE/d.
- Based on your answer in a), what is the percentage in land space saving that can be achieved?
- Compare this with the overall size of a typical WWTP (tip: use google maps for aerial shot of a WWTP near to where your life).

Solution:

- a) *Hourly water flow = 500,000 PE * 120 L/PE/d /24h/d = 2,500 m³/d
Area primary settler = 2,500 m³/d / 2 m³/ m²/d = 1,250 m²
Area micro-sieves = 2,500 m³/d / 100 m³/ m²/d = 25 m²*
- b) *Percentage of reduction = 98% reduction*
- c) *You can obtain the dimensions of the area occupied by settlers for a given wastewater treatment plant by using the "Measure distance" tool from Google Maps. Typically large wastewater treatment plants (e.g. those servicing > 500,000 inhabitant equivalents) will require surface areas over 10,000 m², but this is plant dependent.*

Exercise 8.3. The Canadian city of Halifax is building an activated sludge system at its main wastewater treatment plant that services 170,000 PE. Two resource recovery strategies are considered for the sludge produced from this treatment facility, the first consists of one-stage anaerobic digestion for methane recovery from biogas and the other is polyhydroxyalkanoate (PHA) recovery through a 3-stage process. The 3-stage PHA process consists of 1) anaerobic sludge fermentation to SCCA, 2) aerobic culture selection through a feast/famine process fed with the effluent of 1), and 3) PHA accumulation from the selected culture in 2) using the effluent of 1). Assume standard (i.e. Table 8.1) wastewater flows and characteristics and that 80 gVSS of sludge are produced per m³ of wastewater treated by the facility. Considering that the value of PHA is \$3.5/kg and that the value of methane is \$0.4/m³, where 1 m³ of biogas (with a methane content of 65%) is produced per kg of VSS, while 0.1kg of PHA are produced per kg of VSS in the 3-stage process:

- a) Determine the relative value of the sludge stream using either the PHA recovery or biogas recovery strategy
- b) Discuss the key factors impacting the capital and operational expenditures associated with biogas or PHA production. Which process is likely to incur higher production costs? Why? What would you consider to be the key points impacting your decision on the process to be implemented?

Solution:

- a) *The flow of wastewater will be 108L/PE/d*170,000 people = 18360m³/d
Sludge production is 80gVSS/m³, so 1469kgVSS/d of sludge is produced
Methane: 0.65*1469=955m³/d produced, with a value of \$0.4/m³, therefore \$382/d are generated
PHA: 0.1*1469=147kgPHA/d, with a value of \$3.5/kg, therefore \$514/d are generated*
- b) *PHA production is more lucrative, but will likely have higher capital costs (more complex process) and higher operational costs (aeration demand) that must be considered in the economic balance. Moreover, in the case of biogas it is directly beneficially reused, while for PHA an end-user/client will need to be found.*

Exercise 8.4. Contrarily to popular belief, a large fraction of the COD load entering WWTPs is in the form of toilet paper, depending on the region in the world. For example, the amount in South American countries is typically much lower as it is often prohibited to flush toilet paper in the toilets as the sewer pipes in the building are not designed for this and as such need to be collected separately in a bin. Let us consider USA, with a consumption of toilet paper of 12.7 kg/person/year.

- a) Calculate the concentration of cellulose based COD assuming a daily water consumption of 200 L/per person per day.
- b) Determine the fraction of COD_{cellulose}/COD_{total} assuming a typical municipal wastewater composition.

Solution:

- a) *12.7 kg/person/year equals to 14 kg COD/person/year since the COD content cellulose equals to 1.1 gram COD/gram cellulose. 14,000g divided by 365 * 200 liter/person/day gives 192 mg COD/L!*
- b) *Assuming a COD_{total} concentration of 500-800 mg COD/L, this equals to about 25-40% of the total COD load of a typical WWTP.*

Exercise 8.5. In various places in the world, the excess waste activated sludge after dewatering is being transported to landfills for ultimate disposal. Moreover, not all WWTPs have implemented primary settling as pre-treatment step, as such, in a typical biological nitrogen removal (or biological P removal) configuration all incoming cellulose enters the activated sludge tanks. According to the Foundation for Applied Water Research (STOWA), depending on the WWTP configuration and local conditions (e.g. wastewater composition, local climate, industrial activities in sewer catchment), about 30-70% of the cellulose is being aerobically converted with an accompanying biomass yield of 0.3 kg sludge/kg COD removed. Assume an annual toilet paper usage of 10 kg/PE, 70% aerobic degradation of cellulose, with a COD of 1.1 kg COD/kg cellulose, consider that 0.44 kg O₂ are needed for degradation of 1 kg of COD, a power consumption for aeration of 2.5 kg O₂/kWh for bubble aeration. Based on the above:

- a) Calculate the energy savings that can be achieved for a WWTP with a capacity of 100,000 PE by implementing microsieves as a pre-treatment step.
- b) Calculate the fraction of the incoming toilet paper that ultimate ends up in landfill (in case this is the ultimate disposal route) in case there is no primary treatment.

Solution:

- a) *The daily toilet paper usage is:
10 kg tp/PE/year / 365 d/year = 0.0274 kg tp /PE/d
Assuming that no degradation of the cellulose in the toilet paper occurs in the sewer system, the WWTP with 100,000 PE capacity receives:
0.0274 kg fibres/PE/d * 100000 PE = 2740 kg cellulose/d
Considering that no primary treatment is implemented, all the cellulose are sent to the biological treatment;
Cellulose can be expressed in COD assuming that 1.1 kg COD/kg cellulose, thus:
2740 kg cell/d x 1.1 kg COD/kg cell = 3014 kg COD/d
If 70% of the cellulose (and thus of the COD) is used for biomass growth, the amount of COD aerobically degraded is:
3014 kg COD/d x 0.7 = 2110 kg COD rem/d
If 0.44 kg O₂ are needed for degradation of 1 kg of COD, thus the daily O₂ requirement is:
2110 kg CODrem/d x 0.44 kg O₂/kg COD = 928 kg O₂/d
Considering the power consumption, the maximum amount of daily kWh saving is:
928 kg O₂/d / 2.5 kg O₂/kWh = 371 kWh/d*
- b) *3014 kg COD/d x 0.3 kg sludge/kg CODinf = 904 kg sludge produced/d*

Exercise 8.6. A pilot-scale WWTP is designed to a fully integrated process to valorize the harvested screenings from municipal wastewater and to produce pure marketable cellulose. In this regard, the plant is equipped with an RBF for enhanced TSS separation and further cellulose recovery. Together with solids, cellulose fibers are separated with RBF and thus recovered. The RBF system works at a flowrate of 30 m³/d.

Calculate the maximum cellulose recovery yield considering that:

- 1) The sludge production after 5 hours is 24 kg;
- 2) The % of TS is 20%.
- 3) The percentage of pure cellulose in the sludge, after a post-treatment of sludge washing (to concentrate the amount of fibers), is 35 % of the cellulosic material;

- 4) The specific recovery yield of the cellulosic material in terms of g VS after washing to g TS initially recovered in the sludge is 0.88 gVS/gTS.

Solution:

The amount of sludge produced in per hour is:

$$\frac{g \text{ sludge}}{h} = \frac{kg \text{ sludge}}{h \text{ of test}} \cdot 1000 \frac{g}{Kg} = \frac{24}{5} \cdot \frac{1000g}{Kg} = 4800 \frac{g \text{ sludge}}{h}$$

Then the grams TS produced in an hour are:

$$\frac{g \text{ TS}}{h} = \frac{g \text{ sludge}}{h} \cdot \frac{TS\%}{100} = 4800 \cdot \frac{20}{100} = 960 \frac{g \text{ TS}}{h}$$

With this value it is possible to calculate the recovered solids per cubic meter of treated wastewater as follows:

$$\frac{g \text{ TS}}{m^3} = \frac{\frac{g \text{ TS}}{h}}{\frac{m^3}{h}} = \frac{960}{30} = 32 \frac{g \text{ TS}}{m^3}$$

With the supposed yield, it is possible to calculate the amount of cellulosic material recovered per cubic meter of treated wastewater as:

$$\frac{g \text{ cell. mat.}}{m^3} = \frac{g \text{ TS}}{m^3} \cdot \frac{g \text{ VS (cell. mat.)}}{g \text{ TS}} = 30.3 \cdot 0.88 = 28.2 \frac{g \text{ cell. mat.}}{m^3}$$

Considering that the cellulose content is 35%, then the recovery of pure cellulose is:

$$\frac{g \text{ pure cellulose}}{m^3} = \frac{g \text{ cell. mat.}}{m^3} \cdot \frac{\text{cellulose \%}}{100} = 28.2 \cdot \frac{35}{100} = 9.9 \frac{g \text{ pure cellulose}}{m^3}$$

Exercise 8.7. A given wastewater contains 50 g soluble COD/L, of which 30% are carbohydrates. Assuming that all fermentable fractions of carbohydrates are converted to acetic acid and butyric acid, to be used as substrate for PHA production, what would be their final concentrations in solution, both in g/L and in g COD/L. Assume that all carbohydrates are glucose, and the stoichiometries given in Chapter 7.

Solution:

Assuming that carbohydrates are in the form of glucose;

50 gCOD/L * 30/100 = 15 gCOD/L carbohydrates



15 gCOD/L / 32 gO₂/mol = 0.469 molO₂/L

0.469 molO₂/L / 6 = 0.078 mol/L glucose

0.078 mol/L glucose * 180 g/mol = 14 g/L glucose

Production of acetic acid and butyric acid



14 g Glucose/L / (180 g/mol) = 0.078 mol/L glucose

The amount of acetic acid produced = 0.078 mol/L acetic acid

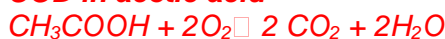
0.078 mol/L acetic acid * 60 g/mol = 4.68 g/L acetic acid

14 g Glucose/L / (180 g/mol) = 0.078 mol/L glucose

The amount of butyric acid produced = 0.078 mol/L acetic acid / 2 = 0.039 mol/L butyric acid

0.039 mol/L butyric acid * 88 g/mol = 3.43 g/L butyric acid

COD in acetic acid



0.078 mol/L acetic acid * 2 = 0.156 mol/L O₂

$$0.156 \text{ mol/L O}_2 * 32 \text{ g/mol} = 4.99 \text{ gCOD/L acetic acid}$$

COD in butyric acid



$$0.039 \text{ mol/L butyric acid} * 5 = 0.195 \text{ mol/L O}_2$$

$$0.195 \text{ mol/L O}_2 * 32 \text{ g/mol} = 6.24 \text{ gCOD/L butyric acid}$$

$$4.99 \text{ gCOD/L acetic acid} + 6.24 \text{ gCOD/L butyric acid} = 11.23 \text{ gCOD}_{\text{tot}}$$

The remaining COD, 3.75 g COD will be released as H_2

Exercise 8.8. The PHA polymeric properties are strongly influenced by the relative PHB vs PHV fractions. Typically, acetate and butyrate are precursors for PHB production, while propionate and valerate are precursors of PHV production. Assuming that the PHB and PHV content are linearly related to the quantity of their SCCA precursors (on a mass basis) produced during acidogenic fermentation, calculate the relative fraction of PHB and PHV produced for the case of an acidogenic feedstock containing 4.1 g/L acetate, 1.6 g/L propionate, 1.1 g/L butyrate and 0.6 g/L valerate. Assume a constant yield coefficient of 0.7 gPHA/gSCCA for each SCCA, while all acetate and propionate are completely consumed by the PHA producing culture, and 85% of the butyrate and valerate are consumed.

Solution:

$$\text{PHB} = 0.7 \text{ gPHB/gSCCA} * (4.1 \text{ g/L Ac} + 1.1 * 0.85 \text{ g/L But}) = 3.52 \text{ g PHB/L}$$

$$\text{PHV} = 0.7 \text{ gPHV/gSCCA} * (1.6 \text{ g/L Pr} + 0.6 * 0.85 \text{ g/L Val}) = 1.48 \text{ g PHV/L}$$

$$\text{PHB/PHA} = 3.52 / (3.52 + 1.48) = 70\% \text{ PHB}$$

$$\text{PHV/PHA} = 1.48 / (3.52 + 1.48) = 30\% \text{ PHV}$$

Exercise 8.9. SCCA are an excellent feedstock for PHA bioplastic production. Considering the supply chain for PHA production, approximately how much organic waste (in COD) would be needed to make an industrially-relevant 5,000 tonnes PHA per year? Assume a SCCA yield of 0.34 gCOD_{SCCA}/gCOD_{fed}, an overall PHA yield of 0.5g biomass/gCOD_{SCCA}, a PHA content of 70% and a total extraction efficiency of 63%.

Solution:

$$\text{Unextracted PHA} = 5,000 \text{ tonnes PHA} / 0.63 = 7,936.5 \text{ tonnes PHA}$$

To calculate the amount of biomass;

$$7,936.5 \text{ tonnes PHA} / 0.7 = 11,337 \text{ tonnes biomass}$$

$$\text{Amount of COD}_{\text{SCCA}} = 11,337 \text{ tonnes biomass} / 0.5 \text{ tonne biomass per tonne COD}_{\text{SCCA}} = 22,675.7 \text{ tonnes COD}_{\text{SCCA}}$$

Considering the SCCA yield;

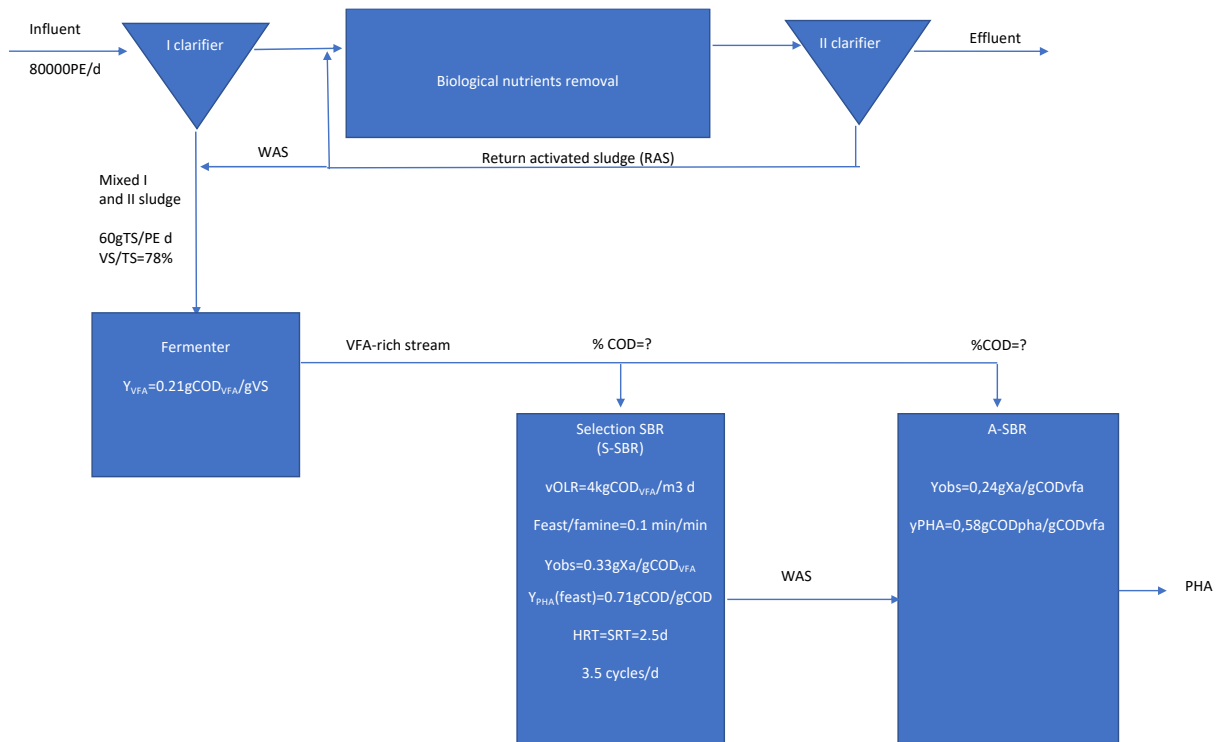
$$22,675.7 \text{ tonnes COD}_{\text{SCCA}} / 0.34 = 66,693 \text{ tonnes COD}_{\text{fed}} \text{ are needed as organic waste}$$

Exercise 8.10. A WWTP with a capacity of 80,000 PE produces around 60 gTS/PE d with a VS/TS ratio of 78%. All the produced sludge is fermented to produce SCCA with an observed fermentation yield of 0.21 gCOD_{SCCA}/gVS_{fed}. The SCCA-rich stream (7,500 mgCOD_{SCCA}/L) is then used for PHA production with an anaerobic feast/famine process. The PHA-production line is composed of 2 different SBRs reactors:

- Selection reactor (S-SBR)
- Accumulation reactor (A-SBR)

A vOLR of 4.0 kgCOD_{SCCA}/m³ d is applied to the S-SBR, which is operated at a feast/famine ratio of 0.1 min/min. The Y_{PHA} under feast conditions is 0.71gCOD_{PHA}/gCOD_{SCCA}, while the Y_{obs} is 0.33gXa/gCOD_{PHA}. The SRT is set at 2.5 days and the SBR works with 3.5 cycles per day. The excess sludge produced from the S-SBR is then fed to the A-SBR for the accumulation test to maximize PHA production.

In the A-SBR, the SCCA-rich stream is added 7 times (once per hour) to achieve an initial COD concentration of around $1\text{gCOD}_{\text{SCCA}}/\text{L}$. The volume of each addition is 0.56m^3 . The PHA yield is about $0.58\text{gCOD}_{\text{PHA}}/\text{gCOD}_{\text{SCCA}}$ and the growth yield is $0.24\text{gXa}/\text{gCOD}_{\text{SCCA}}$. Conversion factor for PHA: $1.67\text{gCOD}/\text{gPHA}$



Calculate:

- 1) The daily SCCA amount produced from the whole WWTP;
- 2) The length of both the SBR cycle and feast/famine of the S-SBR;
- 3) The volume of the S-SBR to sustain a production of $10\text{kgPHA}/\text{d}$, assuming a PHA content in the biomass of 40% (gPHA/gTS);
- 4) The biomass concentration of S-SBR;
- 5) The flowrate of carbon source to S-SBR and A-SBR, respectively (for the production of 10kg PHA);
- 6) The volume of the A-SBR (considering 7 carbon source additions);
- 7) The maximum annual PHA production potential of the whole WWTP.

Solution:

- 1) To calculate the amount of produced SCCA, we need to know the amount of VS produced:

$$TS = 60 \text{ g} \frac{TS}{PE} \text{ d} * 80000 \text{ PE} = 4800000 \text{ g} \frac{TS}{d} = 4800 \text{ kg TS/d}$$

Knowing the VS/TS ratio of 78%

$$VS = 4800 \text{ kg} \frac{TS}{d} * \frac{78}{100} = 3744 \text{ kg VS/d}$$

The fermentation yield is $0.21 \text{gCOD}_{\text{SCCA}}/\text{gVS}$, thus:

$$3744 \text{ kg} \frac{VS}{d} * 0.21 \text{ kg COD}_{\text{VFA}}/\text{kg VS} = 786,24 \text{ kg COD}_{\text{SCCA}}/\text{d}$$

- 2) The S-SBR accomplish 3.5 cycles per day, thus the length of the cycle will be:
 $(24\text{h}/\text{d} * 60\text{min}/\text{h})/(3.5\text{cycles}/\text{d}) = 411.42\text{min}/\text{cycle}$

If the feast/famine ratio is 0.1 min/min the feast length will be given by the following equation:

$$\begin{aligned} \text{Feast} + \text{Famine} &= 411,4 \text{ min} \\ \text{Feast}/\text{Famine} &= 0.1 \\ \text{Feast} &= \text{Famine} * 0.1 \end{aligned}$$

Substituting the Feast term in the initial equation:

$$\begin{aligned} 0.1 * \text{Famine} + \text{Famine} &= 411.4 \text{ min} \\ 1.1 \text{Famine} &= 411.4 \text{ min} \\ \text{Famine} &= 411.4/0.1 = 374 \text{ min} \end{aligned}$$

Subtracting the Famine length to the total cycle length we obtain the Feast length:

$$\text{Feast} = 411.4 \text{ min} - 374 \text{ min} = 37.4 \text{ min}$$

- 3) To calculate the volume of S-SBR, we need to know the amount of active biomass to be produced from S-SBR.

First of all, we need to calculate the amount of COD_{SCCA} necessary for the production of 10kg of PHA.

Knowing that the PHA yield in the accumulation phase is $0.58 \text{gCOD}_{\text{PHA}}/\text{gCOD}_{\text{SCCA}}$, the amount of SCCA will be:

$$10 \text{kgPHA} / (0.58 \text{kgCOD}_{\text{PHA}}/\text{COD}_{\text{SCCA}} / 1.67 \text{kgCOD}_{\text{PHA}}/\text{kgPHA}) = 28.79 \text{ kgCOD}_{\text{SCCA}}$$

We know that the PHA concentration within the biomass is 40%, thus the amount of TS at the end of the accumulation test will be:

$$10 \text{kgPHA} / (0.4 \text{kgPHA}/\text{kgTS}) = 25 \text{kgTS}$$

The active biomass (X_a) is calculated subtracting the amount of PHA from the TS. This biomass is partially produced in the accumulation test ($X_{a_{\text{acc}}}$) and partially derives from the S-SBR ($X_{a_{\text{sel}}}$).

$$25 \text{kgTS} - 10 \text{kgPHA} = 15 \text{kg } X_{a_{\text{sel}+\text{acc}}}$$

We know that the Yobs in the A-SBR is $0.24 \text{g}X_a/\text{gCOD}_{\text{SCCA}}$, so we can calculate the amount of X_a produced during the accumulation test as follows:

$$X_{a_{\text{acc}}} = 28.79 \text{kgCOD}_{\text{SCCA}} * 0.24 \text{g}X_a/\text{gCOD}_{\text{SCCA}} = 6.91 \text{kg}X_a$$

We know that the total amount of X_a produced in the accumulation test is equal to 15kg, thus the amount of X_a that needs to be produced from S-SBR will be:

$$X_{a_{\text{sel}}} = X_{a_{\text{sel}+\text{acc}}} - X_{a_{\text{acc}}} = 15 \text{kg} - 6.91 \text{kg} = 8.09 \text{kg}X_a$$

This is the daily amount of X_a to be produced from S-SBR.

To calculate the volume of S-SBR now we have to consider the Yobs ($0.33 \text{g}X_a/\text{gCOD}_{\text{SCCA}}$) and the substrate storage yield in S-SBR ($0.71 \text{gCOD}_{\text{PHA}}/\text{gCOD}_{\text{SCCA}}$). In this way, we can calculate the total amount of SCCA required for the production of 8.09 kg X_a .

Thus:

$$\text{SCCA} = \frac{8.09 \text{kg}X_a/\text{d}}{\frac{0.33 \text{g}X_a/\text{gCOD}_{\text{SCCA}}}{0.71 \text{gCOD}_{\text{PHA}}/\text{gCOD}_{\text{SCCA}}}} = 34.53 \text{kgCOD}_{\text{SCCA}}/\text{d}$$

Knowing that the vOLR of the S-SBR is $4.0 \text{kgCOD}_{\text{SCCA}}/\text{m}^3 \text{d}$ we can now calculate the volume of the reactor:

$$V = 34.53 \text{kgCOD}_{\text{SCCA}}/\text{d} / 4.0 \text{kgCOD}_{\text{SCCA}}/\text{m}^3 \text{d} = 8.63 \text{m}^3$$

- 4) To calculate the biomass concentration within the S-SBR, we need to know the volume of purged sludge. We know that the SRT is 2.5 days, thus:

$$Q_{\text{purged sludge}} = 8.63\text{m}^3/2.5\text{d} = 3.45\text{m}^3/\text{d}$$

Now we can calculate the biomass concentration within the S-SBR as follows:

$$[X_a] = (8.09\text{kg}X_a/\text{d})/(3.45\text{m}^3/\text{d}) = 2.34\text{kg}X_a/\text{m}^3$$

- 5) We know the amount of SCCA for S-SBR and A-SBR and the carbon source (CS) concentration, so we can calculate the flowrate to the reactors.

$$CS_{\text{sel}} = (34.53\text{kg}COD_{\text{SCCA}}/\text{d})/(7.5\text{g}COD_{\text{SCCA}}/\text{L}) = 4.6\text{m}^3/\text{d}$$

$$CS_{\text{acc}} = (28.79\text{kg}COD_{\text{SCCA}}/\text{d})/(7.5\text{g}COD_{\text{SCCA}}/\text{L}) = 3.84\text{m}^3/\text{d}$$

The relative percentages will be:

$$CS_{\text{sel}} = (4.6\text{m}^3/\text{d})/(4.6\text{m}^3/\text{d} + 3.84\text{m}^3/\text{d}) * 100 = 54.5\%$$

$$CS_{\text{acc}} = (3.84\text{m}^3/\text{d})/(4.6\text{m}^3/\text{d} + 3.84\text{m}^3/\text{d}) * 100 = 45.5\%$$

- 6) To calculate the volume of A-SBR we need to consider the volume of WAS coming from S-SBR and the volume of CS provided during the accumulation phase. Thus:

$$V_{A-SBR} = V_{WAS-SBR} + V_{CS} = 3.45\text{m}^3 + (0.56\text{m}^3 * 7) = 7.37\text{m}^3$$

- 7) To calculate the maximum annual PHA production potential of the whole WWTP, PHA yields and the annual available SCCA for accumulation tests must be taken into account.

Thus:

$$\begin{aligned} \text{SCCAs production} &= (786.24\text{kg}CCOD_{\text{SCCA}}/\text{d}) * (365\text{d}/\text{y}) = 286977\text{kg}COD_{\text{SCCA}}/\text{y} \\ &= 286.7\text{tons}COD_{\text{SCCA}}/\text{y} \end{aligned}$$

We know that the amount of SCCA available for A-SBR is 45.5% of the total SCCA, thus:

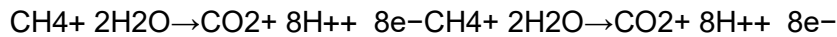
$$VFAs_{A-SBR} = (286.7\text{tons}COD_{\text{VFA}}/\text{y}) * (45.5/100) = 130.45\text{tons}COD_{\text{VFA}}/\text{y}$$

The PHA yield of $0.58\text{g}COD_{\text{PHA}}/\text{g}COD_{\text{SCCA}}$ in the A-SBR is given in the text, thus:

$$\begin{aligned} PHA_{\text{prod}} &= (130.45\text{tons}COD_{\text{VFA}}/\text{y}) \\ &* (0.58\text{g}COD_{\text{PHA}}/\text{g}COD_{\text{VFA}})/(1.67\text{g}COD_{\text{PHA}}/\text{g}PHA) \\ &= 45.3\text{tons}PHA/\text{y} \end{aligned}$$

CHAPTER 9

Exercise 9.1. Consider the following stoichiometry for the oxidation of methane:



Methane is a very stable molecule that provides little energy for cell growth; typically only 20% of available energy is utilized for cell growth. Develop overall mass balance equations for a process where methane is used as an electron donor for biomass production and ammonia is used as a nitrogen source and a negligible decay rate. Note: assume biomass stoichiometry of $\text{C}_5\text{H}_7\text{O}_2\text{N}$ (s).

Solution:

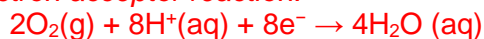
Microbial growth involves chemical transformation coupled to energy generation (catabolism), with energy stored chemically (generally as ATP) to enable cell synthesis (anabolism). Assume 20% of the energy goes towards cell synthesis, therefore 20% of electrons from CH_4 catabolism are used for cell synthesis.

Step 1:

1. Electron donor reaction:



2. Electron acceptor reaction:



3. Cell synthesis reaction:



Step 2:

Use a basis of 100 electrons being transferred to balance catabolism and anabolism. Therefore 100 electrons will be released in equation 1, 80 electrons will be used in equation 2 and 20 electrons will be used for cell growth in equation 3:

$12.5 \times$ equation 1 = 100 electrons in transfer = 80 electrons to energy ($10 \times$ equation 2) and 20 electrons to cell synthesis ($1 \times$ equation 3). Equations are combined in this ratio to give:



Exercise 9.2. Consider the example where bacteria grow using starch as an electron donor and ammonium as a nitrogen source. The cell yield is 0.5 in terms of electrons going respectively to energy (i.e. catabolism) and to cell synthesis (i.e. anabolism). Develop overall mass balance equations for this process. Given the mass balance equations, calculate the amount of starch needed in order to produce 10 tons per day of microbial protein (on a dry solids basis). Note: assume biomass stoichiometry of $\text{C}_5\text{H}_7\text{O}_2\text{N}$ (s).

Solution:

Microbial growth involves chemical transformation coupled to energy generation (catabolism), with energy stored chemically (generally as ATP) to enable cell synthesis (anabolism). An electron cell yield of 0.5 implies that only 50% of the energy goes towards cell synthesis.

Step 1:

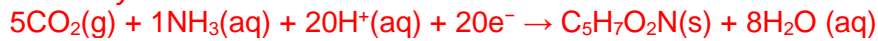
1. Electron donor reaction:



2. Electron acceptor reaction:



3. Cell synthesis reaction:



Step 2:

Balance catabolism and anabolism: 2 x equation 1 = 48 electrons in transfer = 24 electrons to energy (6 x equation 2) and 24 electrons to cell synthesis (24/20 x equation 3). The latter gives the following equation:



Step 3:

Determine the molecular weights of key components:

$$\text{MW starch} = (6 \times 12) + (10 \times 1) + (5 \times 16) = 162 \text{ g/mol}$$

$$\text{MW microbial biomass} = (5 \times 12) + (7 \times 1) + (2 \times 16) + (14 \times 1) = 113 \text{ g/mol}$$

In the balanced chemical reaction, 2 mols of starch produce 1.2 mols of biomass. Therefore, production of 1 ton of biomass requires: $(2 \times 162) / (1.2 \times 113) = 2.39$ ton starch / ton microbial protein. Therefore, 24 metric tons of starch are required to produce 10 ton microbial protein biomass.

Exercise 9.3. Consider the following:

- If the typical composition of hydrogenotrophic biomass is $\text{CH}_{1.74}\text{O}_{0.46}\text{N}_{0.19}$. Present the elemental compositions as mass fractions. If all nitrogen is present as protein, determine the protein content as a fraction of CDM.
- Hydrogen gas is to be generated using electrolysis at a rate of 20 kg H_2 gas per MWh electricity. If a 50 MW hydrolysis cell is used to generate feed for the production of protein biomass, determine the maximum rate of biomass production per hour for a cell yield of 0.3 kg CDM per kg COD-H_2 .
- For the process in (b), determine the mass of nitrogen that must be supplied for complete uptake of H_2 gas.
- If (i) hydrogen at a rate of 20 kg H_2 gas per MWh electricity and nitrogen is produced using Haber-Bosch at an energy cost of 10 MWh/ton N and energy costs are €50/MWh, determine if this process is feasible when bulk microbial protein is valued at €1/kg CDM.

Solution:

- The table below is used to convert the composition of hydrogenotrophic biomass ($\text{CH}_{1.74}\text{O}_{0.46}\text{N}_{0.19}$) into mass fractions of each element. This is achieved by using the atomic weight to determine the mass of each element in 1 C-mole of hydrogenotrophic biomass.

Element	Carbon	Hydrogen	Nitrogen	Oxygen	Total
Atomic Weight	12	1	14	16	
Moles per mole CDM	1	1.74	0.19	0.46	
Mass per mole CDM	12	1.74	2.66	7.36	23.76
Mass Fraction	0.51	0.07	0.11	0.31	1.00

Using the table approach, 1 mole of hydrogenotrophic biomass contains 2.66 g of nitrogen. Using the Jones factor of 6.25 g protein per 1 g nitrogen, 1 C-mole of

hydrogenotrophic biomass contains 16.63 g protein. If 1 C-mole of hydrogenotrophic biomass has a total mass of 23.76 grams, the protein content is 70.0% of the CDM.

b. $50 \times 20\text{kg} = 1 \text{ ton}$ of hydrogen is produced per hour. The latter equals to $\text{H}_2(\text{g}) + 12\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{aq})$
 = 8 grams of COD equivalents per gram hydrogen. Thus, in total 8 tons COD- H_2 equivalents per hour. Considering the cell yield of 0.3 kg CDM per kg COD- H_2 , it follows this is equal to $8 \times 0.3 = 2.4 \text{ ton}$ microbial protein per hour.

c. Based on equation 8, the microbial biomass has the following composition:
 $\text{C}_{4.09}\text{H}_{7.13}\text{O}_{1.89}\text{N}_{0.76}$
 Hence, the total M weight equals to 97.09. Relative mass nitrogen is $10.64 / 97.09 = 10.95\%$, it thus follows that the mass of nitrogen that needs to be supplied per hour (assuming 100% uptake efficiency) of 263 kg N per hour.

d. Energy requirements for hydrogen generation: $50 \text{ MW} \times 1 \text{ hour} = 50 \text{ MWh} \times \text{€}50/\text{MWh} = \text{€} 2500 \text{ per hr}$. The costs associated with Haber-Bosch nitrogen production are: $10 \text{ MWh/ton N} \times 0.263 = 2.63 \text{ MWh} \times \text{€}50/\text{MWh} = \text{€}131.50 \text{ per hr}$. Thus, total costs are $\text{€} 2500 + \text{€}131.50 = \text{€} 2631.50 \text{ per hr}$. It follows that the production costs per ton protein produced are $\text{€} 2631.50 / 2.4 = \text{€}1096$.

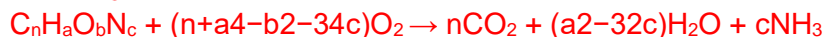
If a bulk microbial protein value of $\text{€}1/\text{kg}$ CDM is assume, protein production costs are higher than the value of the protein product. Note that the above calculation is a simplified representation of the production process with various other economic considerations not taken into account such as drying, sterilization, oxygen supply, mixing/pumping and other nutrient requirements etc.

Exercise 9.4. Consider the following:

- The typical composition of purple phototrophic biomass (PPB) is given as $\text{CH}_{1.8}\text{O}_{0.38}\text{N}_{0.18}$. Write a balanced chemical equation for the oxidation of PPB and use this equation to determine the COD to CDM ratio of PPB.
- If the typical composition of purple phototrophic biomass is $\text{CH}_{1.8}\text{N}_{0.18}\text{O}_{0.38}\text{P}_{0.02}$. Present the elemental compositions as mass fractions. If all nitrogen is present as protein, determine the protein content as a fraction of CDM.
- Research shows that a photobioreactor with a light intensity of 50 W m^{-2} will produce purple phototrophic bacteria at an average areal productivity of $20 \text{ g CDM/m}^2\cdot\text{d}$. Estimate the illuminated surface of the photobioreactor required to produce enough protein to sustain 600 average people (assume 70 kg/ person). What is the energy requirement to light this reactor?

Solution:

- The following equation can be used to balance the chemical equation for the oxidation of PPB:



This results in the following overall equation:



The next step is to determine the molecular weight and the mass of each component involved in the balanced reaction. As demonstrated in the table below.

Species	$\text{CH}_{1.8}\text{O}_{0.38}\text{N}_{0.18}$	O_2	CO_2	H_2O	0.18NH_3
MW	22.4	32	44	18	17
Moles (gmol)	1	1.125	1	0.63	0.18
Mass (g)	22.4	36	44	11.34	3.06

Using the table approach, 22.4g of PPB biomass reacts with 36g of oxygen. Therefore the COD to CDM ratio of PPB is 36g O_2 per 22.4 g CDM or 1.61.

- b. The table below is used to convert the composition of purple phototrophic biomass ($\text{CH}_{1.8}\text{N}_{0.18}\text{O}_{0.38}\text{P}_{0.02}$) into mass fractions of each element. This is achieved by using the atomic weight to determine the mass of each element in 1c-mole of PPB biomass.

Element	Carbon	Hydrogen	Nitrogen	Oxygen	Phosphorous
Atomic Weight	12	1	14	16	31
Moles per mole PPB	1	1.8	0.18	0.38	0.02
Mass per mole PPB	12	1.8	2.52	6.08	0.62
Mass Fraction	0.52	0.08	0.11	0.26	0.03

Using the table approach, 1 mole of PPB biomass contains 2.52 g of nitrogen. Using the Jones factor of 6.25 g protein per 1 g nitrogen. 1 mole of PPB biomass contains 15.75 g protein. If 1 mole of PPB biomass has a total mass of 23.02 grams, the contain content is 68.4% of the CDM.

- c. As described in the introduction: "For physical and mental health, it is important that on average each person can consume some 0.66 gram protein/kg body weight per day (Organization 2002)". It follows that 600 average people with 70kg/person require $70 [\text{kg/person}] \times 0.66 [\text{gram protein} / \text{kg body weight per day}] \times 600 [\text{people}] = 27.72 \text{ kg of protein/day}$.

At 20 g CDM/ $\text{m}^2 \cdot \text{d}$ and a Protein / CDM_{PPB} ratio of 0.68 [g/g], the required illuminated surface equals to 2,038 m^2 . This would consume $2,038 \text{ m}^2 \times 50 \text{ W/m}^2 = 101.9 \text{ kW}$. The latter is equal to $101.9 \text{ kW} \times 24 \text{ hr} = 2446 \text{ kWh/day}$. At a electricity price of \$0.10/kWh this equals approximately \$245 dollars per day or ~\$8.8 / kg PPB produced for irradiation only. Hence, it is of utmost importance to minimize the required energy input for irradiation (on could in theory use sunlight)

Exercise 9.5. Assume that one kg of organic matter dry weight represents approximately 1 kg Chemical Oxygen Demand (COD) (in reality this differs somewhat depending on the type of organics, e.g. fats or sugars), which represents the amount of oxygen needed to oxidize the organic matter present. Generally one kg of COD such as sugar or starch, when consumed by rapidly growing microbial cells, gives rise to 0.4 kg Cell Dry Matter (CDM). The latter, when consisting out of young cells (1-5 days cell residence time), contains approximately 70% protein. Considering the above, how much carbohydrates are required to tie up 1 kg of reactive nitrogen in microbial biomass.

Solution:

Hence 0.28 kg of microbial protein can be expected per kg carbohydrate equivalent subjected to aerobic microbial fermentation. Since protein contains 16% nitrogen on the dry matter, it follows that 1 kg carbohydrate will give rise to the upgrading of $0.28 \times 0.16 = 0.04 \text{ kg reactive}$

nitrogen. In other words, it takes some 20 - 25 kg of carbohydrates to tie up 1 kg reactive nitrogen in microbial biomass.

Exercise 9.6. Assume that one kg of organic matter dry weight represents approximately 1 kg Chemical Oxygen Demand (COD) (in reality this differs somewhat depending on the type of organics, e.g. fats, acetate or sugars), which represents the amount of oxygen needed to oxidize the organic matter present. Considering that one kg of acetate gives rise to 0.66 kg Cell Dry Matter using purple phototrophic bacteria (PPB). The latter contains approximately 70 % protein. Considering the above, how much acetate is required to tie up 1 kg of reactive nitrogen in microbial biomass using PPB.

Solution:

Hence 0.46 kg of microbial protein can be expected per kg carbohydrate equivalent subjected to phototrophic assimilation. Since protein contains 16% nitrogen on the dry matter, it follows that 1 kg acetate will give rise to the upgrading of $0.46 \times 0.16 = 0.074$ kg reactive nitrogen. In other words, it takes around 13 kg of acetate to tie up 1 kg reactive nitrogen in phototrophic microbial biomass.

Exercise 9.7. A soft drink manufacturing process produces 0.5 ML/day of concentrated industrial wastewater with the composition shown in the table below:

Component	Concentration
COD	120 g/L
VFA	70 g/L
Alcohols	20 g/L
TKN	94 mg/L
NH ₄ -N	30 mg/L
Total P	104 mg/L
PO ₄ -P	92 mg/L

- If no external nitrogen is added to the wastewater (i.e. only nitrogen in the wastewater can be used for growth), calculate i) the maximum rate of biomass production and ii) the maximum rate of protein production that can be generated each day using fast growing organotrophic biomass (cell yield of 0.38 kg CDM per kg COD and protein content of 70%).
- Estimate the dose rate of external nitrogen that must be supplied in order to convert all COD in the wastewater into fast growing organotropic biomass. Calculate the biomass production under these conditions.
- If no external nitrogen is added to the wastewater, calculate i) the maximum rate of biomass production and ii) the maximum rate of protein production that can be generated each day using purple phototrophic biomass (cell yield of 0.62 kg CDM per kg COD and protein content of 70%).
- Estimate the dose rate of external nitrogen that must be supplied in order to convert all COD in the wastewater into purple phototrophic biomass. Calculate the biomass production under these conditions.

Solution:

- The maximum rate of biomass production:*

Step 1: Assume that all COD is readily biodegradable and TKN can be incorporated into biomass.

Step 2: Calculate mass of COD and N per day available / required.

COD: Based on the amount of COD present and cell yield, it follows that $500 \text{ m}^3/\text{day} \times$

$120 \text{ kg COD} / \text{m}^3 \times 0.38 \text{ kg CDM per kg COD} = 22.80 \text{ ton biomass}$.
 Considering a protein content of 70%, it follows that the nitrogen content is $70/6.25 = 11.2\%$. Hence, the amount of N required equals to 2.55 ton N.

However, the amount of TKN available: $500 \text{ m}^3/\text{day} \times 94 \text{ g TKN} / \text{m}^3 = 47 \text{ kg Nitrogen}$.
 Hence, nitrogen is the limiting factor (i.e. it should be dosed to the reactor!). The maximum amount of protein that can be produced is $47 \text{ kg N} / 11.2\% = \sim 420 \text{ kg}$.

- The nitrogen that needs to be added to consume all COD and produce 22.80 ton microbial biomass equals to $2.5536 - 0.420 = 2.14 \text{ ton N}$.
- Based on the amount of COD present and cell yield, it follows that $500 \text{ m}^3/\text{day} \times 120 \text{ kg COD} / \text{m}^3 \times 0.62 \text{ kg CDM per kg COD} = 40.80 \text{ ton of purple phototrophic biomass}$.
 Considering a protein content of 70%, it follows that the nitrogen content is $70/6.25 = 11.2\%$. Hence, the amount of N required equals to 4.57 ton N.
- The nitrogen that needs to be added required to produce 40.80 ton microbial biomass equals to $4.57 - 0.420 = 4.15 \text{ ton N}$.

Exercise 9.8. A meat processing plant produces 3 ML/day of industrial wastewater with an average daily composition shown in the table below:

Component	Concentration
COD	5500 mg/L
VFA	1200 g/L
TKN	460 mg/L
NH ₄ -N	230 mg/L
TP	120 mg/L
PO ₄ -P	80 mg/L

- If wastewater discharge costs are €1.0/kg COD, €2.0/kg N and €2.5/kg P, calculate the discharge costs without wastewater treatment.
- If the wastewater is to be treated using purple phototropic bacteria, calculate i) the maximum rate of biomass production and ii) the maximum rate of protein production that can be generated each day (cell yield of 0.62 kg CDM per kg COD and protein content of 70%).
- Using a biomass composition of CH_{1.8}N_{0.18}O_{0.38}P_{0.02}, assume complete conversion of the limiting component and estimate the COD, N and P composition of treated wastewater after production and harvesting of purple phototrophic biomass.
- Using an areal productivity of 20 g CDM/m².d, calculate the required photobioreactor area for this process.
- Initial cost benefit assessments estimate the capital costs for the PPB process at €40/m², biomass production costs are estimated at €1/kg CDM and costs to harvest and process the biomass are estimated at €2/kg CDM. The biomass product is valued at €2/kg CDM. If the plant life is 20 years, and the hurdle return on investment is 15%, determine the preliminary economic feasibility of the process.

Solution:

- Calculate the daily loads of COD, N and P. (note: mg/L = kg/ML)
 COD: $3 \text{ ML/d} \times 5,500 \text{ kg/ML} = 16,500 \text{ kg COD}$ or €16,500/day.
 N (use TKN): $3 \text{ ML/d} \times 460 \text{ kg/ML} = 1380 \text{ kg TKN}$ or €2,760/day.
 P (use TP): $3 \text{ ML/d} \times 120 \text{ kg/ML} = 360 \text{ kg/day}$ or €900/day.
 It follows that the total discharge costs are €20,160/day.

- b. i) the maximum rate of biomass production based on total available COD (you can assume that all COD is readily biodegradable) is $16,500 \text{ kg COD/day} \times 0.62 \text{ kg CDM / kg COD} = 10230 \text{ kg CDM/day}$, ii) with a total protein production of $10,230 \text{ kg CDM / day} \times 0.7 = 7,161 \text{ kg Protein/day}$.
- c. The mass fractions of each element in the biomass are:

Elements	in PPB	M (g/mole)	g/mole PPB	Fraction
C	1	12	$1 \times 12 = 12$	$12/23.02 = 0.521$
H	1.8	1	$1.8 \times 1 = 1.8$	$1.8/23.02 = 0.078$
O	0.38	16	$0.38 \times 16 = 6.08$	$6.08/23.02 = 0.264$
N	0.18	14	$0.18 \times 14 = 2.52$	$2.52/23.02 = 0.110$
P	0.02	31	$0.02 \times 31 = 0.62$	$0.62/23.02 = 0.027$
SUM			23.02	1

From this table it follows that 1 g CDM contains 0.11 g N and 0.027 g P. From question B it follows that $10230 \text{ kg CDM / day}$ is produced and to achieve that one would require $10,230 \times 0.11 = 1125.3 \text{ kg N}$ and $10,230 \times 0.027 = 276.2 \text{ kg P}$.

A CDM production of $10230 \text{ kg CDM / day}$ implies that all COD is incorporated into biomass (effluent COD = 0). It follows from b) that the TKN_{effluent} equals to $1380 \text{ kg TKN} - 1125.3 \text{ kg TKN} = 254.7 \text{ kg N}$ and the P_{effluent} equals to $360 \text{ kg TP} - 276.2 \text{ kg TP} = 83.8 \text{ kg TP}$. The latter equals to effluent concentrations of 84.9 mg TKN/L and 27.9 mg TP/L , respectively.

- d. Consuming all COD would result in 10230 kg CDM-PPB . At $20 \text{ g CDM/m}^2 \cdot \text{d}$, an illuminated surface of $10230 \text{ kg CDM-PPB} / 20 \text{ g CDM/m}^2 \cdot \text{d} = 511,500 \text{ m}^2$ would be required.
- e. Step 1: Calculate the costs:
1. Reactor = $511,500 \text{ m}^2 \times 40 \text{ €/m}^2 = 20,460,000 \text{ €}$.
 2. PPB production costs: $10,230 \text{ [kg CDM-PPB/day]} \times 1 \text{ [€/kg]} \times 365 \text{ [days]} \times 20 \text{ [years]} = 74,679,000$ over 20 years.
 3. PPB harvesting and processing costs: $102,305 \text{ [kg CDM-PPB/day]} \times 2 \text{ [€/kg]} \times 365 \text{ [days]} \times 20 \text{ [years]} = 149,358,000$.

Total costs over 20 years = $€244,497,000$.

Step 2: Revenues:

1. PPB product: $10230 \text{ kg CDM-PPB/day} \times 2 \text{ €/kg} \times 365 \text{ d} \times 20 \text{ years} = 149,358,000$ over 20 years.
2. Discharge costs savings. Please refer to answer from a); $€16,500/\text{day}$ (COD), c) $1125.3 \text{ [kg N/day]} \times 2 \text{ [€/kg]} + 276.2 \text{ [kg TP/day]} \times 2.5 \text{ [€/kg]} = 19,441 / \text{day} \times 365 \text{ [days]} \times 20 \text{ [years]} = 141,920,030$

Total revenue over 20 years = $€291,278,030$.

The return of investment (ROI) we calculate the revenues (here over 20 years) which is $€291,278,030 - €244,497,000 = €46,781,030$. The net revenues divided by the investment costs determine the ROI, which is $€46,781,030 / €244,497,000 \times 100 = 19.1\%$. This is higher than the 15% hurdle and therefore feasible. Note that in practice 'no treatment at all' versus 'one technology' comparison is not 'realistic with a 'variety of treatment methods available that could be used as an alternative to the

production of PPB. Often feasibility studies are conducted comparing several treatment options.

Exercise 9.9. The wastewater generated in a potato factory has the following typical composition: 10 g/L of starch, $\text{NH}_4\text{-N} = 0.5 \text{ g/L}$ and ortho-P = 0.1 g/L. This water, subjected to inoculation with a proper seed culture and aeration in a reactor will in a time period of 2-3 days convert the starch, the ammonium and phosphate present in the water to microbial biomass. Actually, some 4 gram cell dry matter (CDM) per L will be obtained (Yield: 0.4 kg CDW per kg starch converted). Assume a starch removal efficiency of the process of 96%. Considering the above described COD/N/P ratio, yield and typical biomass composition of young cells, calculate the expected effluent concentrations in terms of N and P that can be achieved through assimilation of the N and P into microbial biomass.

Solution:

Considering that the CDW has a protein content of 70%, it will have tied up $4 \times 0.7 \times 0.16 = 0.44$ grams of N and about 0.08 g of P (~2% on the CDW). This implies that when the microbial biomass is adequately separated from the water, the liquid phase (i.e. effluent) will only have a small residuals of starch, $\text{NH}_4\text{-N}$, and P left (i.e. starch $\leq 0.1 \text{ g/L}$, $\text{NH}_4\text{-N} \leq 0.06 \text{ g/L}$ and $\text{P} \leq 0.02 \text{ g/L}$). Hence, the treated process water is appropriate for re-use.

CHAPTER 10

A landfill site produces leachate at a liquid flowrate of 5 m³/h with a total ammoniacal nitrogen concentration of 700 mg NH₄-N/L at pH 9.5 and 80°C ($\rho_l = 971.76 \text{ kg/m}^3$; $\mu_L = 3.537 \times 10^{-4} \text{ Pa}\cdot\text{s}$; $\sigma = 0.0626 \text{ N/m}$). A stripping column is to be designed using a random packed tower containing Plastic tellerettes packing ($C_f = 20$; $a_t = 112 \text{ m}^2/\text{m}^3$; $d_p = 0.0508 \text{ m}$; $\sigma_c = 0.033 \text{ N/m}$; (Crittenden et al., 2005)) to remove 95% of the free ammonia from the leachate using air at 80 °C and 1 atm as the extractant gas ($\rho_G = 1 \text{ kg/m}^3$; $\mu_G = 20.88 \times 10^{-6} \text{ Pa}\cdot\text{s}$). This aims to assist the final polishing of any remaining ammonia from the leachate in a subsequent biological nutrient removal plant.

Phase equilibrium for the dissolution of gaseous NH₃ in water can be described by Henry's Law, $K_{H,NH_3} = 1,818 \text{ Pa/M}$ at 298 K (Sander, 2015), with $\Delta H^0/R$ for the dissolution of ammonia from air into water being 4,100 (Sander, 2015). Diffusivity of ammonia in air $D_G = 0.28 \times 10^{-4} \text{ m}^2/\text{s}$ (Incropera and DeWitt, 2001), Diffusivity of ammonia in water $D_L = 2 \times 10^{-9} \text{ m}^2/\text{s}$ (Perry and Green, 1997; Table 2-372).

Exercise 10.1. Determine Henry's Law constant under the operating conditions.

Solution:

From Equation 10.18:

$$\ln\left(\frac{K(T_2)}{1,818}\right) = 4,100 \cdot \left(\frac{1}{298} - \frac{1}{353}\right)$$
$$\therefore K(T_2) = 15,586 \text{ Pa/M}$$

Exercise 10.2. What is the dimensionless Henry's Law constant?

Solution:

$$K_H = \frac{15,586 \left(\frac{\text{Pa}\cdot\text{L}}{\text{mol}}\right)}{8.314 \left(\frac{\text{m}^3\cdot\text{Pa}}{\text{K}\cdot\text{mol}}\right) \cdot 353(\text{K}) \cdot 10^3 \left(\frac{\text{L}}{\text{m}^3}\right)} = 5.31 \times 10^{-3}$$

Exercise 10.3. What is the minimum gas flowrate for stripping the ammonia?

Solution:

For minimum air flowrate (Q_G), $S = 1$.

$$\text{From equation 10.21, } Q_{G,\min}/Q_L = S/K_H = \frac{1}{5.31 \times 10^{-3}} = 188$$
$$\therefore Q_{G,\min} = 941 \text{ m}^3/\text{h}$$

Exercise 10.4. Determine the diameter of a stripping column appropriate for the application.

Solution:

Use $S = 3.5$ and mid-range gas pressure drop value of 200 Pa/m. From equation 10.21:

$$Q_G = \frac{Q_L \cdot S}{K_H} = \frac{5 \left(\frac{\text{m}^3}{\text{h}}\right) \cdot 3.5}{5.31 \times 10^{-3}} = 3,295 \text{ m}^3/\text{h}$$

Calculate the ratio of L_m and G_m using equation 10.24:

$$\frac{L_m}{G_m} = \left(\frac{Q_L}{Q_G}\right) \cdot \left(\frac{\rho_L}{\rho_G}\right) = \left(\frac{5}{3295}\right) \cdot \left(\frac{972}{1}\right) = 1.474$$

value on the horizontal axis of the Eckert plot (x) using equation 10.22 as follows:

$$x = \frac{L_m}{G_m} \left(\frac{\rho_g}{\rho_l - \rho_g} \right)^{0.5} = 1.474 \cdot \left(\frac{1}{972 - 1} \right)^{0.5} = 0.0473$$

For a nominal gas flow pressure drop of 200 Pa/m, the corresponding value on the vertical axis of the Eckert plot (y) (**Error! Reference source not found.**) is approximately 0.047. Accordingly the area specific air mass flow rate is calculated using equation 10.24:

$$G_m = \left[\frac{y \cdot \rho_G \cdot (\rho_L - \rho_G)}{C_f \cdot \mu_l^{0.1}} \right]^{0.5} = \left[\frac{0.047 \cdot 1 \cdot (972 - 1)}{20 \cdot (3.537 \times 10^{-4})^{0.1}} \right]^{0.5} = 2.25 \text{ kg}/(\text{m}^2 \cdot \text{s})$$

L_m is then calculated from equation 10.25:

$$L_m = \left(\frac{Q_L}{Q_G} \right) \cdot \left(\frac{\rho_L}{\rho_G} \right) \cdot G_m = \left(\frac{5}{3,295} \right) \cdot \left(\frac{972}{1} \right) \cdot 2.25 = 3.32 \text{ kg}/(\text{m}^2 \cdot \text{s})$$

The diameter of the packed column is then calculated from equation 10.26:

$$D_t = \left(\frac{4 \cdot Q_L \cdot \rho_L}{\pi \cdot L_m} \right)^{0.5} = \left(\frac{4 \cdot 5 \left(\frac{\text{m}^3}{\text{h}} \right) \cdot \frac{1}{3600} (\text{h/s}) \cdot 972 \left(\frac{\text{kg}}{\text{m}^3} \right)}{\pi \cdot 3.32 \left(\frac{\text{kg}}{\text{m}^2 \cdot \text{s}} \right)} \right)^{0.5} = 0.72 \text{ m}$$

Exercise 10.5. Determine K_{La} , given the following parameters:

Solution:

This can use the Onda correlations in equation 10.28:

$$\begin{aligned} a_w &= a_t \cdot \left[1 - \exp \left[-1.45 \cdot \left(\frac{\sigma_c}{\sigma} \right)^{0.75} \cdot \left(\frac{L_m}{a_t \cdot \mu_l} \right)^{0.1} \cdot \left(\frac{(L_m)^2 \cdot a_t}{(\rho_L)^2 \cdot g} \right)^{-0.05} \cdot \left(\frac{(L_m)^2}{\rho_L \cdot a_t \cdot \sigma} \right)^{0.2} \right] \right] \\ &= 112 \left(\frac{\text{m}^2}{\text{m}^3} \right) \cdot \left[1 - \exp \left[-1.45 \cdot \left(\frac{0.033}{0.0626} \right)^{0.75} \cdot \left(\frac{3.32 \left(\frac{\text{kg}}{\text{m}^2 \cdot \text{s}} \right)}{112 \left(\frac{\text{m}^2}{\text{m}^3} \right) \cdot 3.537 \times 10^{-4} \left(\frac{\text{kg}}{\text{m} \cdot \text{s}} \right)} \right)^{0.1} \cdot \right. \right. \\ &\quad \left. \left. \left(\frac{\left(3.32 \left(\frac{\text{kg}}{\text{m}^2 \cdot \text{s}} \right) \right)^2 \cdot 112 \left(\frac{\text{m}^2}{\text{m}^3} \right)}{\left(972 \left(\frac{\text{kg}}{\text{m}^3} \right) \right)^2 \cdot 9.81 \left(\frac{\text{m}}{\text{s}^2} \right)} \right)^{-0.05} \cdot \left(\frac{\left(3.32 \left(\frac{\text{kg}}{\text{m}^2 \cdot \text{s}} \right) \right)^2}{972 \left(\frac{\text{kg}}{\text{m}^3} \right) \cdot 112 \left(\frac{\text{m}^2}{\text{m}^3} \right) \cdot 0.0626 \left(\frac{\text{kg} \cdot \text{m}}{\text{m} \cdot \text{s}^2} \right)} \right)^{0.2} \right] \right] = 50.75 \frac{\text{m}^2}{\text{m}^3} \end{aligned}$$

$$\begin{aligned} k_L &= 0.0051 \cdot \left(\frac{L_m}{a_w \cdot \mu_l} \right)^{2/3} \cdot \left(\frac{\mu_l}{\rho_L \cdot D_L} \right)^{-0.5} \cdot (a_t \cdot d_p)^{0.4} \cdot \left(\frac{\rho_L}{\mu_L \cdot g} \right)^{-1/3} \\ &= 0.0051 \cdot \left(\frac{3.32 \left(\frac{\text{kg}}{\text{m}^2 \cdot \text{s}} \right)}{50.75 \left(\frac{\text{m}^2}{\text{m}^3} \right) \cdot 3.537 \times 10^{-4} \left(\frac{\text{kg}}{\text{m} \cdot \text{s}} \right)} \right)^{2/3} \cdot \left(\frac{3.537 \times 10^{-4} \left(\frac{\text{kg}}{\text{m} \cdot \text{s}} \right)}{972 \left(\frac{\text{kg}}{\text{m}^3} \right) \cdot 2 \times 10^{-9} \left(\frac{\text{m}^2}{\text{s}} \right)} \right)^{-0.5} \\ &\quad \cdot \left(112 \left(\frac{\text{m}^2}{\text{m}^3} \right) \cdot 0.0508 \text{ m} \right)^{0.4} \cdot \left(\frac{972 \left(\frac{\text{kg}}{\text{m}^3} \right)}{3.537 \times 10^{-4} \left(\frac{\text{kg}}{\text{m} \cdot \text{s}} \right) \cdot 9.81 \frac{\text{m}}{\text{s}^2}} \right)^{-1/3} \\ &= 8.21 \times 10^{-5} \text{ m/s} \end{aligned}$$

$$\begin{aligned}
k_G &= 5.23 \cdot (a_t \cdot D_G) \cdot \left(\frac{G_m}{a_t \cdot \mu_G} \right)^{0.7} \left(\frac{\mu_G}{\rho_G \cdot D_G} \right)^{1/3} \cdot (a_t \cdot d_p)^{-2} \\
&= 5.23 \cdot \left(112 \left(\frac{\text{m}^2}{\text{m}^3} \right) \cdot 0.28 \times 10^{-4} \left(\frac{\text{m}^2}{\text{s}} \right) \right) \\
&\quad \cdot \left(\frac{2.25 \frac{\text{kg}}{\text{m}^2 \cdot \text{s}}}{112 \left(\frac{\text{m}^2}{\text{m}^3} \right) \cdot 20.88 \times 10^{-6} \left(\frac{\text{kg}}{\text{m} \cdot \text{s}} \right)} \right)^{0.7} \left(\frac{20.88 \times 10^{-6} \left(\frac{\text{kg}}{\text{m} \cdot \text{s}} \right)}{1 \frac{\text{kg}}{\text{m}^3} \cdot 0.28 \times 10^{-4} \left(\frac{\text{m}^2}{\text{s}} \right)} \right)^{1/3} \\
&\quad \cdot \left(112 \left(\frac{\text{m}^2}{\text{m}^3} \right) \cdot 0.0508 \text{ m} \right)^{-2} = 0.056 \text{ m/s}
\end{aligned}$$

Using equation 10.14, the value of the overall mass transfer coefficient is calculated ($K_L a$):

$$\begin{aligned}
\frac{1}{K_L a} &= \frac{1}{k_L a_w} + \frac{1}{K_H \cdot k_G a_w} \\
\frac{1}{K_L a} &= \frac{1}{8.21 \frac{\text{m}}{\text{s}} \cdot 50.75 \frac{\text{m}^2}{\text{m}^3}} + \frac{1}{5.31 \times 10^{-3} \cdot 0.056 \text{ m/s} \cdot 50.75 \frac{\text{m}^2}{\text{m}^3}} = 306 \text{ s} \\
\therefore K_L a &= 3.26 \times 10^{-3} / \text{s}
\end{aligned}$$

Exercise 10.6. Determine height of the stripping column.

Solution:

Using equation 10.27:

$$\begin{aligned}
l &= \frac{Q_L}{A \cdot K_L a} \cdot \left(\frac{S}{S-1} \right) \cdot \ln \left[\frac{1 + (C_{in}/C_{out}) \cdot (S-1)}{S} \right] \\
&= \frac{5 \left(\frac{\text{m}^3}{\text{h}} \right) \cdot \frac{1}{3600} (\text{h/s})}{\left(\frac{\pi D_t^2}{4} \right) \cdot 3.26 \times 10^{-3} / \text{s}} \cdot \left(\frac{3.5}{3.5-1} \right) \cdot \ln \left[\frac{1 + \left(\frac{1}{0.05} \right) \cdot (3.5-1)}{3.5} \right] \\
&= \frac{5 \left(\frac{\text{m}^3}{\text{h}} \right) \cdot \frac{1}{3600} (\text{h/s})}{\left(\frac{\pi \cdot (0.72 \text{ m})^2}{4} \right) \cdot 3.26 \times 10^{-3} / \text{s}} \cdot \left(\frac{3.5}{3.5-1} \right) \cdot \ln \left[\frac{1 + \left(\frac{1}{0.05} \right) \cdot (3.5-1)}{3.5} \right] = 3.92 \text{ m}
\end{aligned}$$

Discussion Question 10.5. Using the principles of a first-order reaction, explain why multiple tanks in series would be a more efficient process to air strip ammonia from a liquid slurry which contains 5,000 mg/L $\text{NH}_3\text{-N}$?

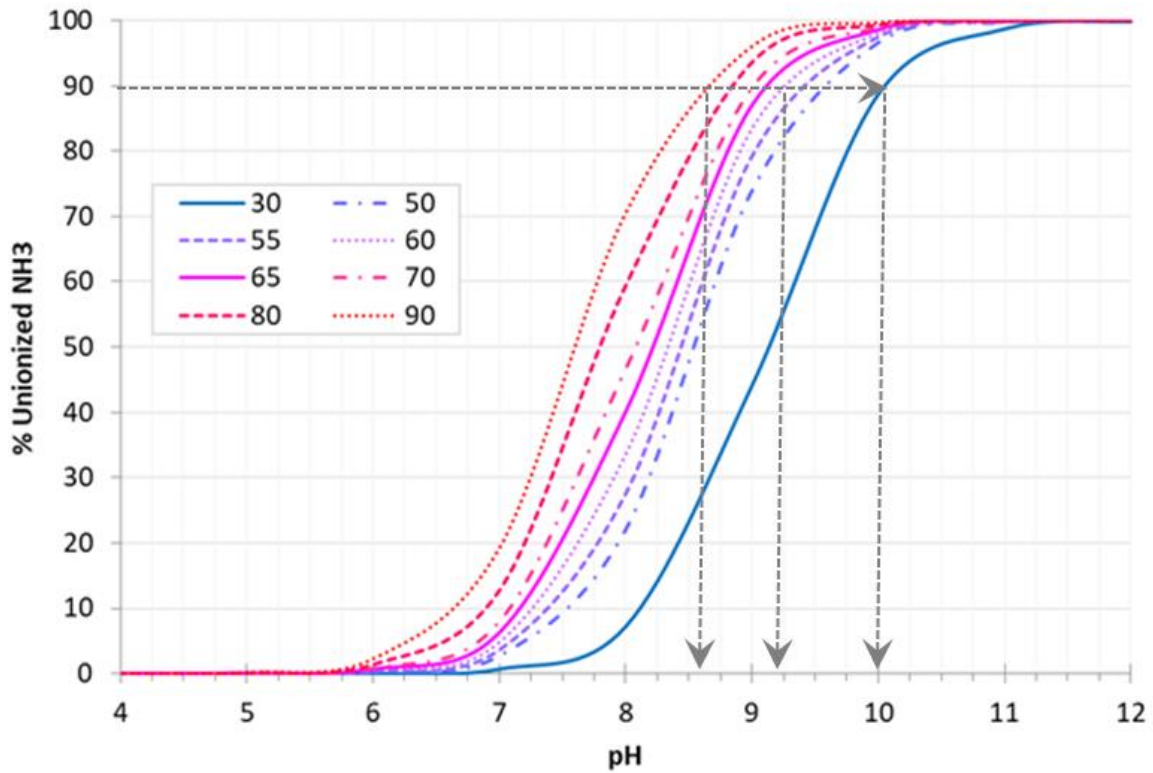
Solution:

To achieve good removal with a single tank scenario, the reactor would maintain a low concentration of ammonia throughout the entire contents of the tank. The driving force for ammonia mass transfer between the liquid to the air would therefore be reduced as the driving force (concentration gradient) is maintained low. With multiple tanks in series, concentration in the contents of the tanks can progressively become lower from the first reactor to the n^{th} reactor in series. This plug flow condition allows for high concentration driving forces at the start of the process and progressively lower towards the final polished effluent.

Discussion Question 10.6. Select 3 different temperatures and pH levels which achieve an ammonia unionization of at least 90% NH_3 . Discuss the implications of how to achieve the conditions from a chemical and thermodynamic perspective.

Solution:

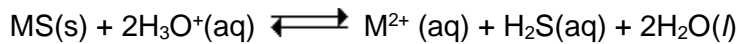
90% unionized ammonia content can be achieved at 90°C with pH 8.58, 60°C with pH 9.24 and 30°C with pH 10.06.



CHAPTER 11

Exercise 11.1. A wastewater containing zinc and iron both at a concentration 0.10 M are aimed to be recovered through chemical sulfide precipitation. Estimate the required pH to precipitate the amount of zinc but not of iron if the initial H_2S concentration is 0.1 M. Use the equation for the metal dissolution in an acidic solution below and rearrange so the single unknown is H_3O^+ . For this, calculate the solubility-product constant in acid (K_{spa}). The K_{sp} values are provided in the table below and in Eq. 11.5 for sulfide dissociation in acid conditions.

$$K_{spa} = \frac{k_{sp}}{k_w k_{sp1}}$$



Data for this question:

Compound	Formula	Ksp
Iron(II) sulfide	FeS	8×10^{-19}
Zinc sulfide (alpha)	ZnS	2×10^{-25}

Solution:

The equation for the dissolution in an acidic solution where the metal ion concentration is 0.1 M and H_2S concentration is 0.1M and H_3O^+ concentration is unknown (x):



$$K_{spa} = \frac{[M^{+2}][H_2S]}{x^2}$$

Rearrange this equation to target H_3O^+ (x):

$$x = \left(\frac{[M^{+2}][H_2S]}{K_{spa}} \right)^{0.5}$$

Using K_{sp} values in the table, calculate the K_{spa} values for FeS:

FeS:

$$K_{spa} = \frac{k_{sp}}{k_w k_{sp1}} = \frac{8 \times 10^{-19}}{(1 \times 10^{-14})(1 \times 10^{-7})} = 8 \times 10^2$$

Substitute the value of K_{spa} for FeS into the Equation:

$$x = \left(\frac{[M^{+2}][H_2S]}{K_{spa}} \right)^{0.5} = \left(\frac{[0.1M][0.1M]}{8 \times 10^2} \right)^{0.5} = 3.54 \times 10^{-3}$$

Concentration of H_3O^+ corresponds to a pH of 2.45

Repeat this process for ZnS:

ZnS:

$$K_{spa} = \frac{k_{sp}}{k_w k_{sp1}} = \frac{2 \times 10^{-25}}{(1 \times 10^{-14})(1 \times 10^{-7})} = 2 \times 10^{-4}$$

Substitute the value of K_{spa} for ZnS into the Equation:

$$x = \left(\frac{[M^{+2}][H_2S]}{K_{spa}} \right)^{0.5} = \left(\frac{[0.1M][0.1M]}{8 \times 10^2} \right)^{0.5} = 7.07$$

Concentration of H_3O^+ corresponds to a pH of -0.85

Exercise 11.2. Estimate the amount of lime ($Ca(OH)_2$) required per year to remove the sulfate and metals from Acid Mine Drainage (AMD) in the table below at a flow rate of $40 \text{ m}^3 \cdot \text{h}^{-1}$. Sulfate concentration in this AMD is $3360 \text{ mg} \cdot \text{L}^{-1}$ [36].

Wastewater source	Acid mine drainage (mg/L) [24]	Wastewater source	Acid mine drainage (mg/L) [24]
Magnesium	342	Nickel	3.78
Aluminium	54.3	Copper	44.9
Chromium	0.12	Zinc	5.9
Manganese	6.05	Cadmium	0.01
Iron	391	Lead	6.9
Cobalt	8.99		

- a) Estimate the amount of sludge generated per year as $CaSO_4$ and $Me(OH)_2$ and the associated costs of disposal if the cost of sludge disposal is €100/ton and the lime cost is €150/ton. Assume a solids content in the sludge of 40%.

- b) Compare this cost with the costs of using biological sulfate reduction instead with ethanol as electron donor. Consider EtOH purity 30%, density 0.95 kg·L⁻¹, and price 100 €·m⁻³.
- c) Based on your calculations above, what is more attractive from an economic point of view, lime dosing or biological sulfate removal.
- d) Provide three non-economic benefits of biological sulfate removal compared with lime dosing.

Solution:

Part A:

In this problem, the lime (added as Ca(OH)₂) is going to form both a metal precipitate (Me(OH)₂) and a calcium sulfate precipitate (CaSO₄). The approach to this problem is to calculate the mass of metal precipitate and the corresponding mass of sulfate precipitate.

The mass of Me(OH)₂ precipitate is calculated by first convert the concentration of each metal from mg/L to mol/L. Each mol of metal will generate 1 mol of Me(OH)₂ precipitate. Therefore, the mass of Me(OH)₂ precipitate can be determined based on the MW of each hydroxide as per the table below.

Next, calculate the corresponding mass of CaSO₄ precipitate. Each mol of Me(OH)₂ generated requires 1 mol of Ca(OH)₂ and will produce 1 mol of CaSO₄. The mass of CaSO₄ is then determined using a MW of 136.14 g/mol, as shown in the table below.

Wastewater source	Acid mine drainage (mg/L)	Atomic weight Me	MW Me(OH) ₂	mmol/L Me	mg/L Me(OH) ₂	mg/L CaSO ₄
Magnesium	342	24.3	60.3	14.074	820.5	1916.0
Aluminium	54.3	27	63	2.011	122.7	273.8
Chromium	0.12	52	88	0.002	0.2	0.3
Manganese	6.05	55	91	0.110	9.8	15.0
Iron	391	55.85	91.85	7.001	629.0	953.1
Cobalt	8.99	59	95	0.152	14.2	20.7
Nickel	3.78	58.7	94.7	0.064	6.0	8.8
Copper	44.9	63.54	99.54	0.707	68.9	96.2
Zinc	5.9	65.4	101.4	0.090	9.0	12.3
Cadmium	0.01	112.4	148.4	0.0001	0.01	0.0
Lead	6.9	207.2	243.2	0.033	8.0	4.5
TOTAL					1688	3300

Next, use mass balancing to determine whether the metals or the sulfate was the limiting material. This will determine if there is residual sulfate (SO₄²⁻) in solution and if additional lime is required. The solution contained 3360 mg/L SO₄²⁻ before treatment. The mass of CaSO₄

precipitate was 3300 mg/L containing 2330 mg/L SO_4^{2-} . Therefore, 1030 mg/L of SO_4^{2-} remains, this requires additional lime and will produce additional $CaSO_4$:

$$\frac{1030 \text{ mg } SO_4^{2-}}{L} \times \frac{136 \text{ mg } CaSO_4}{96 \text{ mg } SO_4^{2-}} = \frac{1460 \text{ mg } CaSO_4}{L}$$

The mass of $CaSO_4$ precipitate per volume of AMD is: $3300 \text{ mg/L} + 1460 \text{ mg/L} = 4760 \text{ mg/L } CaSO_4$

Total precipitate per volume of AMD is: $Me(OH)_2 + CaSO_4 = 4760 \text{ mg/L} + 1688 \text{ mg/L} = 6448 \text{ mg/L}$

Total mass of precipitate is then determined from the flow rate:

$$\frac{6448 \text{ mg solids}}{L} \times \frac{1 \text{ kg solids}}{1 \times 10^6 \text{ mg solids}} \times \frac{1000 \text{ L}}{1 \text{ m}^3} \times \frac{40 \text{ m}^3}{h} = \frac{257.9 \text{ kg solids}}{h}$$

Sludge production is 257.9 kg/h. If the sludge contains 40% solids, the total mass for disposal is 430 kg/h corresponding to 5649 tons per year at a cost of 564,870 € per year

Total lime required is

$$\frac{3360 \text{ mg } SO_4^{2-}}{L} \times \frac{40 \text{ mg } Ca}{96 \text{ mg } SO_4^{2-}} \times \frac{74 \text{ mg } Ca(OH)_2}{40 \text{ mg } Ca} = \frac{2590 \text{ mg } Ca(OH)_2}{L}$$

$$\frac{2590 \text{ mg } Ca(OH)_2}{L} \times \frac{1 \text{ kg } Ca(OH)_2}{1 \times 10^6 \text{ mg } Ca(OH)_2} \times \frac{1000 \text{ L}}{1 \text{ m}^3} \times \frac{40 \text{ m}^3}{h} = \frac{103.6 \text{ kg solids}}{h}$$

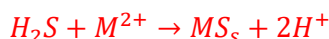
The lime requirement is 103.6 kg/h, this corresponds to 906.9 tons per year at a cost of 136,033 € per year.

Therefore the total cost of lime treatment is:

Cost of lime + cost of sludge disposal = 700,903 € per year

Part B:

For a process using biological sulfate reduction with ethanol as the carbon source, hydrogen sulfide is generated according to Equation 11.14. The hydrogen sulfide then forms a metal precipitate (MeS):



Based on Equation 11.14, each mol of ethanol will reduce 1.5 mols of sulfate and this will then produce 1.5 moles of H_2S and 1.5 mols of MeS. The total sulfate in the process is:

$$\frac{3.360 \text{ g } SO_4^{2-}}{L} \times \frac{1 \text{ mol } SO_4^{2-}}{96 \text{ g } SO_4^{2-}} \times \frac{1000 \text{ L}}{1 \text{ m}^3} \times \frac{1 \text{ mol EtOH}}{1.5 \text{ mol } SO_4^{2-}} \times \frac{40 \text{ m}^3}{h} = \frac{933 \text{ mol EtOH}}{hr}$$

Next, convert from mol ethanol to volume of ethanol solution using MW, concentration and density:

$$\frac{933 \text{ mol EtOH}}{\text{hr}} \times \frac{46 \text{ g mol EtOH}}{1 \text{ mol EtOH}} \times \frac{100 \text{ g EtOH}}{30 \text{ g EtOH}} \times \frac{1 \text{ L EtOH}}{950 \text{ g EtOH}} = \frac{151 \text{ L EtOH}}{\text{hr}}$$

The volume of 30% ethanol solution required is 0.151m³ per hour, corresponding to 1320 m³ per year at a cost of 131,963 € per year.

Similar to Part A, the mass of MeS is calculated by first converting the concentration of each metal from mg/L to mol/L. Each mol of metal will generate 1 mol of MeS precipitate. Therefore, the mass of MeS precipitate can be determined based on the MW of each hydroxide as per the table below.

Wastewater source	Acid mine drainage (mg/L)	Atomic weight Me	MW MeS	mmol/L Me	mg/L MeS
Magnesium	342	24.3	56.3	14.074	792.4
Aluminium	54.3	27	59	2.011	118.7
Chromium	0.12	52	84	0.002	0.2
Manganese	6.05	55	87	0.110	9.6
Iron	391	55.85	87.85	7.001	615.0
Cobalt	8.99	59	91	0.152	13.9
Nickel	3.78	58.7	90.7	0.064	5.8
Copper	44.9	63.54	95.54	0.707	67.5
Zinc	5.9	65.4	97.4	0.090	8.8
Cadmium	0.01	112.4	144.4	0.0001	0.01
Lead	6.9	207.2	239.2	0.033	8.0
TOTAL					1640

The mass of MeS precipitate per volume of AMD is 1640 mg/L MeS. Total mass of precipitate is then determined from the flow rate:

$$\frac{1640 \text{ mg MeS}}{\text{L}} \times \frac{1 \text{ kg MeS}}{1 \times 10^6 \text{ mg MeS}} \times \frac{1000 \text{ L}}{1 \text{ m}^3} \times \frac{40 \text{ m}^3}{\text{h}} = \frac{65.6 \text{ kg MeS}}{\text{h}}$$

The MeS sludge production is 65.6 kg/h. If the sludge contains 40% solids, the total mass for disposal is 164 kg/h corresponding to 1436 tons per year at a cost of 143,647 € per year.

The total cost of biological sulfate reduction is:

Cost of ethanol + cost of sludge disposal = 275,610 € per year

Part C:

Biological sulfate reduction is significantly more attractive economically.

Part D:

Biological sulfate reduction utilizes a pollutant already present in the wastewater. Biological sulfate reduction avoids transportation of hazardous sulfide chemicals.

Biological sulfate reduction can be conducted at ambient temperature and flexible flow rate conditions.

Exercise 11.3. Given the operational parameters of the Thiopaq® process (Section 11.6.3) at a flowrate of $30 \text{ m}^3 \cdot \text{h}^{-1}$ and an initial and final sulfate concentrations at $15 \text{ g} \cdot \text{L}^{-1}$ and $3 \text{ g} \cdot \text{L}^{-1}$, respectively. Calculate the consumption of H_2 in $\text{m}^3 \cdot \text{h}^{-1}$ in the biological sulfate reduction stage (Eq. 11.16).

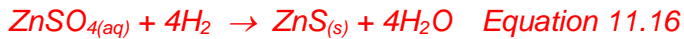
Solution:

First, determine the mass of sulfate reduced in the bioreactor per hour:

$$\text{Sulfate reduced} = (\text{Concentration in} - \text{Concentration out}) \times \text{flowrate}$$

$$\text{SO}_4^{2-} \text{ reduced} = \left(\frac{15 \text{ g SO}_4^{2-}}{\text{L}} - \frac{3 \text{ g SO}_4^{2-}}{\text{L}} \right) \times \frac{50 \text{ m}^3}{\text{hr}} \times \frac{1000 \text{ L}}{1 \text{ m}^3} = \frac{360000 \text{ g SO}_4^{2-}}{\text{h}} = \frac{3750 \text{ mol SO}_4^{2-}}{\text{h}}$$

In the bioreactor, sulfate reducing bacteria convert the $\text{ZnSO}_{4(\text{aq})}$ into $\text{ZnS}_{(\text{s})}$ using hydrogen as electron donor according to the reaction:



Based on Equation 11.16, 4 mols of Hydrogen are required for 1 mol of sulfate:

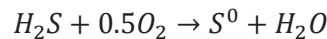
$$\frac{3750 \text{ mol SO}_4^{2-}}{\text{h}} \times \frac{4 \text{ mol H}_2}{1 \text{ mol SO}_4^{2-}} = \frac{15000 \text{ mol H}_2}{\text{hr}}$$

Next, use the ideal gas law to convert from mol of H_2 to a volumetric flow rate of H_2 :

$$\text{Volume H}_2 = \frac{15000 \text{ mol H}_2}{\text{hr}} \times \frac{8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \times 298 \text{ K}}{101300 \text{ Pa}} = 367 \frac{\text{m}^3}{\text{h}}$$

Exercise 11.4. Given that the Thiopaq® process reported a recovery of $8.5 \text{ ton} \cdot \text{d}^{-1}$ of ZnS :

- a) How much air is used to oxidize all sulfides remaining from the calculation of exercise 11.3 in the sulfide oxidizing stage? Assume sulfides are oxidized according to:



- b) Given air pump efficiency of 50%, energy consumption: $110 \text{ Wh} \cdot \text{Nm}^{-3}$, electricity cost: $0,05 \text{ €} \cdot \text{kWh}^{-1}$. What is the cost of the aeration?

Solution:

Part A

From exercise 11.3, it was determined that 3750 mol/h of sulfate was removed during the process, this corresponds to 3750 mol/h of Sulfur. Convert this to a mass of sulfur, using the molecular weight (32 g S per mol S):

$$\frac{3750 \text{ mol SO}_4^{2-}}{\text{h}} \times \frac{1 \text{ mol S}}{1 \text{ mol SO}_4^{2-}} \times \frac{32 \text{ g S}}{1 \text{ mol S}} = \frac{120,000 \text{ g S}}{\text{hr}} = \frac{120 \text{ kg gS}}{\text{hr}}$$

Next determine the mass of sulfur removed as ZnS. For this calculation, the molecular weight of ZnS is 97 g per mol and each mol of ZnS contains 1 mol of S with a mass of 32g:

$$\frac{8.5 \text{ ton ZnS}}{d} \times \frac{1 d}{24 h} \times \frac{1000 \text{ kg ZnS}}{1 \text{ ton ZnS}} \times \frac{32 \text{ g S}}{97 \text{ g ZnS}} = \frac{116.84 \text{ kg gS}}{hr}$$

Based on this calculation, 116.84 kgS is removed via precipitation as ZnS. Using a mass balance, the amount of S removed through aeration was 3.16 kg/h.

$$\frac{3.16 \text{ kgS}}{h} \times \frac{1000 \text{ mol S}}{32 \text{ kgS}} \times \frac{1 \text{ mol O}_2}{2 \text{ mol S}} = \frac{49.4 \text{ mol O}_2}{hr}$$

Next, use the ideal gas law to convert from mol of O₂ to a volumetric flow rate of air:

$$\text{Volume O}_2 = \frac{49.4 \text{ mol O}_2}{hr} \times \frac{8.314 \frac{J}{\text{mol}\cdot K} \times 298K}{101300 \text{ Pa}} = 1.21 \frac{m^3}{h}$$

$$\text{Volume Air} = 5.8 \frac{m^3}{h}$$

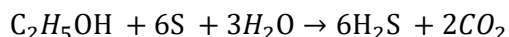
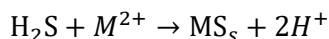
Part B:

The airflow required is 5.8 Nm³/h. First convert this to airflow per year and then calculate a power cost using 110 W.h per Nm³:

$$\frac{5.8 \text{ Nm}^3 \text{ air}}{h} \times \frac{24 h}{d} \times \frac{365 d}{y} \times \frac{110 \text{ W}\cdot h}{1 \text{ Nm}^3 \text{ air}} \times \frac{1 \text{ kW}\cdot h}{1000 \text{ W}\cdot h} = \frac{5541 \text{ kW}\cdot h}{yr}$$

However, the efficiency of the air pump is 50%, therefore the actual power required is 11082 kW.h per year. For an electricity cost of 0,05 €·kWh⁻¹, the aeration cost is 554 € per year.

Exercise 11.5. In 2014, the plant from the company Paques, THIOTEQ™ Metal technology, started operation at a goldmine located in the Dominican Republic to recover copper sulfide from an acidic process water stream. The process consists of two stages: a chemical (precipitation) stage and a biological process where sulfide is produced from elemental sulfur (instead of sulfate) and ethanol. A simplified representation of the governing reactions for metal precipitation and for hydrogen sulfide production can be described as follows:



The technology is able to recover 20,000 ton of Cu per year at the goldmine. Based on this amount, estimate the following:

- The amount of S that is being added.
- The amount of ethanol that is being added (ethanol: 30%, density: 0.95 kg·L⁻¹) in order to reduce sufficient sulfur to sulfide for Cu precipitation. Assume a 100% ethanol conversion efficiency.
- What is the advantage of using S instead of sulphate as in the Thiopaq® technology? Hint: how much ethanol would have to be added if SO₄²⁻ would be the electron acceptor?

d) Despite the advantage highlight in c), discuss a disadvantage from a process point of view.

Solution:

Part A

The chemical precipitation stage of the Paques, THIOTEQ™ Metal technology uses hydrogen sulfide to precipitate metals according to the equation:



where M^{2+} is a metal, such as Zn^{2+} , Cu^{2+} , Pb^{2+} and Ni^{2+} . According to this equation, 1 mol of Cu will precipitate with 1 mol of S. Therefore, convert the mass of Cu recovered per year to mols.

$$\frac{20,000 \text{ ton Cu}}{\text{year}} \times \frac{1,000,000 \text{ g Cu}}{1 \text{ ton Cu}} \times \frac{1 \text{ mol Cu}}{63.5 \text{ g Cu}} = \frac{3.15 \times 10^8 \text{ mol Cu}}{\text{year}}$$

Next, use the mols per year of Cu to calculate the required addition of S in mol/yr

$$\frac{3.15 \times 10^8 \text{ mol Cu}}{\text{year}} \times \frac{1 \text{ mol S}}{1 \text{ mol Cu}} = \frac{3.15 \times 10^8 \text{ mol S}}{\text{year}}$$

Next, use the molecular weight of S to convert from mol/y S to kg/y S

$$\frac{3.15 \times 10^8 \text{ mol S}}{\text{year}} \times \frac{32 \text{ g S}}{1 \text{ mol S}} \times \frac{1 \text{ ton S}}{1,000,000 \text{ g S}} = \frac{10,080 \text{ ton S}}{\text{year}}$$

The total mass of sulfur required is 10,800 ton per year. This corresponds to 1150 kg/h.

Part B

In this example, the biological stage of the Paques, THIOTEQ™ Metal technology uses ethanol to reduce sulfur to hydrogen sulfide, according to the equation:



Based on this equation, 1 mol of ethanol can reduce 6 mols of sulfur. From Part A, the process requires 1150 kg/h of sulfur. Convert this to mols of S and therefore mols of ethanol required:

$$\frac{1150 \text{ kg S}}{\text{hr}} \times \frac{1000 \text{ mol S}}{32 \text{ kg S}} \times \frac{1 \text{ mol EtOH}}{6 \text{ mol S}} = \frac{5992 \text{ mol EtOH}}{\text{hr}}$$

Next, convert from mol ethanol to volume of ethanol solution using MW, concentration and density:

$$\frac{5992 \text{ mol EtOH}}{\text{hr}} \times \frac{46 \text{ g mol EtOH}}{1 \text{ mol EtOH}} \times \frac{100 \text{ g Solution}}{30 \text{ g EtOH}} \times \frac{1 \text{ L Solution}}{950 \text{ g Solution}} = \frac{967 \text{ L EtOH Solution}}{\text{hr}}$$

The volume of 30% ethanol solution required is 967 L per hour.

Part C

The generation of hydrogen sulfide from sulfate, with Ethanol as the carbon source was described by Equation 11.14.



Based on Equation 11.14, each mol of ethanol will produce 1.5 mols of H₂S (compared to 6 mols of H₂S using elemental sulfur. Therefore the amount of ethanol consumed for the same production of H₂S is 4 times larger, corresponding to 3869 L/hr.

Exercise 11.6. Give the redox equation for sulfate reduction with methanol, assuming that methanol is oxidized to HCO₃⁻. Write sulfide as HS⁻.

Solution:



Exercise 11.7. A wastewater contains sulfate (2.5 g·L⁻¹) and zinc (1 g·L⁻¹ Zn²⁺) and will be treated biologically. Methanol (CH₃OH) is selected as electron donor for sulfate reduction. Calculate how much methanol (g·L⁻¹) needs to be added considering that:

- all zinc precipitates as zinc sulfide
- an excess of 200 mg·L⁻¹ total sulfide is targeted
- 5% of the consumed methanol is used as carbon source
- no hydrogen sulfide is stripped

How much sulfate is left in the effluent?

Solution:

1 g/l of Zn²⁺ (M=65.38 g/mol) corresponds to 15.3 mM Zn²⁺. As this is precipitated as ZnS, 15.3 mM sulfide is needed, assuming the remaining Zn²⁺ in solution is negligible compared to the influent concentration. An excess of 200 mg/l sulfide (M= 32 g/mol) corresponds to 6.25 mm sulfide. Thus, a total of 21.55 mM of sulfide is needed. To produce this by sulfate reduction, $4/3 \cdot 21.55 = 28.73$ mM of methanol is required stoichiometrically. Because 5% of consumed methanol is used as carbon source, in total $28.73/0.95 = 30.25$ mM methanol or 0.97 g/L is needed.

2.5 g/l of sulfate (M= 96 g/mol) corresponds to 26.0 mM, of which 21.55 mM is reduced to sulfide. Thus, in the effluent 4.5 mM or 0.43 g/L sulfate remains. Note that in reality a small fraction of sulfate is used as sulfur source for growth of the sulfate reducing bacteria. This anabolic need is however negligible with the catabolic consumption.

Exercise 11.8. Zinc needs to be removed to a level of 0.1 mg·L⁻¹. What is the theoretically required total sulfide level (in µg·L⁻¹) to achieve this, assuming equilibrium for ZnS precipitation is reached. The pH is 7, the pK_{sp} for ZnS is 24.7.

Solution:

$$[\text{Zn}^{2+}] \cdot [\text{S}^{2-}] = 10^{-24.7} \text{ M}^2 \quad (\text{p}K_{\text{sp}} = 24.7)$$

The target Zn²⁺ concentration is 0.1 mg/l, or $1.52 \cdot 10^{-6} \text{ M Zn}^{2+}$.

$$\text{At equilibrium, } [\text{S}^{2-}] = \frac{10^{-24.7}}{1.52 \cdot 10^{-6}} = 1.30 \cdot 10^{-19} \text{ M}$$

$$[\text{S}_{\text{tot}}] = [\text{S}^{2-}] \cdot \left(1 + \frac{[\text{H}^+]}{K_{a2}} + \frac{[\text{H}^+]^2}{K_{a1} \cdot K_{a2}} \right) = 1.30 \cdot 10^{-19} \cdot \left(1 + \frac{10^{-7}}{10^{-17.4}} + \frac{(10^{-7})^2}{10^{-7} \cdot 10^{-17.4}} \right) = 6.6 \cdot 10^{-9} \text{ M} = 0.21 \text{ µg/l}$$

Exercise 11.9. It turns out that besides zinc, there is also copper (1 g·L⁻¹ Cu²⁺) present in the waste stream. CuS has a pK_{sp} of 36.2.

- Will CuS precipitate at the pH and total sulfide concentration at which the zinc precipitates under Exercise 11.8?
- What consequence will the presence of 1 g·L⁻¹ Cu²⁺ have on zinc precipitation?

c) How would you solve the problem that emerged in the answer of part b?

Solution:

In Exercise 11.8, the concentration of Zn^{2+} and S^{2-} at equilibrium were calculated. Because CuS has a higher K_{sp} than ZnS, CuS will also precipitate. The 1 g/l of Cu^{2+} ($M= 63.5$ g/mol) corresponds to $15.7 \cdot 10^{-3}$ M Cu^{2+} . With the S^{2-} concentration calculated at question c:

$$[Cu^{2+}] \cdot [S^{2-}] = 1.3 \cdot 10^{-19} \cdot 15.7 \cdot 10^{-3} = 2.05 \cdot 10^{-21} M^2$$

- As the maximum solubility product equals $10^{-36.2} M^2$, as given by the K_{sp} of CuS, is much lower, CuS will precipitate.
- To precipitate all Cu^{2+} , 15.7 mM of additional sulfide is needed. Therefore, 15.7 mM of sulfate needs to be reduced to provide the sulfide for CuS precipitation. For ZnS precipitation, 15.3 mM sulfate is consumed (see answer Exercise 11.6). Thus, in total 31.0 mM or 3.0 g/l of sulfate is needed. However, only 2.5 g/l is available; sulfate is limiting.
- An additional sulfur source is needed. Elemental sulfur is a good choice as it requires less electron donor (here methanol) compared to sulfate or other more oxidized sulfur species, like sulfite or thiosulfate.

Exercise 11.10. Zinc and copper sulfide precipitate simultaneously in the process. At which pH is selective precipitation possible?

Solution:

We are looking for the pH at which CuS still precipitates but ZnS not. At that pH, the Zn^{2+} in solution is 1 g/l or 15.3 mM Zn^{2+} , while the total sulfide (S_{tot}) concentration is 200 mg/L or 6.25 mM. The S^{2-} concentration needs to be lower than:

$$[S^{2-}] = \frac{10^{-24.7}}{15.3 \cdot 10^{-3}} = 1.30 \cdot 10^{-23} M$$

Because in the following equation, all parameters except the proton concentration is known, the latter can be calculated by iteration:

$$[S^{2-}] = \frac{[S_{tot}]}{1 + \frac{[H^+]}{K_{a2}} + \frac{[H^+]^2}{K_{a1} \cdot K_{a2}}}$$

It turns out that at a pH of 1.86, the zinc will not precipitate.

CHAPTER 12

Exercise 12.1. Table 1 shows the waste management hierarchy. Provide at least two examples per step in the waste hierarchy ladder for the water sector as a whole. Can you provide two examples for each of the following sectors within the water industry; (i) drinking water production, (ii) municipal wastewater management and industrial (waste) water management?

Solution:

1. *Quantitative prevention / Refuse: There are plenty of examples that can be mentioned. These include reduction in water consumption, decrease in chemical consumption through optimized process control, washing of cloth at lower temperatures, shorter showers, source separation of urine, avoidance of tissues entering the sewer etc.*
2. *Intensify use / Rethink: Examples include pre-treatment of sludge to enhance biogas production, introduction of more efficient/compact treatment approaches.*
3. *Qualitative prevention / Reduce: Examples include using materials that can be re-used after end-of-service life, use of low carbon materials, energy efficient aerators/pumps/mixers etc. Use of coagulants with a lower environmental impact and/or higher potential for re-use. Use of calcite rather than sand during pellet softening.*
4. *Product Reuse (in its original function): water reclamation processes, iron pellets for As-removal,*
5. *Repair / Refurbish: pumps, repair pipes underground (for instance by relining them on the inside)*
6. *Reuse parts / Remanufacture: cut (new) pipes, change use of drinking water pipes to wastewater transportation pipes*
7. *Recycle parts / Repurpose: cut (new) pipes, change use of drinking water pipes to wastewater transportation pipes*
8. *Material recycling: calcite pellets for e.g. glass-industry or (re-)use as seeding material, coagulants made from iron- or alum sludge, phosphate recovery for agricultural use.*
9. *Use as fuel / Recover: biogas production, incineration of sewage sludge*
10. *Incineration as disposal route with material recovery: Recovery of phosphate, coagulants and heavy metals from sludge ash.*
11. *Incineration as disposal route without material recovery: incineration of sludge, spent activated carbon.*
12. *Landfilling: landfilling of biosolids, grit removal, sand, As-containing iron sludge from groundwater.*

Exercise 12.2. The most commonly used coagulants in drinking water treatment are iron salts (either with chloride or sulfate as counter anion) or aluminum salts in the form of aluminium sulfate (often referred to as alum) and Poly-Aluminium-Chloride (PAC). The choice differs depending on the region. For example, in Australia alum is predominantly used, where as in countries such as the Netherlands and the US iron based salts are used more often. The latter is often directly related to the price of the coagulant, as both types of coagulants are capable of reaching desired water quality standards. In some regions alum is cheaper and readily available and in some iron salts are cheaper and readily available (i.e. the presence of iron and alum smelters greatly affect the price). In the context of 'circular resources', despite the fact that for your location iron salt coagulants to be used in drinking water treatment are 30% more expensive than alum based salts, provide several arguments why iron based salts ultimately would be considered the best choice for the urban water infrastructure at large?

Solution:

There are more options available for multiple use of iron rich drinking water sludge within the urban water infrastructure as it can be used for both control of sulfide in sewers, (the main cause for sewer corrosion), sulfide control in digesters as well as phosphate removal at

WWTP and ingredient in the cement industry for the production of clay bricks. Alum can only be used for the removal of phosphate. Equally important, iron has more reuse options than aluminum. A good example has been discussed in this chapter, i.e. iron pellets.

Exercise 12.3. In the question above, you have provided several reasons why the choice of iron based coagulants would be preferable for the urban water infrastructure at large. However, you might have given a different answer if you were the OH&S manager of the drinking water plant. Describe the OH&S concerns that is associated with transport, handling and storage of concentrated chemicals.

Solution:

The transport, handling and storage of concentrated chemicals can come with serious occupational health and safety concerns. To illustrate this, in some places it is not allowed to store concentrated chemicals such as FeCl_3 (42 wt %) in urban areas, thereby hindering the use of FeCl_3 as a sewer corrosion control method. One can imagine that one chemical is easier / safer to handle and, something that should always be taken into consideration and decisions ultimately taken by utilities and/or companies go well beyond economics, sustainability and recovery potential and also include ease of operation, robustness and health and safety aspects.

Exercise 12.4. The first implementation of the waste management hierarchy dates back as 1975 when it was included in the Waste Framework Directive (1975/442/EEC), and ever since has become one of the key pillars of environmental regulation that has been embedded in various national regulatory principles and guidelines as well international treaties and covenants. Nevertheless, as witnessed by our current way of wastewater management, in many instances the waste management hierarchy is not followed. Provide at least three reasons why this is the case.

Solution:

Elements of a good response include: (i) Process economics; process that enables efficient recovery / reuse is too expensive. (ii) Appropriate regulation that allows the reuse of the recovery material is not in place. (iii) There is no market demand for the recovered product. (iv) Reusing a product is not possible in terms of the specs on hygiene and human health. (v) The environmental impact of e.g. a resource recovery route is in fact less positive). This might be the case situations where the materials can be regenerated, but this regeneration process consumes, for example, a lot of energy, water or chemicals.

Exercise 12.5. A drinking water utility uses alum as coagulant at a large scale drinking water treatment plant (i.e. 500.000 PE). Currently, the produced sludge is stored on-site since regulation allows it and it is from an economic point of view (by far) the cheapest option. Moreover, there is sufficient space to store the sludge for another 30 years. Nevertheless, the utility is afraid that the regulation will change as such that on-site storage is prohibited. Calculate the amount of sludge produced on a yearly basis used by the water utility and the financial impact it would have in case the sludge would need to be landfilled. In your answer, assume an alum dosing rate of 7 mg Al^{3+} /L (see chapter 3 for more detail), a daily water consumption of 130 liter per person per day, a sludge moisture content of 70% and a landfill gate fees of \$100 dollar per ton product (i.e. thus wet ton sludge). What about the situation where landfilling is not allowed?

Solution:

Step 1. 7 mg Al^{3+} /L equals to $(27 + 3 \times 17) / 27 = 20.22$ mg $\text{Al}(\text{OH})_3$ /L water treated.

Step 2. 130 liter/day \times 500.000 (pe) = 65 ML/day

Step 3. 65 ML/day \times 20.22 kg/ML = ~ 1314 kg $\text{Al}(\text{OH})_3$ (s) per day (1.3 ton per day) or 480 ton (as dry solids) annually.

Step 4. 480 ton / 0.30 (i.e. moisture content is 70%) = ~ 1600 wet ton $\text{Al}(\text{OH})_3$ per year.

Step 5. $1600 \times \$100 = \$160,000$ per year.

In cases where landfilling is not allowed one would need to find or develop another destination for this sludge. A common route is to 'climb' the waste hierarchy ladder. This would mean in this case looking for waste incineration as a disposal route. As this sludge contains reasonable amounts of alum, one should look for incineration route with metal recovery. For alum-sludge, this might be the cement industry (cement contains alum as an important ingredient). Note that alum sludge from drinking water production plants typically have low P concentrations. In case where the P concentrations in alum sludge are substantial mono-incineration may become the preferred option.

CHAPTER 13

Question 13.1. What are the predominant concerns and targets of regulators? (leadership, utility management)

Solution:

After having read the comprehensive body of regulations governing the use of recovered resources from water and wastewater, think of the concerns and intentions of policy makers and interpret them in your own words. Which goods are protected by regulations and which behaviour is favoured by legal incentives? As a critical citizen, do you think the regulative body is complete or do feel that important human or natural goods are not sufficiently covered? How are the regulations linked to the global agreements like the Sustainable Development Goals or the Climate Agreement?

Question 13.2. How would you explain the legislative framework to colleagues or third parties with limited specific knowledge? (operators, utility management)

Solution:

In your role as an operator or manager of a utility, think of having to explain the legislative framework to third parties in your own words in 15 minutes, for instance in a presentation. Think of the structural approach in Europe with policies, directives and regulations and think of the restrictions and incentives. How is the Circular Economy addressed by regulations, if at all?

Question 13.3. What is the difference between EU regulations and regulations of your country (operators, utility management)

Solution:

Once you have read and understood the body of legislation in the European Union, check if you have equivalent regulations in the jurisdiction where you operate. The check should include regulations that have similar intentions and cover similar subjects, even if the explicit targets and wording are quite different from what EU regulators have adopted. Find out the differences, explain them with your own words. What is your opinion about the differences – do you think that the European regulations can serve as a model for other countries?

Question 13.4. Which regulations could support resource recovery initiatives? (leadership, utility management)

Solution:

Imagine you want to improve the environmental performance of your water activity, you have limited financial resources and your activity should generate additional revenues or reduce the cost of operating your facility. Reviewing the regulations, which type of regulations could contribute to your financial targets? For instance, about 100 struvite plants operate globally in wastewater treatment plants saving maintenance costs because of preventing scaling and incrustations in pipes and tanks of EHBP plants. In many cases, recycling struvite pays back even if the product is given away for free.

Question 13.5. Which areas of the water and wastewater treatment sector are preferred targets for resource recovery? (leadership, utility management)

Solution:

Current legislation for water and wastewater treatment focuses on removal (not re-use) – of contaminants, nutrients, organic matter, etc. If you think of recovery and recycling, how would you select and which area would you chose? To what extent would you consider legislation

and to what extent would you consider other drivers, e.g. operating costs? Which other arguments could influence your decision?

Question 13.6. Can anaerobic digestion contribute to reduce greenhouse gas emissions and abate global warming? (leadership, utility management)

Solution:

You have learned that policies aim at achieving renewable energy targets and prevent emissions to air and water bodies. Renewable energy can be recovered by anaerobic digestion of sewage sludge. Do you think that anaerobic digestion can make a relevant contribution to the renewable energy targets? How could anaerobic digestions concurrently contribute to pollution prevention?

Question 13.7. Which legislative bodies need to be considered if undertaking activities of recovery and recycling of energy and nutrients? (leadership, utility management)

Solution:

If you conceive a resource recovery and recycling activity, you need to plan compliance with the legislative framework outlined in this chapter. However, not all regulations are relevant for your planned activity. Please specify regulations you need to comply with for a) an energy recovery activity or b) a nutrient recovery activity. Find out, which regulations need to be considered for every activity - regardless of the resource to be recovered – and which regulations are only relevant for specific recycling activities?

CHAPTER 14

(No Exercises)

CHAPTER 15

Exercise 15.1. How should a campaign to introduce water reuse at household level in the MENA region be designed?

Solution:

Any public awareness intervention should be designed by taken the following steps into consideration:

- *Conduct research to understand household knowledge, perceptions, and attitudes towards water reuse so that the campaign is designed to address any fears, confusion, etc. of households.*
- *It should be designed in collaboration with relevant government authorities to align and capture key components of relevant policies and regulations,*
- *Include importance of water reuse (what are the pressing water needs in the country/city/town) and tailor around the following themes: for example, water scarcity combined with growing urban water needs make water reclamation and innovative water allocations for reuse important and necessary for the region.*

*A good reference: Lazarova et al. 2013. Milestones in water reuse: The best success stories. IWA. 408pp. Open access at <https://iwaponline.com/ebooks/book/581/Milestones-in-Water-Reuse-The-Best-Success-Stories>. Refer to **Chapter 3: NEWater: A key element of Singapore's water sustainability** for a great example of how effective public education and communication helped Singapore gain public trust for wastewater reuse for potable purposes.*

Exercise 15.2. Could you describe why it is so challenging to change behaviour of e.g. African farmers who use untreated wastewater due to the lack of safer alternative water sources?

Solution:

The following are some factors limiting behaviour change among farmers using untreated wastewater:

- *Limited awareness of health and environmental risks of using untreated wastewater and lack of governmental resources to support required educational measures.*
- *Financial benefits of using untreated wastewater by farmers outweigh that of using treated water because untreated wastewater is currently/ mostly 'free'.*
- *Whilst some governments have regulations on wastewater reuse, enforcement is largely lacking due to lack of resources, low prioritization.*
- *Additional research is required to comprehensively understand the full gamut of approaches needed to trigger and sustain behavior change of users of untreated wastewater.*

Reference: See Otoo, Miriam; Drechsel, Pay. (Eds.) 2018. Resource recovery from waste: business models for energy, nutrient and water reuse in low- and middle-income countries. <http://www.iwmi.cgiar.org/Publications/Books/PDF/resource-recovery-from-waste.pdf> . Business Model 22: Corporate Social Responsibility (CSR) as a driver of change – page 733.

Exercise 15.3. Select a country where farmers use wastewater for agricultural production. Determine which of these measures (economic or social (marketing) incentives, such as access to credit, labelling/branding, dedicated marketing chains, tax exemptions, and institutional support, like the provision of extension services, awards, or tenure security) would be the best in supporting behavior change and justify why?

Solution:

Refer to: Business Model 22: Corporate Social Responsibility (CSR) as a driver of change – page 733 in for the example in Ghana. Otoo, Miriam; Drechsel, Pay. (Eds.) 2018. Resource recovery from waste: business models for energy, nutrient and water reuse in low- and middle-income countries. <http://www.iwmi.cgiar.org/Publications/Books/PDF/resource-recovery-from-waste.pdf> .

Exercise 15.4. Even with existing regulations, can you explain the reluctance of agricultural producers in using treated wastewater for irrigation?

Solution:

Similar answer to Question 2. For additional cases refer to Chapter 18. Business Models for Increasing Safety in Informal Wastewater Irrigation page 728, in Otoo, Miriam; Drechsel, Pay. (Eds.) 2018. Resource recovery from waste: business models for energy, nutrient and water reuse in low- and middle-income countries. <http://www.iwmi.cgiar.org/Publications/Books/PDF/resource-recovery-from-waste.pdf> .

Exercise 15.5. What regulations need to be changed to allow/ incentivize biosolids land application?

Solution:

*One of the most influential legal drivers of resource recovery and reuse in Europe was the establishment of the **Landfill Directive** (1999/31/EC), which defines landfills as the last option for waste treatment and disposal. The directive imposes, for example, staged landfill reduction targets for the biodegradable fraction of municipal solid waste. Because the Landfill Directive limits the landfill capacity, this is pushing countries to identify alternative waste management options, including reuse. For example, California's policy prohibiting landfilling of untreated sewage sludge drove its beneficial reuse as 'Class A biosolids'.*

Other regulatory factors include emissions caps, carbon taxes or carbon trading schemes; incentives related to the share of alternative (green) energy

Refer to Chapter 19. The Enabling Environment and Finance of Resource Recovery and Reuse. Boxes 19, 22 and 24 in: Otoo, Miriam; Drechsel, Pay. (Eds.) 2018. Resource recovery from waste: business models for energy, nutrient and water reuse in low- and middle-income countries. <http://www.iwmi.cgiar.org/Publications/Books/PDF/resource-recovery-from-waste.pdf> for more details.

Exercise 15.6. Where risk awareness is low, and not easy to develop, how best can farmers be motivated to trigger adoption of risk mitigation measures?

Solution:

Where risk awareness is low and farmers and other stakeholders along the food chain do not see a reason for engaging in safety practices, they might however change their behavior for other values or benefits which can contractually be agreed on Examples are:

- **Tenure security:** Many users of wastewater farm along streams on public land with limited tenure security if any, and constant fear of eviction. Land release, zoning and tenure security are thus powerful incentives when demanding the implementation, e.g. of best praactices, especially those which require farm-based infrastructure.
- **Credit on condition:** A similar incentive is the provision of low-interest credit to farmers who are applying safe irrigation methods. It remains the duty of the authorities to monitor farmers' compliance with their contractual obligations.
- **Fear of exposure:** Where safety regulations cannot be monitored by authorities, media exposure (naming and shaming) can be a powerful alternative to steer compliance. Urban farmers in Ghana feared media exposure as it can trigger ad hoc policy response like eviction from the land.

Exercise 15.7. Select a country and assess the potential for wastewater-based aquaculture. Determine socio-economic factors that can support and/or limit consumer demand.

Solution:

*Refer to **Chapter 15. Business Models beyond Cost Recovery: Leapfrogging the value chain through aquaculture** in : Otoo, Miriam; Drechsel, Pay. (Eds.) 2018. Resource recovery from waste: business models for energy, nutrient and water reuse in low- and middle-income countries.*

<http://www.iwmi.cgiar.org/Publications/Books/PDF/resource-recovery-from-waste.pdf> for case examples from Africa and Asia.

Exercise 15.8. Assess the current level of formal and informal use of septage in agriculture in your country. Evaluate the factors supporting and limiting its formal use.

Solution:

Refer to **SWOT Analyses of case examples in Chapter 11. Business Models on Compost production for sustainable service delivery**; and **Chapter 12. Business Models for outsourcing fecal sludge to the farm** in : Otoo, Miriam; Drechsel, Pay. (Eds.) 2018. *Resource recovery from waste: business models for energy, nutrient and water reuse in low- and middle-income countries.* <http://www.iwmi.cgiar.org/Publications/Books/PDF/resource-recovery-from-waste.pdf>.

Some factors supporting formal reuse of fecal reuse include:

1. Increasing urban populations using onsite sanitation systems and thus quantities of generated fecal sludge
2. Legalization of use of treated fecal sludge
3. Decreasing land fertility and rising fertilizer prices

Limiting factors include:

1. New sewage lines developed in underserved areas can destroy the 'fecal sludge' market.
2. Legalization may imply additional business costs for farmers, such as registration, marketing and branding, etc.

CHAPTER 16

Exercise 16.1. Suppose a new vendor is found for the calcite-seed pellets (from the revised innovative scenario described in Figure 16.5 and 16.6), which would reduce transport requirements to the treatment plant by 50%. Calculate the overall environmental impact of revised innovative scenario before and after this transportation savings in units of Ecopoints (Pts).

Solution:

Figure 16.5 represents the data inventory for the “revised innovative scenario”, which is also shown in Table 16.3 (under the heading “Innovative revised”). The total environmental impact of the revised innovative scenario can be calculated from the data in Figure 16.5.

Revised innovative scenario total impacts (data from Figure 16.5):

$$2.07 + 0.47 + 0.184 + 0.0712 + 1.79 - 4.47 - 5.38 = -5.26 \text{ Pts}$$

New revised innovative scenario total impacts with reduced transportation emissions to the plant:

$$(2.07/2) + 0.47 + 0.184 + 0.0712 + 1.79 - 4.47 - 5.38 = -6.30 \text{ Pts}$$

Exercise 16.2. Suppose additional research showed that the innovative revised process described in Section 16.4.2 eliminates losses to the sewer. Based on the data in Table 16.3 and Figure 16.5, what is the new single score resulting from the LCA of the “innovative revised” scenario with no calcium carbonate loss to the sewer?

Solution:

Figure 16.5 represents the data inventory for the “revised innovative scenario”, which is also shown in Table 16.3 (under the heading “Innovative revised”). The total environmental impact of the innovative scenario can be calculated from the data in Figure 16.5.

Total impacts from the revised innovative scenario with no loss to sewer (data from Figure 16.5):

$$2.07 + 0.47 + 0.184 + 1.79 - 4.47 - 5.38 = -5.34 \text{ Pts}$$

Exercise 16.3. A drinking water production site generates 150,000 m³ of water and 680 tons of CaCO₃ per day. The calcium carbonate recovery offsets conventional calcium carbonate production. The environmental impacts of calcium carbonate production can be extracted from Figure 16.5. Determine the unit impacts of conventional calcium carbonate production (in units of Pts per ton CaCO₃) and the environmental benefits of its recovery (in units of Pts per year).

Solution:

From Figure 16.5, 111 kg of calcium carbonate results in 0.47 Pts of impact.

$$[(0.47 \text{ Pts}) / (111 \text{ kg})] * (1,000 \text{ kg/ton}) = 4.23 \text{ Pts per ton of CaCO}_3 \text{ (ReCiPe Endpoint V1.13).}$$

$$(680 \text{ tons of CaCO}_3 \text{ per day}) * (4.23 \text{ Pts per ton of CaCO}_3) * (365 \text{ days per year}) = 1.05 \times 10^6 \text{ Pts per year}$$

Exercise 16.4. You are performing a quick scan analysis of a process that requires the following materials and processes for construction and across its lifetime: 3,9 tons of reinforcing steel, 179 m³ of concrete, and 16,600 MWh of electricity. Over the same lifetime, nutrient recovery and distribution to agriculture offset 139 tons of nitrogen fertilizer and 55 tons of phosphorus fertilizer. Given the unit impacts below, (a) determine the relative global warming impact of steel, concrete, and electricity (determine the total impacts of the three, and each's contribution to that total as a percentage) and (b) determine what percentage of impacts are offset by both nitrogen fertilizer offsets and phosphorus fertilizer offsets.

- Nitrogen fertilizer: 11,5 kg-CO₂ eq. per kg N
- Phosphorus fertilizer: 2,1 kg-CO₂ eq. per kg P
- Reinforcing steel: 2,5 kg-CO₂ eq. per kg steel
- Concrete: 398 kg-CO₂ eq. per m³ concrete
- Electricity: 0,64 kg-CO₂ eq. per kWh

Solution:

(a) Determine the total global warming potential of steel, concrete, and electricity, and the three added together.

Steel: (3,900 kg of reinforcing steel) * (2.5 kg-CO₂ eq. per ton steel) = 9,750 kg-CO₂ eq.
 Concrete: (179 m³ of concrete) * (398 kg-CO₂ eq. per m³ of concrete) = 71,300 kg-CO₂ eq.
 Electricity: (16,600 MWh of electricity) * (1,000 kWh per MWh) * (0.64 kg-CO₂ eq. per kWh)
 = 1.059 x 10⁷ kg-CO₂ eq.
 Total: 1.067 x 10⁷ kg-CO₂ eq.

Determine the percentage contribution from each of the three.

Steel percentage: (100%) * (9,750 kg-CO₂ eq.) / (1.067 x 10⁷ kg-CO₂ eq.) = 0.1%
 Concrete percentage: (100%) * (71,300 kg-CO₂ eq.) / (1.067 x 10⁷ kg-CO₂ eq.) = 0.7%
 Electricity percentage: (100%) * (1.059 x 10⁷ kg-CO₂ eq.) / (1.067 x 10⁷ kg-CO₂ eq.) = 99.2%

(b) Determine the impact offsets from nitrogen and phosphorus fertilizers.

Nitrogen: (139,000 kg of N) * (11.5 kg-CO₂ eq. kg N) = 1.60 x 10⁶ kg-CO₂ eq.
 Phosphorus: (55,000 kg of P) * (2.1 kg-CO₂ eq. kg P) = 1.14 x 10⁵ kg-CO₂ eq.

Determine percentage of impacts that are offset by N and P fertilizers.

N offset percentage: (100%) * (1.60 x 10⁶ kg-CO₂ eq.) / (1.067 x 10⁷ kg-CO₂ eq.) = 15.0%
 P offset percentage: (100%) * (1.14 x 10⁵ kg-CO₂ eq.) / (1.067 x 10⁷ kg-CO₂ eq.) = 1.1%

Exercise 16.5. A resource recovery and treatment process results in fugitive emissions of nitrous oxide (N₂O) and methane (CH₄). Ultimately, 0,5% of influent nitrogen is released as N₂O and 2 g of CH₄ is released per m³ treated. If the characterization factors of N₂O and CH₄ are 298 g-CO₂ eq. per g N₂O and 28 g-CO₂ eq. per g CH₄, what is the total global warming potential resulting from fugitive emissions (in units of g-CO₂ per m³ treated) for a wastewater with 35 mg-N·L⁻¹ in the influent?

Solution:

Methane:
 (2 g CH₄/m³) * (28 g-CO₂ eq./g CH₄) = 56 g-CO₂ eq./m³

Nitrous oxide:
 [(0.005 g-N as N₂O)/(g-N in influent)] * (46 g-N₂O/14 g-N) * (35 g-N/m³) * (298 g-CO₂ eq./g N₂O) = 171 g-CO₂ eq./m³