

13

Production Integrated Water Management and Decentralized Effluent Treatment

13.1

Introduction

Until now, the main point of interest in this book has been biological wastewater treatment. In this chapter we want to expand our perspective to the development of new production processes with reduced consumption levels of water and raw materials and with reduced production of wastewater. For this purpose, we have to direct our interest towards an entire production process and we have to consider new methods to save water and different, mostly non-biological ways to treat water.

Figure 13.1 provides a systematic view to make the following discussions in this chapter more readily understood.

It is necessary to limit the problem to a single state and it is also prudent to discuss the problem with respect to water while keeping in mind that water as well as all impurities may change their state.

Water pollution and wastewater treatment are typically divided into the two different fields of application, i.e. industrial and municipal wastewater. In this chapter, we will consider the production and treatment of industrial wastewater (Fig. 13.1).

Process integrated water management is characterized by three management procedures:

1. Minimization of water use may already be an important aim, but it may be that water reuse is not possible or the cases are restricted and the advantages are too small. Only if two or three processes have coupled, multiple use of water can offer a chance for considerable saving. Therefore, a separate discussion of point 1 is necessary.
2. The development of new processes and the optimization of existing or new ones with the aim of saving water, materials and energy must be the first step of water management. The price for fresh water, the costs for wastewater treatment and the charges for discharging into surface waters must be considered to find the best way for a *sustainable development* which is a balance of economical success, environmental protection and social acceptance (Fig. 13.2)
3. The regeneration and recycling of water should be taken into account where there is a short supply of fresh water, which makes it necessary to close water cycles at least partly. Point 3 should be discussed together with point 1.

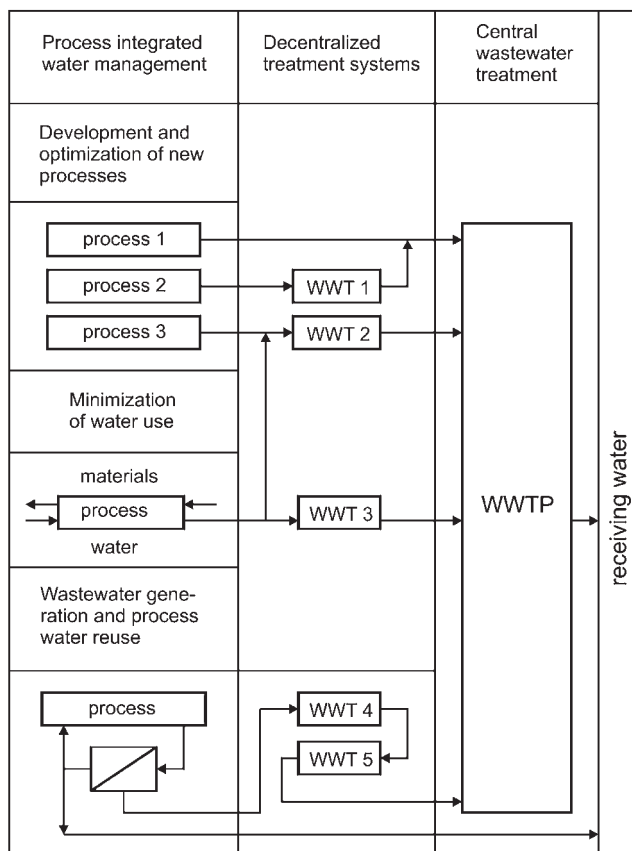


Fig. 13.1 Schematic of industrial water management as process integrated water management, distributed treatment systems and central wastewater treatment.

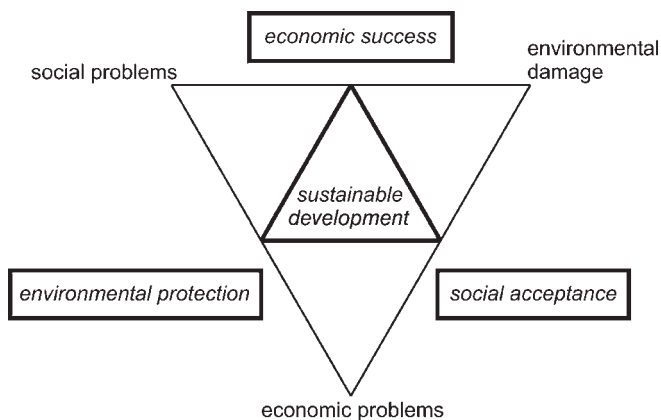


Fig. 13.2 Sustainability (Christ 1996, 1999).

Decentralized effluent treatment systems can be divided in those with and those without reuse. There are two motivations to treat effluents in a decentralized manner:

- The water is only loaded by components which can be separated easily at low cost, which makes it possible to discharge the treated water directly into a river at no additional cost. The costs may be significantly lower than the amount which would have to be paid to the central WWTP. Another case may be applicable for a highly loaded effluent which can be treated anaerobically without significant sludge production and without aeration costs. It may be cheaper to treat this effluent anaerobically together with several similarly loaded effluents in comparison to a single aerobic stage.
- Following decentralized treatment, the water may be reused in further processes which do not need water with freshwater quality or it can be sent to a larger aerobic industrial or municipal WWTP.

In this chapter, we will explain what process integrated water management and decentralized effluent pretreatment are and how they can be applied in specific industries such as the chemical, pharmaceutical, food, textile, drinks, paper and cellulose, iron and steel industries. To these topics annual meetings take place at University Bremen, Germany (Räbiger 1999). We find the most examples for process integrated water management within the chemical industry. Therefore, this industry is suitable to give examples for the following discussion.

13.2

Production Integrated Water Management in the Chemical Industry

13.2.1

Sustainable Development and Process Optimization

13.2.1.1 Primary Points of View

For a simple and clear overview, we want to discuss the following problems arising during technical-scale chemical synthesis, using an example of a one-step reaction in water:



It may be possible to produce a mixture of the main product C and the byproduct D in water under *laboratory conditions*. Additionally, we are often left with remaining educts A and B as a result of an incomplete reaction and/or a non-stoichiometric addition. For a homogeneously catalyzed reaction:



the catalyst is a part of the effluent which also contains an auxiliary, such as a surfactant.

Furthermore, the target or byproduct can be converted during a subsequent reaction, producing a further byproduct E:



In a *technical-scale synthesis* large amounts of raw materials are used which frequently contain impurities that can also be transformed by reactions ($N_1 \rightarrow N'_1$, N_2 inert). The wastewater produced contains all these materials; and the product C must therefore be separated. Complete separation of C is not economical and thus the target product also contributes additional pollution left in the wastewater. Chemical companies are often interested in changing this situation by developing new processes or by optimizing existing ones, particularly if they were developed several decades ago.

It may be possible to use:

- New ways of chemical synthesis.
- Enzymatic methods or conversions by microorganisms.
- New raw materials with lower impurities content.
- New catalysts with higher selectivity.
- New conditions for the reaction (T, p, pH).
- New methods for saving water (Sections 13.2.2 and 13.2.3) as well as relieving end-of-pipe treatment.
- More effective methods of product separation from all other materials.

Modernization of existing processes or development of new ones along these lines is not only done to lower the cost of production and waste management but also to obtain products of higher purity and to reduce side-effects of pharmacological products.

13.2.1.2 Material Flow Management

The aims described in Section 13.2.1.1 can only be reached if material and energy balances are studied for existing processes and for new concepts. We restrict the following discussion, thus, to a *material (or mass) flow analysis*. Some fundamentals of mass balances were already explained in the section above. This analysis can be divided into several steps:

1. All influent and effluent flow rates in the liquid, solid and gas state must be determined.
2. The concentration of all important components must be measured in these different streams: the influent raw materials A and B and the effluent components C and D (Eq. 13.1), the catalysts and auxiliaries (Eq. 13.2), the byproduct E (Eq. 13.3) and all important impurities N_1 , N_2 and N'_1 .
3. Do these components change their state by crystallization, condensation or evaporation?
4. Write mass balances for all components and test them by using measurements.

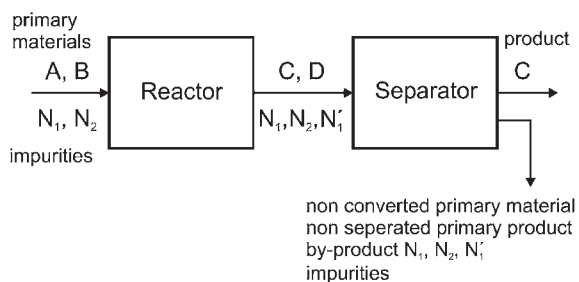


Fig. 13.3 General schematic of a production process.

After successful tests, the calculation of some characteristic parameters can start. In order to achieve a simpler analysis

- All flow rates are summarized $Q_{\Sigma} = \Sigma Q_i$.
- We assume there is no change of state.
- Mean concentrations are calculated from mass balances at mixing points, i.e. for the influent:

$$C_{oi} = \frac{\sum_{i=1}^n Q_i C_i}{Q_0} \quad (13.4)$$

Figure 13.3 presents a simple scheme describing this situation.

The following considerations follow explanations by Christ (1999), who used masses $m_i = c_i V_i$.

Stoichiometric Yields

In taking the discussion further, we will introduce stoichiometric coefficients into Eq. (13.1). Normalized to 1 mol A, we obtain:



$Y_{C/A}^{\circ}$ mol C/mol A is the *stoichiometric yield* of the target product C relative to the educt A. It can be calculated from measured values for the converted mass of A m_A and the mass of C formed m_C . Using the molar masses of A and C we have:

$$Y_{C/A}^{\circ} = \frac{m_C M_A}{m_A M_C} \frac{\text{mol C}}{\text{mol A}} \quad (13.6)$$

The stoichiometric yield has some disadvantages. It gives no information about:

- Other educts contained in Eq. (13.5).
- Other raw materials which may be contained in the total influent mass.
- Subsequent products which may be produced by further reactions.
- Auxiliary materials present, e.g. solvents, surfactants, etc.

Thus, further yield coefficients must be defined.

Consideration of Secondary Materials

B, the second educt in Eq. (13.5), gives:

$$Y_{C/A+B}^{\circ} = \frac{\frac{m_C/M_C}{\frac{m_A}{M_A} + \frac{m_B}{M_B}} \frac{\text{mol C}}{\text{mol A} + \text{mol B}}}{\quad} \quad (13.7)$$

$Y_{C/A+B}^{\circ}$ is smaller than $Y_{C/A}^{\circ}$ and is decreased remarkably if a larger number of primary raw materials is used:

$$Y_{C/\Sigma PM}^{\circ} = \frac{\frac{m_C/M_C}{\sum_{i=1}^n \frac{m_i}{M_i}}}{\quad} \quad (13.8)$$

With Eq. (13.7) or Eq. (13.8), only the first of the four points mentioned above can be considered.

Further definitions regarding the kind and amount of the secondary materials N_1 and N_2 will be introduced which frequently can only be measured using the units of mass instead of moles. Some of these components are often unknown and their number may be high.

For the *real balance yield*, the result is:

$$Y_{C/A+B+\Sigma N} = \frac{m_C}{m_A + m_B + m_{N1} + m_{N2}} \frac{g}{g} \frac{C}{(A + B + \Sigma N)} \quad (13.9)$$

For higher masses of N_1 and N_2 , the result is remarkably low compared to $Y_{C/A+B}^{\circ}$. The relation of both is given by the specific real balance yield:

$$Y_{\text{spec}} = \frac{Y_{C/A+B+\Sigma N}}{Y_{C/A+B}^{\circ}} \frac{g}{g} \frac{C}{(A + B + \Sigma N)} \frac{(\text{mol A} + \text{mol B})}{\text{mol C}} \quad (13.10)$$

and indicates the influences of all secondary materials. For $\Sigma N \gg A + B$, the specific real balance yield may be for example $Y_{\text{spec}} = 0.15$, influenced by the high amount of secondary raw materials present. From an economical and ecological point of view, a different raw material with a lower amount of secondary substances should be used.

Altogether, there are three important points which should be considered when assessing raw materials: the quality, the price and the cost for environmental protection.

13.2.1.3 Production of Naphthalenedisulfonic Acid

Aromatic sulfonic acids are produced in large scale plants and are used as surfactants. Naphthalenedisulfonic acids are important intermediate substances for the production of azo dyes (see Section 9.5). Most can only be biodegraded with great difficulty and naphthalene-1,5-disulfonic acid is not biodegradable at all (Krull and Hempel 1994). Only after chemical oxidation with ozone can mineralization by a subsequent aerobic biological treatment be successful (Breithaupt et al. 2003).

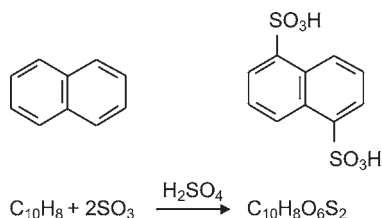


Fig. 13.4 Formation of 4,8-naphthalene-disulfonic acid.

Some fundamental microbiological studies were published by Nörtemann and Knackmus (1988) and some important biotechnological research by Krull et al. (1991). The following example is discussed in detail by Christ (1999). During the technical synthesis of a desired naphthalenedisulfonic acid (i.e. 4-8-NDSA; Fig. 13.4), temperature, concentration of H_2SO_4 and SO_3 as well as mean retention time are optimized to obtain the target product at a concentration as high as possible. Nevertheless, some other undesired derivatives of NDSA are formed and increase the wastewater load after separation of the desired product.

This process is presented by Fig. 13.5a. Naphthalene is treated with H_2SO_4 and SO_3 at 50–60 °C. After addition of NaOH and Na_2SO_4 , NSA precipitates as a sodium salt and can be filtered out.

Besides the target product, several other sodium salts of NSA remain in the filtrate as byproducts. Yet a large amount of different derivatives from NSA and NDSA

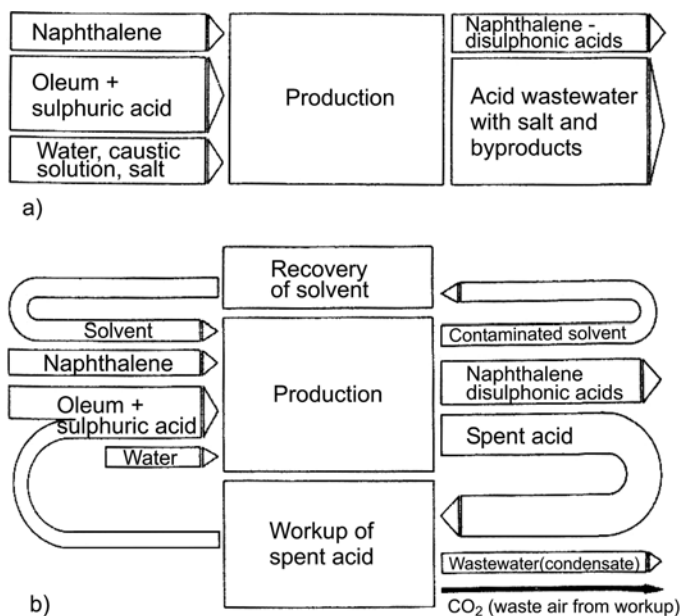


Fig. 13.5 Bayer AG processes for naphthalenedisulfonic acid production: (a) old process (before 1989, 3000 t a⁻¹ COD); (b) new process (after 1989, 3 t a⁻¹ COD; Christ 1999).

remained in the filtrate and increased the COD load of the wastewater remarkably, to levels of 3000 t a^{-1} COD.

Only a small amount of this COD could be mineralized in the biological end-of-pipe treatment plant. A modification of the process was absolutely necessary.

The first step for developing a new process was to find a catalyst with a higher selectivity in favor of the product 4-8-DNSA (Bueb et al. 1990). A team from Bayer AG succeeded by replacing the formerly used iron chloride–sulfur catalyst with an iron chloride catalyst. The result was the production of fewer byproducts. But the use of this new catalyst was only possible if sulphuric acid was no longer used as the reaction medium.

The new solvent for naphthalene and SO_3 , a chlorinated hydrocarbon, allowed a reduction of the reaction temperature. The dehydrating action of SO_3 led to the formation of higher molecular structures. The anhydride bridges must be hydrolyzed in the next step by adding the reaction mixture to water. This results in an aqueous sulfonic acid solution, the organic solvent can be separated, and the free sulfuric acid is precipitated by addition of sulfonic acid followed by cooling. After filtration of the precipitated product, the remaining "mother liquor" is regenerated as spent sulfuric acid and recycled.

In the old process, wastewater was produced which contained:

- A high concentration of naphthalene disulfonic acids as byproducts,
- Excess sulfonic acid,
- Inorganic salts for the salting out of the product with subsequent filtration, re-suspension and spray drying.

In the new process:

- The portion of the desired product is increased by using a new catalyst with a higher selectivity.
- An organic solvent for naphthalene and SO_3 replaces the sulfonic acid which can be regenerated and recycled.
- A portion of the acid used is cleaned by distillation and recycled.
- The salting-out is replaced by a membrane, yielding a dye-free permeate and a concentrate which is spray-dried.

The permeate can be reused as feed water; and its COD is reduced about 80% in comparison to the filtrate of the former process. The condensed vapor of this distillation process is the only wastewater, with a COD load of only 3 t a^{-1} . The costs of production are reduced because of the reduced costs for wastewater treatment; and the yield and product quality are somewhat higher than before.

13.2.1.4 Methodology of Process Improvement

A systematic approach is necessary if an old process is to be changed to reduce its high costs, such as the costs of wastewater treatment, exhaust gas handling and solid waste disposal. This will be explained using Table 13.1.

Table 13.1 Different points which must be considered when a new process is to be developed.

Point	Consideration
1	New biotechnological process? 1.1 Catalyzed by an immobilized enzyme? 1.2 Converted by suspended or immobilized microorganisms?
2	New chemical process? 2.1 New method of synthesis Different raw materials Different catalyst with reduced amount of by-products Different reaction conditions (T, p, pH) Other solvent (organics instead of water) 2.2 New methods of product recovery • Precipitation, filtration • Distillation, condensation • Concentration, spray drying • Ultrafiltration, reverse osmosis 2.3 Recycling of solvent (water, organics) after removal of impurities Recycling of concentrates with remaining product, primary materials, and catalysts 2.4 Recovery of a by-product to use as a starting material in a further process Recovery of an auxiliary for reuse

For a high wastewater flow rate and a high COD concentration, an estimation of the treatment costs lets us know whether it is better to treat it in an end-of-pipe plant or in a decentralized effluent treatment system.

13.2.2

Minimization of Fresh Water Use

13.2.2.1 Description of the Problem

A number of different processes must be supplied with water. This water may be used

- for heat transfer processes (cooling, evaporation, condensation, etc.),
- for mass transfer processes (washing, absorption/desorption, distillation/condensation, reaction, etc.).

The rising costs of energy, fresh water and wastewater treatment make it necessary to save both energy and water (Pauli 1997). The following considerations are to be made for water management.

The problem is presented by Fig. 13.6, showing four different water-using processes in parallel, each of them using water for mass transfer processes.

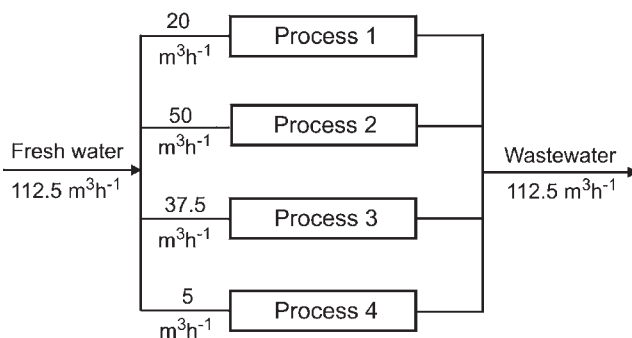


Fig. 13.6 Fresh water use in each of the four processes leading to a fresh water flow rate of $112.5 \text{ m}^3 \text{ h}^{-1}$.

Following the discussion of Wang and Smith (1995), Smith et al. (1994) and Baetens (2002), we will at first assume that 112.5 t h^{-1} fresh water are used for all four processes. The mass transfer data are given in Table 13.2.

Table 13.2 Example for process data of the process of Fig. 13.7.

Process No. j	Mass load of contaminant $Q c_{\text{out}}$ (kg h^{-1})	Concentrations		Water flow rate Q ($\text{m}^3 \text{ h}^{-1}$)
		c_{in} (kg m^{-3})	c_{out} (kg m^{-3})	
1	2	0	0.1	20
2	5	0	0.1	50
3	30	0	0.8	37.5
4	4	0	0.8	5
	$\Sigma 41$			$\Sigma 112.5$

For process 1 with a given contaminant mass load of $Q_1 c_{1,\text{out}} = 2 \text{ kg h}^{-1}$ impurities and a given concentration of $c_{1,\text{out}} = 0.1 \text{ kg m}^{-3}$, a flow rate of $Q_1 = 20 \text{ m}^3 \text{ h}^{-1}$ results. Correspondingly for the mass loads of processes 2, 3 and 4 (Table 13.2), given as 5, 30 and 4 kg h^{-1} , flow rates of 50, 37.5 and $5 \text{ m}^3 \text{ h}^{-1}$ can be calculated, which yields a sum of:

$$\sum_{j=1}^4 Q_j = 112.5 \text{ m}^3 \text{ h}^{-1} \quad (13.11)$$

How much water do we need if we do not operate the four processes in parallel and look for a more economical water use?

13.2.2.2 The Concentration/Mass Flow Rate Diagram and the Graphical Solution

In a water-using mass transfer process, different components are transported to the water (Fig. 13.7a). In the following, we will study only one component. The index i for different compounds can now be omitted.

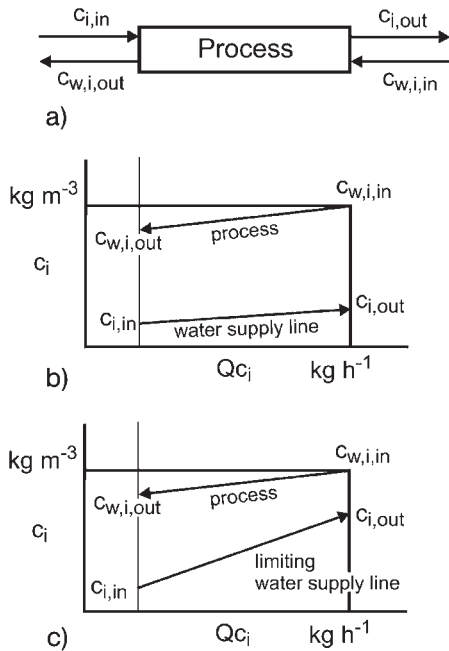


Fig. 13.7 Concentration/mass flow rate diagram. (a) Schematic of a water using process for impurity. (b) A water-using process in a concentration/mass flow rate diagram, with the water profile not limited for one impurity. (c) The water profile is limited (one impurity).

The concentration of this component (the impurity) decreases inside the process system and increases in the water. This can be demonstrated using a concentration/mass flow rate diagram (Fig. 13.7b). The slopes of the straight lines are the reverse of the flow rate Q . The water flow rate is very high, resulting in a low increase in the concentration c_i . In Fig. 13.7c, the water flow rate Q is reduced down to the lowest possible value which is still sufficient to meet the required reduction of c_{in} to c_{out} . The lower straight lines are called *water supply lines* and the limiting line in Fig. 13.7c is the *limiting water supply line*. Any water supply line which is below the limiting water supply line will satisfy the process requirements. However, there are also possibilities to save water. How we can find a method to save the greatest possible amount of fresh water without reducing the transferred impurities if there are four processes with different c_{in} and flow rates Q_j ?

We want to approach the solution step by step. The first step is to construct a concentration/mass flow rate diagram as in Fig. 13.7, one for each of the four processes presented by Fig. 13.6 and Table 13.2.

All four water supply lines start at the point $(c_i = 0, Q_j c_i = 0)$, but they end at different points $c_{i,out}$, showing different slopes Q_j (Fig. 13.8 and Table 13.2). The total water flow rate is $\Sigma Q_j = 112.5\ m^3\ h^{-1}$.

The next step is a discussion with the process operators which may result in higher permissible c_{in} values for processes 2, 3 and 4 (Table 13.3).

If such a system of process water management is to be realized, the total water flow rate would have to be increased to $170\ m^3\ h^{-1}$ (Table 13.3), much more than if using fresh water for each process ($112.5\ m^3\ h^{-1}$, Table 13.2). However, the following considerations will show a way to reduce this water flow rate remarkably.

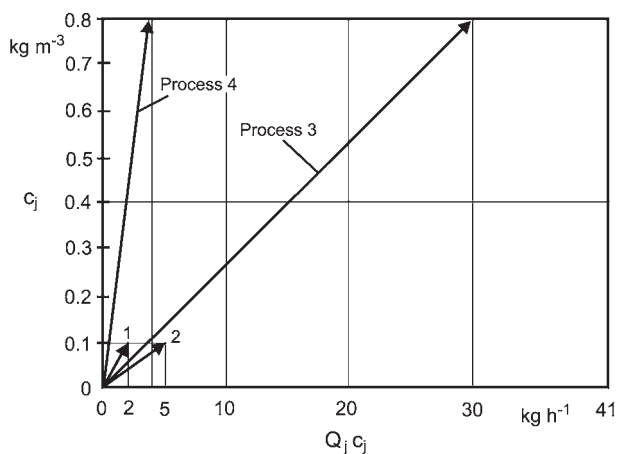


Fig. 13.8 The four processes j connected in parallel with a fresh water use of $112.5 \text{ m}^3 \text{ h}^{-1}$ presented in a concentration/mass flow rate diagram.

Table 13.3 Example for limiting process data (see Fig. 13.9a).

Process No. j	Mass load of contaminant $Q_j c_{\text{out}}$ (kg h^{-1})	Concentrations		Water flow rate Q_j ($\text{m}^3 \text{ h}^{-1}$)
		c_{in} (kg m^{-3})	c_{out} (kg m^{-3})	
1	2	0	0.1	20
2	5	0.05	0.1	100
3	30	0.05	0.8	40
4	4	0.4	0.8	10
	$\Sigma 41$			$\Sigma 170$

As a part of the analysis we constructed *one* concentration/mass flow rate diagram for the *four* processes, but there are still no connections between the straight lines (Fig. 13.9a).

The discontinuities in concentrations can be avoided by connecting the points as follows (Fig. 13.9b, based on Table 13.3).

The water for *process 1* must be clean ($c_{1,\text{in}} = 0 \text{ kg m}^{-3}$). So the first straight line will not be changed but the second straight line for *process 2*, starting at $c_{2,\text{in}} = 0.05 \text{ kg m}^{-3}$, meets the first line at $Qc_{2,\text{in}} = 1.0 \text{ kg h}^{-1}$. The straight line for process 3 follows from Table 13.3, by calculating the slope using $\Delta c_j = 0.4 - 0.1 = 0.3 \text{ kg m}^{-3}$ and $\Delta Q_j c_j = 21 - 9 = 12 \text{ kg h}^{-1}$, giving slope $= 0.3/12 \text{ h m}^{-3}$ and thus $Q = 1/\text{slope} = 40 \text{ m}^3 \text{ h}^{-1}$. Figure 13.9b presents the concentration/mass flow rate diagram for a system of four processes characterized by requirements presented by Table 13.3. This curve is called the *limiting composite curve*.

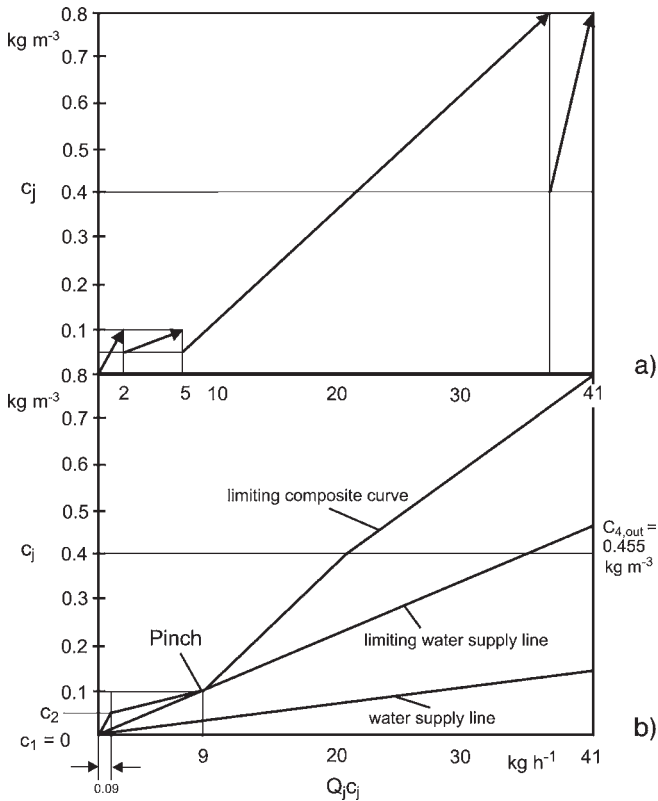


Fig. 13.9 Limiting composite curve. (a) Limiting water profile. (b) Limiting composite curve with water supply line defining the minimum water flow rate.

In analogy to Fig. 13.7, which presents the concentration/mass flow rate diagram for only one process, it is very interesting to find the limiting water supply line. The straight line with the lower slope plotted in Fig. 13.9b shows a water supply with a relatively high flow rate Q . The lowest possible flow rate $Q_{\min}$ can be calculated from the limiting water supply line which touches the limiting composite curve without crossing the line. This point is called a *pinch* (Wang and Smith 1994).

The slope of this limiting water supply line can be calculated using $c_{\text{in}} = 0 \text{ kg m}^{-3}$ and $c_{\text{out,max}} = (41 \cdot 0.1)/9 = 0.455 \text{ kg m}^{-3}$.

$$\frac{c_{\text{out,max}} - c_{\text{in}}}{Q_{\min} \cdot c_{\text{out,max}}} = \frac{0.455}{41} \text{ m}^{-3} \text{ h} \quad (13.12)$$

$$Q_{\min} = 90 \text{ m}^3 \text{ h}^{-1}$$

If we compare this optimized water demand with that of processes connected in parallel we would save:

$$\frac{112.5 - 90}{112.5} = 20\% \quad \text{if using clean water and}$$

$$\frac{170 - 90}{170} = 47\% \quad \text{if using partly polluted water}$$

But what network of processes do we have to build in order to save this amount of water?

13.2.3

The Network Design Method

The inlet and outlet concentrations of the impurity c_{in} and c_{out} and the concentration/mass flow rate diagram with the pinch point form the basis of the recommendations for the network design (see Table 13.3), which yields a minimum wastewater flow rate of $90 \text{ m}^3 \text{ h}^{-1}$ (Fig. 13.9b). This form of data is used for the construction of a network (Fig. 13.10). Note that there may be more than one way to design a network.

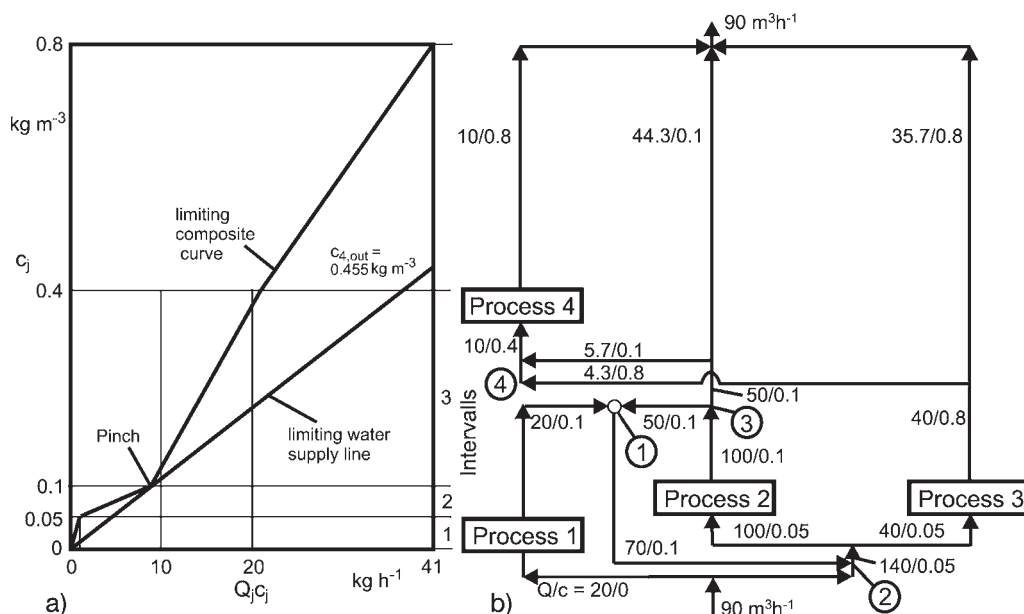


Fig. 13.10 The design of the water management system. (a) Limiting composite curve with limited water supply line for $Q = 90 \text{ m}^3 \text{ h}^{-1}$. (b) Final design of the wastewater network with four processes for $Q = 90 \text{ m}^3 \text{ h}^{-1}$.

We distinguish three intervals. For the following considerations, we must conform to Table 13.3 and Fig. 13.10.

Interval 1 (0–0.05 kg m⁻³)

Only process 1 is considered within interval 1. As follows from Table 13.3, the concentration increases from $c_{1,\text{in}} = 0$ to $c_{1,\text{out}} = 0.1 \text{ kg m}^{-3}$, giving a water flow rate $Q_1 = 20 \text{ m}^3 \text{ h}^{-1}$, with $70 \text{ m}^3 \text{ h}^{-1}$ flowing directly to segment 2.

Interval 2 (0.05–0.1 kg m⁻³)

There are two processes located in interval 2. As follows from Table 13.3, the influent concentration of both processes 2 and 3 should be $c_{2,\text{in}} = c_{3,\text{in}} = 0.05 \text{ kg m}^{-3}$. However, the concentration coming from interval 1 is 0 kg m^{-3} and the flow rate is $70 \text{ m}^3 \text{ h}^{-1}$. In order to get 0.05 kg m^{-3} , the same flow rate of $70 \text{ m}^3 \text{ h}^{-1}$ and an effluent concentration of process 1 and 2 of 0.1 kg m^{-3} must be recycled. After mixing $70/0$ with $70/0.1$, $140/0.05$ is obtained, which is then divided into $100/0.05$ for process 2 and $40/0.05$ for process 3. Fundamentally, at each of the mixing points 1, 2, 3 and 4, the balances for water (the equation of continuity) and for the impurity (mass balance) can be formulated and solved to calculate the unknown flow rate or concentration. The relatively simple example presented in Fig. 13.10 makes a simpler solution possible.

Interval 3 (0.1–0.4 kg m⁻³)

Only process 4 is located in interval 3. The water flow rate for this process is $10 \text{ m}^3 \text{ h}^{-1}$ and the influent concentration is 0.4 kg m^{-3} (Table 13.3). We only get these conditions after mixing portions of the effluents from process 2 and process 3. For this purpose, we need two balances for water and for the impurity, as mentioned above:

$$Q'_2 + Q'_3 = Q_4 \quad (13.13)$$

Impurity:

$$Q'_2 c_{2,\text{out}} + Q'_3 c_{3,\text{out}} = Q_4 c_{4,\text{in}} \quad (13.14)$$

where $c_{2,\text{out}} = 0.1 \text{ kg m}^{-3}$, $c_{3,\text{out}} = 0.8 \text{ kg m}^{-3}$, $c_{4,\text{in}} = 0.4 \text{ kg m}^{-3}$. Q_2 follows to:

$$Q_2 = \frac{Q_4 c_{4,\text{in}} - Q_3 c_{3,\text{out}}}{c_{2,\text{out}}} \quad (13.15)$$

$$Q_3 = Q_4 - Q_2 \quad (13.16)$$

$$Q_2 = \frac{Q_4 (c_{4,\text{in}} - c_{3,\text{out}})}{c_{2,\text{out}} - c_{3,\text{out}}} \quad (13.17)$$

13.3

Decentralized Effluent Treatment

13.3.1

Minimization of Treated Wastewater

13.3.1.1 Description of the Problem

We assume that a production unit of a factory generates four wastewater streams which are polluted by nearly the same components, giving a COD which can be removed by the same method or type of treatment. The treatment must take place before discharging the treated water into an end-of-pipe treatment plant (WWTP). The COD must be removed down to c_e . An example of such a situation is given in Fig. 13.11, showing WWTP 1, 2, 3 and 4 as a situation of a development for a decentralized treatment system. It is assumed that the costs of the pretreatment are proportional to the flow rate. Therefore, the aim of the optimization is to minimize the treated flow rate. This assumption is only one of several possible objectives. However, it makes it easier to explain the procedure. In Fig. 13.11, four different ways to reach the objective are discussed.

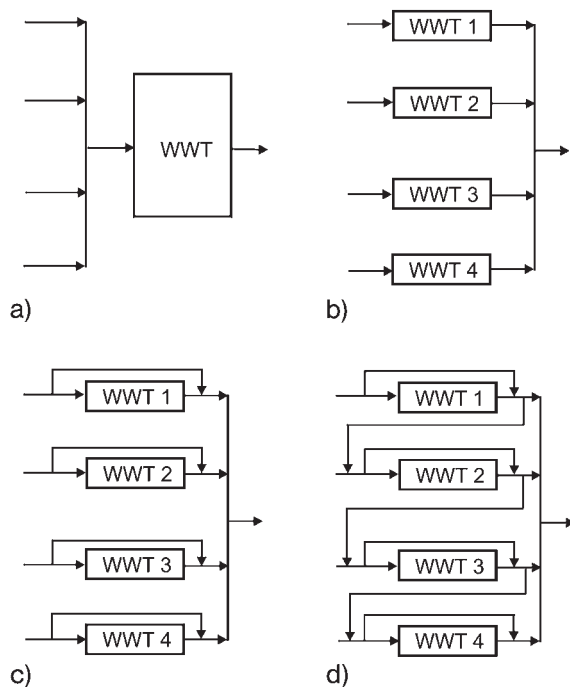


Fig. 13.11 Decentralized effluent pretreatment systems. (a) One treatment process. (b) Four parallel treatment processes. (c) Four parallel treatment processes with bypasses. (d) Four treatment processes partly connected in parallel, partly in series with bypasses.

In Fig. 13.11a, the streams flow into one treatment plant, where they are mixed and treated together. This method is problematic because a stream with a high flow rate and a low concentration may be mixed with a stream with a low flow rate and a very high concentration.

A better way may be to treat the four streams separately (Fig. 13.11b). The retention time in treatment plant 1 (TP 1) can now be lower because of the low COD and the high flow rate. In contrast, it may be possible to treat another stream in TP 2 or TP 3 using a higher retention time. But there are several reasons to be dissatisfied with this treatment concept and we have not decreased the reactor volume.

This is possible if we reduce the COD in each TP below c_e , pumping only part of the four streams each in parallel to the TPs and mixing them all together to obtain the required c_e (Fig. 11.13c).

A further way to reduce the reactor volume is presented by Fig. 13.11d. The TPs are connected in parallel and in series. The part of the wastewater which is treated in parallel can be decreased by increasing the part being treated in series. Several possibilities are given to optimize this treatment process. The part of the recycled wastewater in WWT 1 can influence that of the following WWTs. A strategy is necessary to find an optimized solution to a given problem. The method described in the next section was published by Wang and Smith (1994).

13.3.1.2 Representation of Treatment Processes in a Concentration/Mass Flow Rate Diagram

Initially, we want to discuss the influence of a bypass on only one treatment plant. The lower line in Fig. 13.12 shows the wastewater stream with an influent concentration c_{in} , for example, in g L^{-1} COD and a lower flow rate Q .

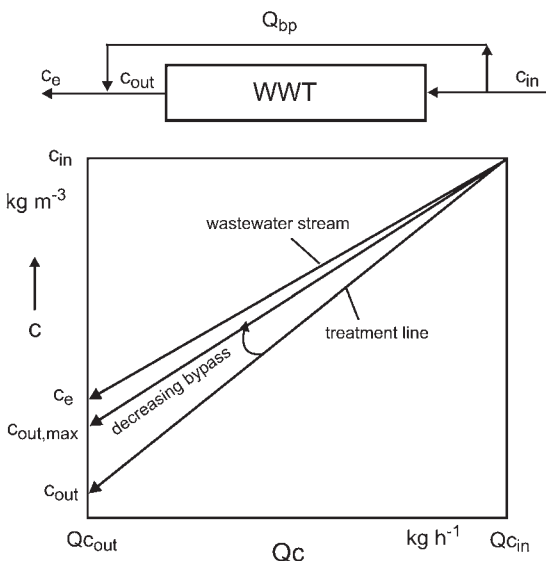


Fig. 13.12 Concentration/mass flow rate diagram for one treatment plant with bypass.

An effluent concentration c_e is given. The rest of the flow rate flows through the bypass. The concentration c_{out} before mixing with the bypass wastewater is relative low owing to the relative high mean retention time inside the reactor. With decreasing bypass, c_{out} increases and finally reaches $c_{out,max}$, the highest allowed effluent concentration, which should not be exceeded. $c_{out,max}$ can be calculated using a mass balance and the given concentration c_e .

In the next step, several treatment plants either without bypass (Fig. 13.11b) or with bypass (Fig. 13.11c) are connected in parallel. The concentration/mass flow rate diagrams for four plants are presented in Fig. 13.13. In Fig. 13.13a, the effluent concentrations are lower than c_e in three of the four plants because all the wastewater goes directly through the treatment plants. By adjusting bypass flow rates, the situation presented in Fig. 13.13b can be obtained: the effluent concentrations in all four treatment systems agree at c_e .

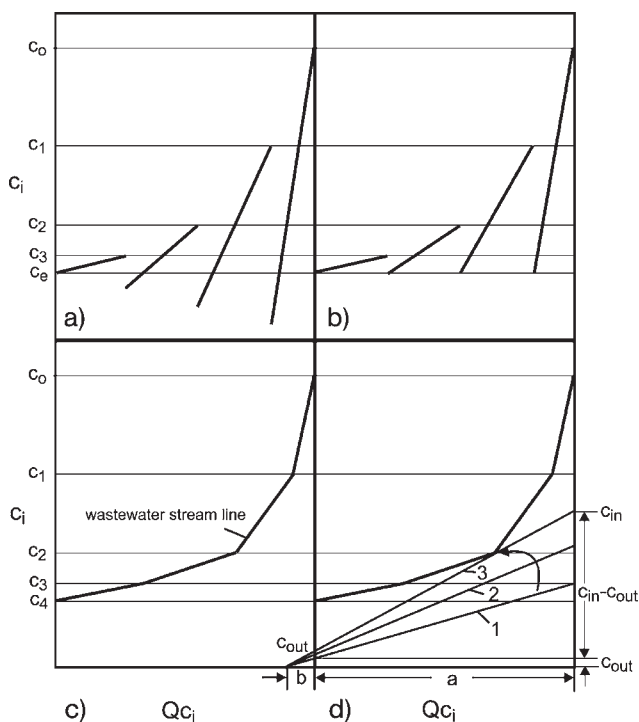


Fig. 13.13 Decentralized effluent pretreatment process in the concentration/mass flow rate diagram. (a) (Treatment in) parallel plants, partly with lower effluent concentration than the required c_e . (b) (Treatment in) parallel plants, all with the required effluent concentrations c_e . (c) (Treatment by) using the parallel/series portion and the bypasses of all four plants. (d) Construction of the treatment lines for higher flow rates (curve 1 and curve 2) and for the lowest possible flow rate Q (curve 3).

Up to here, all WWTs have been connected in parallel. Now, we wish to combine the lowest points in Fig. 13.13b by connecting the highest point of the first plant with the lowest point of the second plant. To do this, we will change: (a) the parallel/series portion and (b) the bypass of all four plants. This changes the flow rates in each of the plants as well as the concentrations of the influent wastewater, giving c_1 , c_2 , c_3 and c_4 (Fig. 13.13c).

13.3.1.3 The Lowest Wastewater Flow Rate to Treat

Now we search for the treatment line with the lowest flow rate. To achieve this, we have to know the desired degree of removal:

$$\alpha = \frac{c_{in} - c_{out}}{c_{in}} \quad (13.18)$$

The highest removal α follows from curve 3:

$$\frac{c_{in} - c_{out}}{c_{in}} = \frac{a}{a + b} = \alpha = \text{const} \quad (13.19)$$

it characterises the three triangle in Fig. 13.13d. The lowest treatment line 1 and the middle line 2 are possible solutions of the wastewater treatment, but the flow rates Q_1 and Q_2 , the reciprocal inclinations, are relatively high. Only treatment line 3, which touches the wastewater stream line, represents a solution of the problem using the lowest possible flow rate Q_3 (Fig. 13.13d). A straight line with a larger slope crosses the wastewater stream line at two points (not plotted here). It represents an impossible solution because mass balances are not fulfilled (Wang and Smith 1994).

After obtaining the fundamental solution for Q_{min} , c_{in} and c_{out} , a study of the design of the treatment system must follow. We will not go further into details here and will take up this question in Problem 13.2. We are convinced that there is a need to use this type of method to save water in industry.

13.3.2

Processes for Decentralized Effluent Treatment

The target of this optimization procedure is to reduce the amount of wastewater to the lowest possible level. This can be performed

- for continuous production processes and
- for batch processes with large storage tanks which can be employed to realize nearly constant flow rates during filling.

Often, discontinuous treatment processes must be used and other optimization methods are needed. Physico-chemical processes are especially suited (Bueb et al. 1990, Kollatsch 1990), e.g.:

- stripping
- distillation, rectification
- extraction
- adsorption, absorption
- precipitation, flocculation
- wet oxidation
- evaporation
- incineration, etc.

In future, some membrane technology processes will become useful alone or in combination with a bioreactor (Chapter 12) or with one of the processes mentioned above. Fundamentally, all biological treatment processes discussed in detail in Chapters 5 to 11 may be interesting, if the cost is low compared with other treatment processes.

PROBLEM 13.1

For a reaction given by Eq. (13.5), the masses and molar masses of the educts A and B and the product C are:

$$m_A = 50 \text{ kg}, M_A = 70 \text{ g mol}^{-1}$$

$$m_B = 22 \text{ kg}, M_B = 140 \text{ g mol}^{-1}$$

$$m_C = 45 \text{ kg}, M_C = 74 \text{ g mol}^{-1}$$

The masses of the secondary materials N_1 and N_2 are:

$$m_{N1} = 25 \text{ kg and } m_{N2} = 17 \text{ kg}$$

Calculate the stoichiometric yields, $Y_{C/A}^o$ and $Y_{C/A+B}^o$, the real balance yield $Y_{C/A+B+\Sigma N}$ and the specific real balance yield Y_{spec} .

Solution

$$Y_{C/A}^o = \frac{m_C M_A}{m_A M_C} = \frac{45 \cdot 70}{74 \cdot 50} \frac{\text{mol C}}{\text{mol A}} = 0.942 \triangleq 94.2\%$$

$$Y_{C/A+B}^o = \frac{m_C/M_C}{\frac{m_A}{M_A} + \frac{m_B}{M_B}} = 0.698 \triangleq 69.8\%$$

$$Y_{C/A+B+\Sigma N}^o = \frac{m_C}{m_A + m_B + m_{N1} + m_{N2}} = \frac{45}{50 + 22 + 25 + 17} = 0.395 \triangleq 39.5\%$$

$$Y_{\text{spec}} = \frac{Y_{C/A+B+\Sigma N}}{Y_{C/A+B}^o} = \frac{0.395}{0.698} = 0.566 \triangleq 56.6\%$$

Results:

- 69.8% of the moles from both educts are obtained as product C;
- 39.4% of the mass from all primary and secondary materials are obtained as product C;
- the specific real balance yield Y_{spec} can be increased by using better raw materials from 56.6% up to 100%.

PROBLEM 13.2

The calculation of stoichiometric relations is surely a very simple example for the first part of material flow management. The next part is the study of the main mass balances, i.e. the foundation for process optimization.

For this problem, the flow rates and inlet concentrations for three effluent streams are given in Table 13.4 (Wang and Smith 1994). The total flow rate is $90 \text{ m}^3 \text{ h}^{-1}$.

The limit effluent concentration must be $c_e = 20 \text{ mg L}^{-1}$ DOC. Only a part of this wastewater is to be treated to a removal degree of $\alpha = 0.99$ and as low a flow rate as possible should be treated. The composite curve with the three wastewater streams is shown in Fig. 13.14.

The total mass flow rate in the influent is $Qc_{\text{in}} = 17.8 \text{ kg h}^{-1}$ DOC. The limiting wastewater stream line goes through the pinch (0.1/5.8) and forms two similar triangles with the ordinate and abscissa of Fig. 13.14.

Calculate the limit flow rate of the treated water and design a network for the water system.

Table 13.4 Wastewater streams for Problem 13.2 (Wang and Smith 1994).

Stream No. j	Flow rate Q_j ($\text{m}^3 \text{ h}^{-1}$)	Concentration c_j (kg m^{-3})
1	40	0.4
2	30	0.1
3	20	0.03

Solution

Comparing the largest and the smallest triangle in Fig. 13.14 and using $c_{\text{out}} = 0.01 \cdot c_{\text{in}}$, it follows that:

$$\frac{c_{\text{in}}}{17.8 + a} = \frac{c_{\text{out}}}{a} = \frac{0.01 c_{\text{in}}}{a}$$

and it can be calculated that: $a = 0.18 \text{ kg h}^{-1}$ COD.

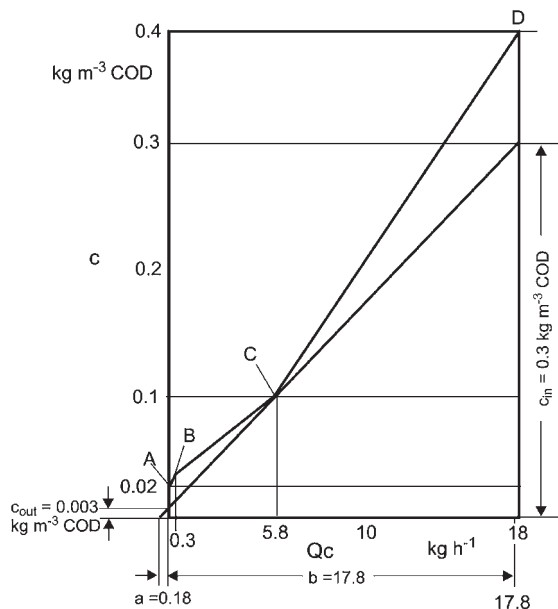


Fig. 13.14 Construction of the limiting water supply line for a given removal $\alpha = 0.99$ (and three processes).

From the upper smaller and the largest triangles:

$$\frac{c_{in} - 0.1}{17.8 - 5.8} = \frac{c_{in}}{17.8 + 0.18}$$

$c_{in} = 0.300 \text{ kg m}^{-3} \text{ COD}$ is obtained as the allowed influent concentration for the flow rate of:

$$Q = \frac{17.8}{0.3} = 59.33 \text{ m}^3 \text{ h}^{-1}$$

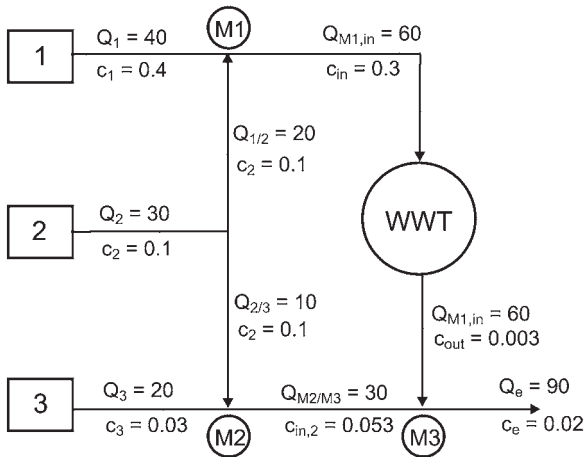
Only $59.33 \approx 60 \text{ m}^3 \text{ h}^{-1}$, respectively $\sim 66.6\%$ must be treated.

An obvious solution would be to treat the effluent from process 1. But the flow rate is too low and the concentration is too high. A better strategy is to use a part of the effluent from process 2 for mixing with the effluent of process 1 and a second part for mixing with the effluent from process 3 (Fig. 13.15).

Starting with $c_{in} = 0.3 \text{ kg m}^{-3} \text{ DOC}$ and $\alpha = 0.99$, c_{out} is obtained from:

$$\alpha = \frac{c_{in} - c_{out}}{c_{in}}, c_{out} = c_{in} (1 - \alpha), c_{out} = 0.003 \text{ kg m}^{-3}$$

To obtain $Q_{1,2}$, the flow rate from process 2 is mixed with that of process 1; and a further mass balance at mixing point M1 is:



All concentrations as kg m^{-3} DOC and
all flow rate as $\text{m}^3 \text{h}^{-1}$

Fig. 13.15 Construction of a water network considering the results of Fig. 13.14

$$Q_1 c_1 + Q_{1/2} c_2 = Q_{M1,in} c_{in}$$

giving:

$$Q_{1/2} = \frac{Q_{M1,in} c_{in} - Q_1 c_1}{c_2}$$

with:

$$c_2 = 0.1 \text{ kg m}^{-3} \text{ DOC.}$$

It then follows that: $Q_{1/2} = 20 \text{ m}^3 \text{h}^{-1}$.

With two further mass balances, we are able to test whether the limit of $c_e = 0.020 \text{ kg m}^{-3} \text{ DOC}$ is upheld:

1. The concentration after mixing effluent from processes 2 and 3 at mixing point M2 is:

$$20 \cdot 0.03 + 10 \cdot 0.1 = 30 \cdot c_{in,2}$$

$$c_{in,2} = \frac{20 \cdot 0.03 + 10 \cdot 0.1}{30} = 0.053 \text{ kg m}^{-3} \text{ DOC}$$

2. The concentration after mixing at mixing point M3 is:

$$30 \cdot 0.053 + 60 \cdot 0.003 = 90 \cdot c_e$$

$$c_e = \frac{30 \cdot 0.053 + 60 \cdot 0.003}{90} = 0.019 \approx 0.020 \text{ kg m}^{-3} \text{ DOC}$$

The proposed network for the treatment of three wastewater streams is suitable to undercut the required limit of:

$$c_e = 0.020 \text{ kg m}^{-3} \text{ DOC} > 19 \text{ mg L}^{-1} \text{ DOC}$$

Thus, 30 m^3 of the wastewater must not be treated.

References

- Baetens, D. **2002**, Water pinch analysis: minimisation of water and wastewater in the process industry, *Water Recycling and Resource Recovery in Industry*, Lens, P., L. H. Wilderer, P. and Asano, T. (Eds.), IMA Publishing, 207–222.
- Breithaupt, T.; Reemtsma, T.; Jekel, M.; Storm, T.; Wiesmann, U. **2003**, Combined biological treatment/ozonation of wastewater for the mineralization of non-biodegradable naphtholine-1,5-disulfonic acid, *Acta Biotechnology* 23, 321–333.
- Bueb, M.; Finzenhagen, M.; Mann, T.; Müller, K. **1990**, Verminderung der Abwasseremission in der chemischen Industrie durch Verfahrensumstellungen und Teilstrombehandlungen, *Korrespondenz Abwasser* 37, 542–558.
- Christ, C. **1996**, Integrated environmental protection reduces environmental impact, *Chemical Technology Europe* 3, 19.
- Christ, C. (ed) **1999**, *Production Integrated Environmental Protection and Waste Management in the Chemical Industry*, Wiley-VCH, Weinheim.
- Kollatsch, D. **1990**, Industrielles Wassersparen und Abwasserreinigen schaffen neue Dimensionen, *Korrespondenz Abwasser* 37, 560–564.
- Krull, R.; Hempel, D.C. **1994**, Biodegradation of naphthalene sulfonic acid-containing sewage in a two-stage treatment plant, *Bioprocess Engineering* 10, 229–234.
- Krull, R.; Nörtemann, B.; Kuhm, A.; Hempel, D.C.; Knackmuss, H.-J. **1991**, Der bakterielle Abbau von 2,6-Naphthalindisulfonsäure mit immobilisierten Mikroorganismen, *gwf Wasser-Abwasser* 132, 352–354.
- Nörtemann, B.; Knackmuss, H.-J. **1988**, Abbau sulfonierter Aromaten, *gwf Wasser-Abwasser* 129, 75–79.
- Pauli, G. **1997**, Zero emissions: the ultimate goal of cleaner production, *J. Cleaner Prod.* 5, 109–113.
- Räbiger, N. **1999**, Future Aspects – Clean Production, *Biotechnology Vol. 11a*, Environmental Processes I, J. Winter (ed.), Wiley-VCH, Weinheim, 561–577.
- Smith, R.; Petela, E.; Wang, Y.P. **1994**, Water, water everywhere ..., *The Chemical Engineer* 12, 21–24.
- Wang, Y.-P.; Smith, R. **1994**, Design of distributed effluent treatment systems, *Chem. Eng. Sci.* 49, 3127–3145.
- Wang, Y.P.; Smith, R. **1995**, Wastewater minimization with flowrate constraints, *Trans. IchemE* 73, 889.