

Bauhaus-Universität Weimar

in co-operation with DWA

Deutsche Vereinigung für Wasserwirtschaft, Abwasser und Abfall e.V.

Further education

1. Edition

Correspondence course Water and the Environment

Subject matter

Applied process engineering in industrial wastewater treatment



Bauhaus-Universität Weimar

EXCERPT

Applied process engineering in industrial wastewater treatment

1. Edition

Deutsche Vereinigung für Wasserwirtschaft, Abwasser und Abfall e.V.
(DWA)

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Chapter 2 - Wastewater treatment in the food industry

Chapter 3 - Other industries using predominantly organic constituents

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WATER AND THE ENVIRONMENT**

WW 54

**Applied process engineering in industrial wastewater
treatment**

1. Edition

Chapter 3

Mechanical / physical processes

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3 Other industries using predominantly organic constituents

This chapter examines sectors subsumed under 'other agricultural industry' whose raw materials are essentially based on agricultural products. It will present manufacturing processes, material flows, and examples of wastewater treatment.

Sectors subsumed under 'other agricultural industry'

3.1 Textile industry

3.1.1 Characterisation of the sector

The textile sector firstly processes raw fibres to produce yarns, flock fabrics, linear fabrics, woven fabrics, knitwear, fleeces, textile floor coverings, and other textile sheeting materials; secondly, it also refines / finishes these products.

Based upon the type of raw fibre used, the products of the textile industry are essentially subject to further processing in three sub-areas:

Sub-areas of the textile industry

- The clothing industry (approx. 30 %)
- The manufacture of textiles for house and home (approx. 37 %)
- The manufacture and/or further processing of technical textiles (approx. 33 %)

Germany currently has approximately 90 companies that process fibres and yarns, approximately 325 companies that manufacture sheeting materials, and around 400 companies that finish raw textile goods [2].

At this point we will take a closer look at textile finishing. This requires a multiplicity of stages which are subject to change, depending on the source materials (such as cotton, wool, linen, viscose, acetate rayon, various synthetic fibres and mixed fibres), the form in which they are presented (such as yarn, weave or piece goods) and the respective fashion trend.

Stages in textile finishing

Figure 3.2 shows the most important stages in textile finishing, which – apart from singeing – are also significant in terms of water management:

- Singeing: this refers to the thermal removal of fine fibres projecting from the woven fabric.
- Desizing: removal of the auxiliaries (sizes) required for the manufacture and processing of yarn; these include starch, starch derivatives, higher alcohols, polyvinyl alcohols, polyacrylates, and carboxymethyl cellulose. The process is generally undertaken with hot water plus added enzymes and tensides.
- Boiling or bucking: the removal of extraneous materials and contaminants such as fats, waxes, lignin and pectin substances. This is undertaken with hot water plus added sodium hydroxide or in some cases sodium carbonate.

- Bleaching: in order to increase its whiteness, the item is treated with sodium hypochlorite, sodium chlorite, or hydrogen peroxide.
- Mercerising: in order to increase its tear-resistance and dyeability, the item is stretched and treated briefly with sodium hydroxide (NaOH).
- Dyeing / printing: dissolved or dispersed dyes are applied to the item. Dyeing uses aqueous dye solutions or dispersions, while printing makes use of dye pastes with a relatively high viscosity. The dye solution is referred to as a dye bath or dye liquor.



Fig. 3.1: Exhaustion dyeing with an NT jigger (Image: thiestextilmaschinen.de, Thies GmbH)

- Finishing: various mechanical and/or chemical treatment processes are used to achieve the desired usage properties for the item in question, such as crease-resistance, antistatic or water-repellent behaviour, and so forth.

Textile auxiliaries

The wide range of raw materials used to make textiles together with the long list of requirements when it comes to their appearance and usage properties mean that textile finishing deploys a multitude of dyes and chemicals, i. e. textile auxiliaries. Most of the textile auxiliaries on the market are listed in the Textile Auxiliaries Buyers' Guide [12].

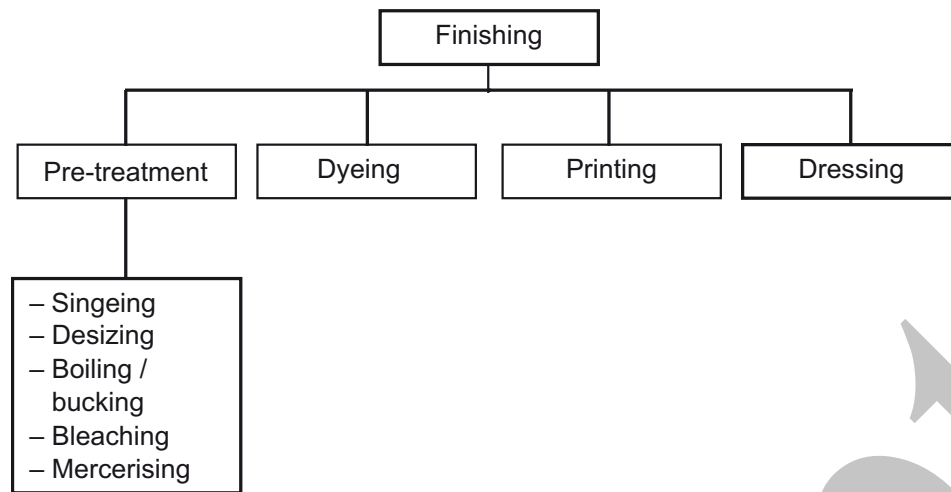


Fig. 3.2: Essential stages in textile finishing

3.1.2 Wastewater volume / composition, plus requirements

The textile industry uses a lot of water and hence also produces a large volume of wastewater, because almost all of the finishing processes are carried out using aqueous solutions or suspensions which subsequently remain in the form of wastewater.

Proceeding from the overview of essential stages in textile finishing shown in *Figure 3.2*, *Figure 3.3* uses the example of cotton finishing to present the material flows that are relevant in the context of water management and the resultant partial flows of wastewater that are assigned to the various stages. In each case, the process stages shown are sub-divided into the treatment itself and the subsequent washing and rinsing stages used to remove excess dyes and textile auxiliaries.

*Cotton finishing:
partial material
flows and partial
wastewater flows*

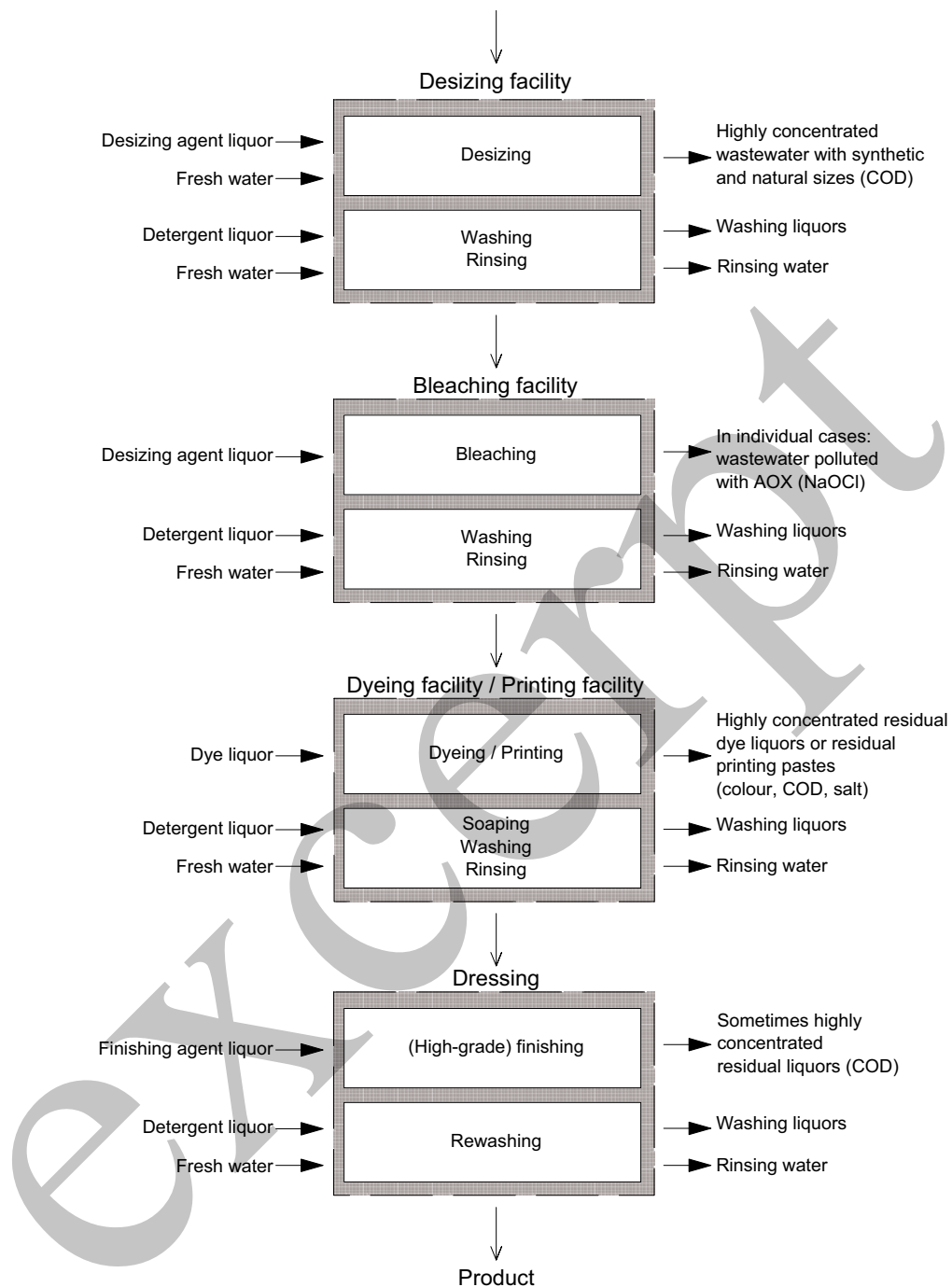


Fig. 3.3: Essential stages in cotton finishing, plus the associated material flows

Depending on the manufacturing process, the actual treatment stages sometimes produce relatively small amounts of very highly concentrated partial flows and residual liquors. Particular mention should be made of the following:

- Residual liquors from desizing: these liquors manifest high levels of organic contamination as a result of the sizes that have subsequently been removed and the enzymes and tensides that have been added.

- Residual liquors from boiling: these liquors manifest high levels of organic contamination and are strongly alkaline as a result of contaminants and substances mixed in with the fibres which have subsequently been removed, together with the sodium hydroxide that has been added.
- Residual liquors from bleaching: these liquors manifest high levels of organic contamination as a result of substances mixed in with the fibres which have subsequently been removed, and are often badly polluted with AOX if chlorine bleach has been used.
- Acid or alkaline residual dye liquors plus wastewater from washing once printing has been completed: these liquids are very coloured and manifest high levels of organic contamination due to non-absorbed dyes and dye auxiliaries such as acids, bases, salts and other textile auxiliaries. If certain classes of dye are used, they can also manifest a high AOX, heavy metal or sulphide content.
- Residual liquors from finishing: these liquors often manifest high levels of organic contamination due to non-absorbed (mostly synthetic) textile auxiliaries.

The subsequent washing and rinsing process also produces small amounts of medium- to highly concentrated washing liquors and – depending on the number of rinsing stages – relatively large amounts of weakly polluted rinsing water.

The volume of wastewater produced by a textile finishing business (and its composition) are to a large extent determined by the substrate used, the mode of operation, how the process is managed, and further influencing factors; this makes it impossible to provide any average or typical data.

Influencing factors

Some important partial flows are concentrates from the finishing processes, which manifest very major pollution. They include [2]:

Concentrates from the finishing processes

- desizing liquors (COD: 3,000–80,000 mg/l depending on the washing technique / how the process is managed)
- wastewater produced by continuous pre-treatment of knitted fabrics / knitwear made from synthetic fibres (hydrocarbon content in the g/l range)
- residual dye pad liquors (COD and dye content: 5,000–100,000 mg/l)
- residual print pastes (COD: 100,000–350,000 mg/l)
- residual finishing liquors (COD: 5,000–200,000 mg/l)
- residual liquors from coating / covering and lining
- residual liquors from coating the back of carpets

Washing processes usually produce partial flows that are much less polluted. The first rinsing water can still manifest noteworthy COD content, whereas the final rinsing water often manifests very low COD concentrations (< 200 mg/l).

Table 3.1 summarises research data relating to total untreated wastewater from 50 textile finishing businesses [13].

Research data from 50 textile finishing businesses

Table 3.1: Range of fluctuation in the composition of total untreated wastewater from 50 textile finishing businesses (1995-1999) [2]

Parameter	Unit	Range of values
pH value	-	5–13
Conductivity	$\mu\text{S/cm}$	300–9500 ¹⁾
Temperature	$^{\circ}\text{C}$	15–60
COD	$\text{mg O}_2/\text{l}$	400–5,000
TOC	mg C/l	150–1,600
BOD ₅	$\text{mg O}_2/\text{l}$	80–1,500
COD/ BOD ₅	-	2.3–7
AOX	mg Cl/l	0.05–8 ²⁾
Hydrocarbons	mg/l	< 0.1–110 ³⁾
Organically bonded nitrogen	mg N/l	6–80 ⁴⁾
Ammonium	mg N/l	< 0.1–120 ⁵⁾
Anionic tensides	mg/l	2–24
Non-ionic tensides	mg/l	5–50
Trichloromethane	$\mu\text{g/l}$	0.3–170 ⁶⁾
Sulphite	mg/l	< 0.5–90 ⁷⁾
Total copper	mg/l	< 0.001–1.5 ⁸⁾
Total zinc	mg/l	0.02–1.1
Total chromium	mg/l	< 0.005–2 ⁹⁾

¹⁾ In the case of wastewater, mainly from dyeing cellulose fibres with reactive or direct dyes, for which large quantities of neutral salts are used.

²⁾ Values above 1 mg/l are the exception; high values generally occur when using halogenated dyes that have relatively low fixation rates (< 80 %). Values > 1 mg/l are also caused by using chlorine-separating bleaches or by free chlorine resulting from the use of sodium hypochlorite. Apart from sodium chlorite to bleach synthetic fibres, the wastewater must not contain chlorine-separating bleaching agents.

³⁾ High values generally occur as a result of substances containing hydrocarbons being washed-out when pre-treating polyester or polyamide.

⁴⁾ High values occur if larger quantities of residual resin finishing liquors with ethylene urea derivatives are drained off or when crease-resistant finishes (likewise ethylene urea derivatives) are washed out.

⁵⁾ High values occur in the case of reactive- and dye bath printing (including coloured discharge printing) if relevant quantities of urea are used.

⁶⁾ High values occur when NaOCl bleach is used. Apart from sodium chlorite to bleach synthetic fibres, the wastewater must not contain chlorine-separating bleaches (e. g. NaOCl).

⁷⁾ High values occur when relevant quantities of sodium dithionite are used, e. g. in the case of dye bath dyeing or from the reductive post-treatment of polyester dyes.

⁸⁾ Values above 0.5 mg/l are the exception. Higher values can occur during printing.

⁹⁾ Values above 0.2 mg/l are the exception. Higher values can occur when dyeing wool or polyamide with chromium complex dyes or post-chroming dyes.

Appendix 38 of the Wastewater Ordinance (*AbwV*) stipulates the requirements for wastewater from textile manufacturing and textile finishing prior to discharge into a water body and/or prior to blending with other wastewater. *Requirements for the point of discharge*

Table 3.2: Appendix 38 Part C; requirements for wastewater at the point of discharge [1]

COD [mg/l]	BOD ₅ [mg/l]	Total P [mg/l]	NH ₄ -N [mg/l]	Total N as sum of ammonia N, ni- trite N and nitrate N [mg/l]	Sul- phite [mg/l]	Pigmentation (SAC) [m ⁻¹]	Toxicity to fish eggs (T _{egg}) [-]
160	25	2	10	20	1	Yellow range (436 nm): 7 Red range (525 nm): 5 Blue range (620 nm): 3	2

Table 3.3: Appendix 38 Part D; requirements for textile wastewater prior to blending with other wastewater [1]

AOX [mg/l]	Total chromium [mg/l]	Copper, nickel [mg/l]	Sulphide [mg/l]	Tin, zinc [mg/l]
0.5	0.5	0.5	1.0	2.0

3.1.3 Wastewater avoidance / treatment

Twenty of the approximately 400 textile finishing businesses in Germany are currently direct dischargers; the remainder are indirect dischargers which discharge into municipal wastewater treatment plants [2].

In addition to a multiplicity of universal measures to save water and thus reduce operating costs, the textile industry also makes efforts to reduce water consumption with the precise aim of lowering the volume of wastewater and/or the wastewater load. For example:

Avoidance measures

- Recovery / recycling (e. g. via ultrafiltration) of sizes while at the same time using the permeate for washing processes or the redeployment of sizing agents.
- Reducing the use of chemicals by testing and optimising formulae
- steam drying of the lye and recirculation into the mercerisation facility
- The preferred use of dyeing processes that enable optimal exploitation of the dye bath
- The increased use of dyes which are free of heavy metals and which can be easily fixed in the fibres; this reduces the concentration of dyestuffs in the wastewater
- Reducing the liquor ratio (ratio of textile to water) when dyeing

- Using dyes that are low in AOX or free of AOX
- Recycling of dyeing and finishing liquors
- Minimising the use of textile auxiliaries that are not readily biodegradable and/or toxic
- The combined use of water and compressed air when cleaning printing templates
- The steam drying of highly concentrated partial flows of wastewater plus separate disposal of residues
- Optimisation of rinsing and washing processes
- Reuse of weakly polluted rinsing water and cooling water

Reuse of weakly polluted rinsing water in the dyeing industry

The following process diagram illustrates the reuse of weakly polluted rinsing water in the dyeing industry. Highly concentrated residual dye liquors and the first rinsing baths (which can possibly be treated and reused) are then left for discharge.

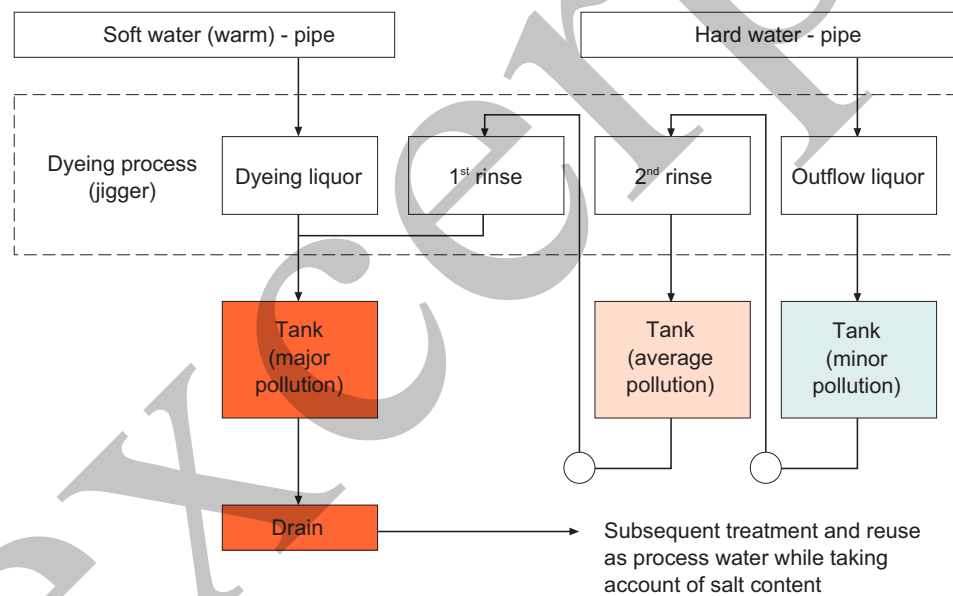


Fig. 3.4: Process diagram showing the reuse of weakly polluted rinsing water in a dyeing facility [9]

Wastewater treatment

In addition to mechanical procedures (such as the use of mesh screens), physical / chemical processes can be used to pre-treat textile wastewater. A mixing and balancing tank should be included as a way of balancing concentrations and quantities. The mutual neutralisation of alkaline and acid partial flows reduces the consumption of chemicals and thus the extent to which the wastewater is polluted with salts. The pH value of the blended wastewater is generally alkaline. If at all possible, one should refrain from neutralising alkaline wastewater because neutralisation can be achieved by using the CO_2 formed during the biological stage of municipal treatment plants. This reduces the extent to which the wastewater is polluted with neutral salts, which for economic reasons cannot be eliminated.

The co-treatment of textile wastewater in a municipal sewage plant becomes critical if it constitutes a high COD percentage of the total load of the treatment plant. The colouring plus a much higher percentage of persistent COD then become problematic. In individual cases, the AOX concentration of the textile wastewater can impact on the discharge concentration of the municipal treatment plant.

The following example illustrates the co-treatment of textile wastewater in a municipal sewage plant. In the original plans, the ratio of local authority to local industry in terms of the COD wastewater load was 1 to 3.5 [10]. The wastewater purification concept contains the following stages:

- Anaerobic treatment of a partial flow of highly concentrated sizes in the sludge digester where polyvinyl alcohol (PVA) is to a large extent degraded.
- Pre-treatment of the blended textile wastewater in a highly charged activation/aeration stage
- Ozonisation of the biologically pre-treated textile wastewater (ozone is produced on the spot from pure oxygen)
- Joint treatment of municipal and pre-purified textile wastewater in a weakly charged activation / aeration stage
- Adsorption via powdered activated carbon (PAC)
- Multimedia filtration (flocculation filtration) including dosing of polyelectrolytes and iron chloride.

Figure 3.5 shows the process diagram.

Depending on the pollution derived from the textile industry, ozonisation and adsorption can be enabled or disabled. Treatment with ozone to a very large extent removes any colour from the wastewater. The residual COD concentrations satisfy the minimum requirements stipulated by Appendix 1 of the Wastewater Ordinance (*AbwV*).

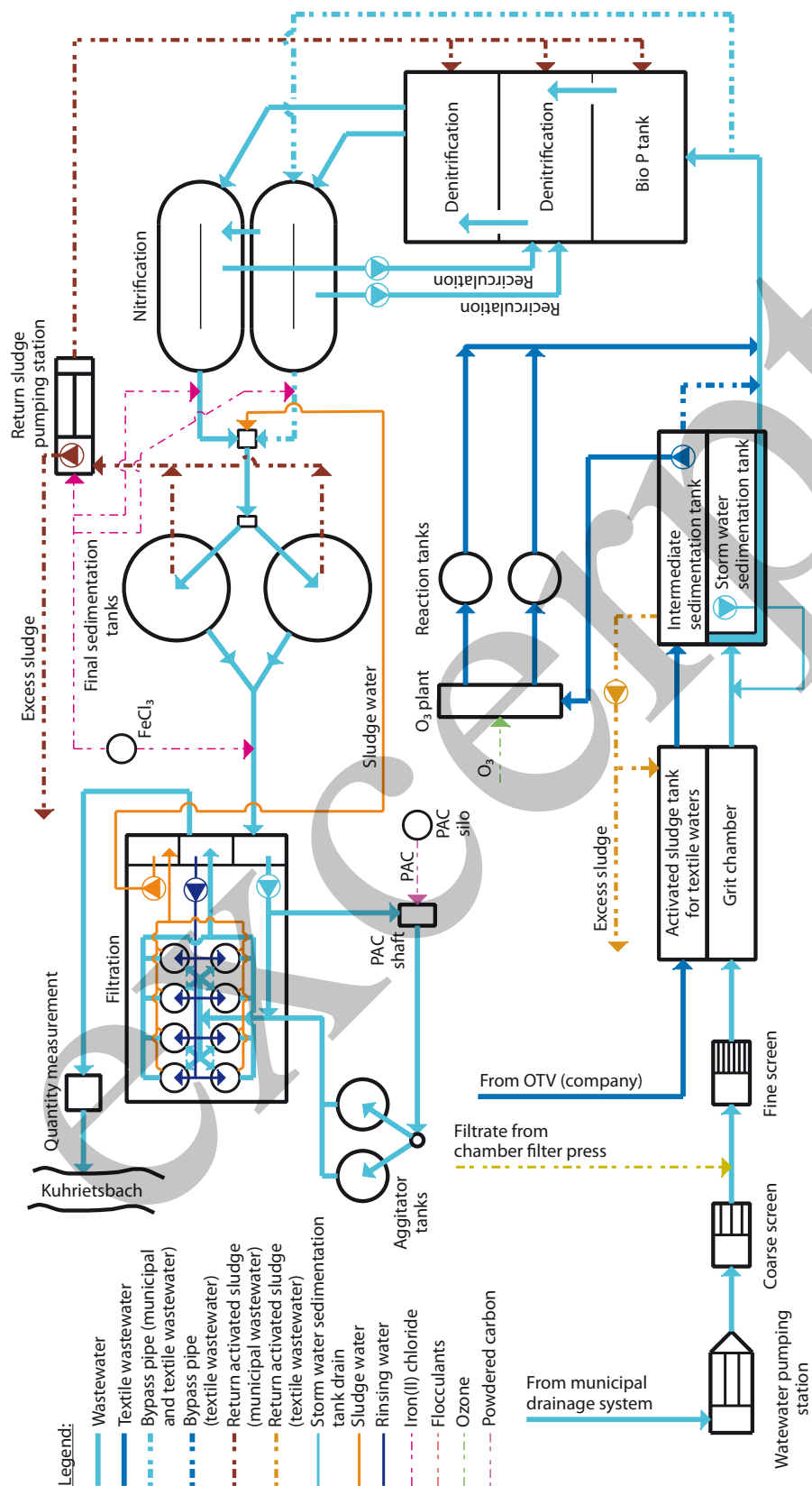


Fig. 3.5: Process diagram of a municipal treatment plant with a high percentage of textile wastewater (Image: Tutthahs & Meyer)

3.2 Wastewater from leather manufacturing

3.2.1 Characterisation of the sector

The EU is the biggest supplier of leather on the international market. Italy is the most important country in Europe with regard to the number of companies and employees as well as production volume and turnover. Italy is responsible for 15 % of global production of cow and calf leather and 65 % of the leather produced in the EU. The development of the leather industry in other regions of the world such as Asia and the American continent means that the EU's market share of leather production is declining. [14]

Most leather-producing companies in Europe are small or medium-sized enterprises (SMEs). The most important buyer of tanning products in the EU is the shoemaking sector, which accounts for 50 %. Roughly 70 % of the German leather industry in 1999 was devoted to upholstery (furniture and automobiles) and roughly 25 % went to the shoemaking industry. The remainder (5 %) was divided up between leather goods, leather clothing (including gloves) and numerous other areas such as technical leather goods, sports items, riding gear and saddles. The processing of sheepskins and goatskins, which for the most part are imported as semi-finished goods, has declined to roughly 3 % of total output. The pig leather industry, which constituted around 50 % of total production in the former GDR, is no longer of any consequence. [4]

Hides and pelts are by-products of abattoirs, and represent the raw material for leather manufacturing. Hide comprises three layers: the epidermis, the dermis and the hypoderm. Only the dermis can be used to make leather, and it mostly consists of a fibrous protein, namely collagen. The absorption of tanning agents means it will keep for a considerable length of time, i. e. it will be transformed into leather.

In the past, most tanneries used to preserve the hides and pelts with salt before processing. Preservation with salt is on the decline, albeit unavoidable if the item has to be stored temporarily. An ever greater percentage of hides and pelts are nowadays delivered to the tannery within a few hours of the animal being slaughtered, and are immediately processed.

The production processes when manufacturing leather can be sub-divided into four main groups:

Stages in production

- The storage of hides and pelts
- Processes within the beamhouse (the area of a tannery where hides are pre-treated prior to actual tanning)
- Tanning
- Wet finishing subsequent to tanning (e. g. dyeing, greasing and drying)
- Finishing

Prior to tanning

Prior to tanning, the (possibly preserved) raw materials that have been delivered are subject to the following stages: soaking, liming (including hair removal by applying an alkaline treatment solution), deliming (treatment with inorganic or organic acids or their salt), bating and pickling (immersion in a solution of salt and acid). The first stages in the beamhouse serve to remove constituents that are superfluous when making leather. The idea is that the dermis should also be opened up by these preparatory tasks in readiness for the actual tanning process.

Tanning

Tanning can use mineral tanning agents (e. g. chromium tanning) or plant-based and synthetic tanning materials (bark tanning); oil tanning, aldehyde tanning, quinone tanning (chamois tanning) and combined tanning processes are also deployed. Out of all these processes, chromium tanning is the most commonly used method (approx. 85 %). Only the complex salts of trivalent chromium can be used for tanning purposes [4]. Tanning alters the animal hide in such a way that it won't rot when damp, won't get sticky in heat, and won't break when it's cold. Once tanning has been completed, the hides and pelts constitute an intermediate product which can be marketed (described as 'wet blue' in the case of chromium tanning because of the blue colour, and 'wet white' in the case of chromium-free tanning because of the white colour).

Fur production

Unlike leather manufacturing, the hairs are preserved when furs are produced. Fur production uses the term 'fur dressing' to describe the tanning process.

3.2.2 Wastewater volume / composition, plus requirements

Several individual stages in one single container

It is customary in leather manufacturing to leave the hides, pelts (the term for hides after liming) or 'wet blue' in one single container while several individual stages are carried out; it is also normal to change the process water. Each of the following stages is therefore often carried out in one single container:

- (1) Soaking, liming, washing
- (2) Deliming, bating, pickling, chromium tanning
- (3) Washing, neutralising, washing, dyeing, greasing, fulling, re-tanning, washing

Different assignments can be made, depending on the mechanical processes involved (defleshing, splitting, sammying, shaving, and intermediate drying).

Each production container is generally connected to one discharge channel (or two at most) because it makes no sense to separate the wastewater into every individual liquor. This leads to process wastewater of a similar nature (alkaline and acid) merging to form partial flows which are then – depending on their level of pollution – treated specifically or combined to form a total flow.

Table 3.4: Composition of total wastewater flows in chromium leather manufacturing (standard ranges, process-dependent deviations, formula and possible water consumption) [4]

Process stages	-	(1) to (3)	(3)
Source material	-	Raw hide	Wet blue
Parameter	Unit	-	-
Reference weight	Mg	Weight of raw hide	Shaved weight
Wastewater volume	m ³ /Mg	20–30	15–30
pH value	-	9.5–11.5	3.8–5.6
BOD ₅	mg/l	2,400–3,600	1,900–4,000
COD	mg/l	4,000–9,000	3,100–10,000
Organic N	mg/l	400–800	
NH ₄ -N	mg/l	120–250	80–400
Sulphide	mg/l	50–200	<< 0.1
Chromium (III)	mg/l	100–400	35–380

The sulphide content and chromium(III) compound content are characteristic features of tannery wastewater. In-house measures can minimise the quantities produced (e. g. via recycling of residual liquor, chromium recovery, sulphide recovery, closed loop recycling).

Characteristic features of tannery wastewater

The multiple use of chromium baths requires more analyses to be carried out if one is to avoid any adverse effect on the quality of the leather. Multiple use of this kind is possible when manufacturing less high-quality leather (e. g. split leather), where it is deployed in a variety of ways. Salts and organic contaminants will accumulate in the bath, so it has to be discarded once it has been used for a longer period of time (3–4 months). When manufacturing high-quality leather (upper leather), the multiple use of tanning baths leads to loss of quality, so this process is not used in such cases.

Multiple use of chromium baths

The chromium content of the wastewater can be minimised if the liquors are depleted: the chromium that has been introduced into the liquor is to a very large extent fixed in the hide. Furthermore, chromium is recovered via precipitation and breaking down the chromium-containing precipitation sludge to form sulphuric acid. Once the desired pH value has been established with sodium hydroxide and other chemicals, the chromium(III) sulphate solution is reused in the tanning process. These procedures help to reduce the chromium-containing sludges, which would otherwise need to be disposed of as hazardous waste.

Appendix 25 of the Wastewater Ordinance (*AbwV*) stipulates the requirements for wastewater from leather manufacturing and fur finishing.

Requirements for the wastewater

Table 3.5: Appendix 25 Part D: requirements for wastewater prior to blending [1]

Process	Parameter, concentration
Soaking, liming and deliming, each including rinsing	Sulphide: 2 mg/l
Tanning, wet finishing, each including rinsing; Leather fibreboard manufacturing	Total chromium: 1 mg/l

3.2.3 Wastewater treatment

Partial flow treatment or total flow treatment

Wastewater treatment makes a distinction between the treatment of partial flows and the treatment of the total flow. Whether partial flow treatment or total flow treatment make sense (particularly for chromium and sulphide) depends on the respective local and operational circumstances. Treatment can occur in batch or continuous flow processes. Wastewater from the leather industry can easily be biologically purified and tends to be discharged indirectly. Local conditions may make it necessary to treat waste gases. The sources of foul-smelling waste gases (e. g. hydrogen sulphide, ammonia) can be storage tanks, sulphide oxidation, or sludge treatment.

Level of efficiency during treatment

The data in the following table indicates typical values for the level of efficiency when treating wastewater derived from leather manufacturing. The figures relate to conventional process liquors for the production of finished leather from raw hide.

Table 3.6: Levels of efficiency when treating wastewater derived from leather manufacturing [14]

Parameter % or mg/l	COD		BOD ₅		Settleable solids		Chromium	S ₂ -	N _{total}	
	%	mg/l	%	mg/l	%	mg/l	mg/l	mg/l	%	mg/l
Pre-treatment										
Grease separation (dissolved air flotation plant)	20–40									
Sulphide oxidation (liming and washing liquors)	10							10		
Chromium precipitation							1–10			
Physical/chemical treatment										
Mixing + sedimentation	25–35		25–35		50–70		20–30		25–35	
Mixing + chemical treatment + sedimentation	50–65		50–65		80–90		2–5	2–10	40–50	
Mixing + chemical treatment + flotation	55–75		55–75		80–95		2–5	2–5	40–50	
Biological treatment										
Primary or chemical treatment + activated sludge treatment	85–95	200–400	90–97	20–60	90–98	20–50	< 1	< 1	50	150
Primary or chemical treatment + activated sludge treatment including nitrification and denitrification	85–95	200–400	90–97	20–60	90–98	20–50	< 1	< 1	80–90	30–60

EXCERPT

3.3 Wastewater from paper and cellulose manufacturing

3.3.1 Paper consumption and the paper industry in Germany

The consumption of paper is constantly rising: per capita consumption in Germany for 2004 totalled 230 kg as opposed to 189 kg in 1996 and 32.2 kg in 1950. This figure subsumes all paper goods, i. e. including books, magazines, kitchen roll and toilet paper. There are many reasons for this steady increase: in addition to the ever greater number of newspaper / magazine titles and advertising brochures, people are somewhat blasé in their attitudes toward paper as a raw material.

Table 3.7: Paper production in Germany in 2005 [15]

	Production in Gigagram (Gg)
Newsprint	2,451
Other graphic papers	8,087
Paper, card and cardboard for packaging	8,498
Hygiene papers	1,188
Speciality papers	1,455
Total	21,679

In 2005, the 114 companies in Germany produced a total of 21.7 Tg of paper. During the same period, turnover in this sector (cellulose and paper) amounted to 13 billion euros, and approx. 45,850 people were employed in the industry. A total of approx. 3,000 different grades of paper are manufactured. *Table 3.7* provides an overview of the most important grades of paper expressed as percentages of total production.

3.3.2 The use and processing of raw materials

Fibres and bulking agents which are insoluble in water account for more than 95 % of the materials used to produce paper. The demand for fibres is covered exclusively by renewable raw materials, mainly wood; one either uses mechanical or chemical/mechanical processes to defibre the wood to form groundwood pulp, or chemical processes to open up the wood and form cellulose). *Table 3.8* provides an overview of the raw materials used in 2005.

Demand for fibres is covered exclusively by renewable raw materials

Table 3.8: Consumption of raw materials in Germany in 2005 [15]

	Use in Gg	%
Waste paper	14,413	56.6
Cellulose	4,976	19.6
Mechanical wood pulp and semi-cellulose	1,677	6.6
Other fibres	33	0.1
Other materials	4,347	17.1
Total	25,466	100

The main types of fibre used to manufacture paper are waste paper pulp, cellulose, and mechanical wood pulp. Other fibres such as rags from recycled fabrics, cotton fibres, linters, wool, synthetic organic fibres and inorganic fibres are used in only a few specialised products and are of secondary importance [11]. In 2006, the rate of waste paper reuse (ratio of waste paper consumption to the production of paper and cardboard) was 67.4 %, which is a record for any country. The paper recycling rate (ratio of waste paper collected to the amount of paper and cardboard consumed) totalled 75 %. Quality requirements dictate the existence of vastly differing individual grades of paper, meaning that newsprint and packaging contained up to 100 % waste paper, whereas graphic papers contained only 26 %.

Paper and cellulose production differ fundamentally in terms of the manufacturing process as well as the type and quantity of wastewater they produce. Similar to the production of groundwood pulp or the treatment of waste paper, cellulose is often produced in dual-purpose mills that also manufacture paper (integrated paper mills). Cellulose manufacturing and pulp products create considerable wastewater and pollution at the respective site. Before we explain the actual paper manufacturing process, we will therefore begin by looking at the essential procedures involved in preparing/producing the raw materials.

3.3.2.1 Cellulose production

Cellulose production entails the separation of any concomitant substances from the plant material (mainly wood). In the case of wood, this principally means lignin and hemicelluloses. Generally speaking, more than 50 % of the wood material is brought into solution and the pulping is supplemented with a bleach that removes colouring compounds (mainly the residual lignin). Two processes are predominantly used:

Sulphate process

The *sulphate process* uses an aqueous solution of sodium hydroxide and sodium sulphide to achieve pulping. One can use steam drying and incineration to treat the spent cooking liquor (black liquor) and thereby recover the pulping chemicals (following additional chemical conversion).

In the case of the *sulphite process*, pulping is achieved via a hydrogen sulphite solution (cooking acid) which contains an excess of dissolved SO_2 . After pulping, the cellulose is generally subjected to further treatment (removal of cooking liquid and contaminants) and is then bleached, usually in several stages. In the past, chlorine was essentially used as an oxidation agent for bleaching, but it is customary nowadays to use oxygen (mostly supported with hydrogen peroxide) [11].

Sulphite process

In addition to smaller partial flows, cellulose production principally creates two wastewater flows: the vapour condensates from the sulphite process and the wastewater from the bleaching stages, which in the case of the sulphate process constitutes the majority of the wastewater. Paper mills in Germany mainly buy in cellulose as a commercial product. There are only a few mills that produce nothing but cellulose, and some with integrated cellulose production. In the case of the latter, the cellulose that is produced is usually only thickened and not dewatered before being used to make paper, which means that the organic contaminants dissolved in the pulp/cellulose suspension enter the paper manufacturing process and a clear separation of the wastewater pollutants is no longer possible.

3.3.2.2 Production of groundwood pulp

The pulp produced as raw material for paper manufacturing as a result of mechanically defibering wood is called groundwood pulp. The individual processes differ with regard to the type of mechanical defibering used: trunks/logs can be defibered with grinding stones, while woodchips are defibered between grooved metal plates that move in parallel, i. e. so-called refiners. The processes also differ as a consequence of the various pressures and temperatures under which defibering occurs. In order to manufacture white papers, the groundwood pulp must subsequently be bleached, which can be achieved via a hydrosulphite bleach, an oxidising bleach with hydrogen peroxide, or a combination of the two processes. After it has been graded, the (possibly) bleached and condensed material is transferred to the paper machine as finished pulp. The dissolved organic compounds contained in the groundwood pulp suspension are thus introduced into the paper machine's water cycle.

3.3.2.3 Waste paper processing

Waste paper – like groundwood pulp – is generally processed in paper mills. This is frequently achieved via straightforward defibering and subsequent grading, during which various temperatures and pressures are applied. The waste paper is initially broken down in a pulper and any rope-forming components are separated off. Return water from the paper machine is mostly used to break the paper down, and grading is accomplished in centrifugal separators. The quality of the waste paper pulp that is produced in this way is inadequate for higher-quality paper products, so the printing inks and other contaminants have to be removed via de-inking (which mostly entails the chemical removal of the printing ink and separation via flotation).

The waste paper pulp that is produced (DIP = de-inked pulp) is often also bleached and then largely dewatered or fed into the paper machine as a suspension.

3.3.2.4 Other additives

In addition to the fibres, inorganic bulking agents that are insoluble in water are often added in order to alter the paper's pore structure. Some examples of white bulking agents are kaolin, calcium carbonate or talcum. Depending on the grade of paper, a multitude of different auxiliaries are used to produce other attributes: size (glaze) to make it easier to write on the paper, resins and/or mixed polymers to increase wet strength, and so forth. The method of production often requires additional auxiliary materials and additives in order to optimise the process or actually enable modern paper machines to function at high speeds. All these substances can influence wastewater purification.

3.3.3 Description of the paper manufacturing process

The role of water during manufacture

Water likewise plays a crucial role in the actual paper manufacturing process: it serves as a suspension- and transport medium for fibres and bulking agents, as a solution medium for chemical auxiliaries, and as a medium to form the hydrogen bridge bonds between the fibres. These hydrogen bridge bonds constitute the essential components that make the product stable and rigid. Paper as it is generally understood can therefore not be manufactured without water. Depending on the grade, between 250 and 1,000 l water per product are needed to process the fibres and form the fibre mat on the paper machine wire. However, the majority of this can be recycled, so the specific water consumption is much lower. In principle, wastewater accumulates during this process solely in the form of excess circulation water which is displaced when fresh water is added [11].

Manufacturing process

The manufacturing process is shown in the following diagram (*Figure 3.6*): water is added to the fibres and they are initially dispersed in periodically or continuously functioning facilities. Depending on the grade of paper to be produced, they are then milled to a greater or lesser degree to form a material that possesses the desired quality. Different fibres are mixed together, and bulking agents, size, dyes and other paper auxiliaries are added. After dilution, consistency control and grading, the pulp is transferred to the paper machine wire, which is a constantly rotating belt on which the fibres settle and form the paper web.

The following illustration shows the general paper manufacturing process with a special focus on water management. After an initial dewatering on the wire, the percentage of water is further reduced in special presses to a dry matter content of 40–55 %; it is eventually brought to its final water content (less than 10 %) via thermal drying using cylinders that are heated from the inside with steam.

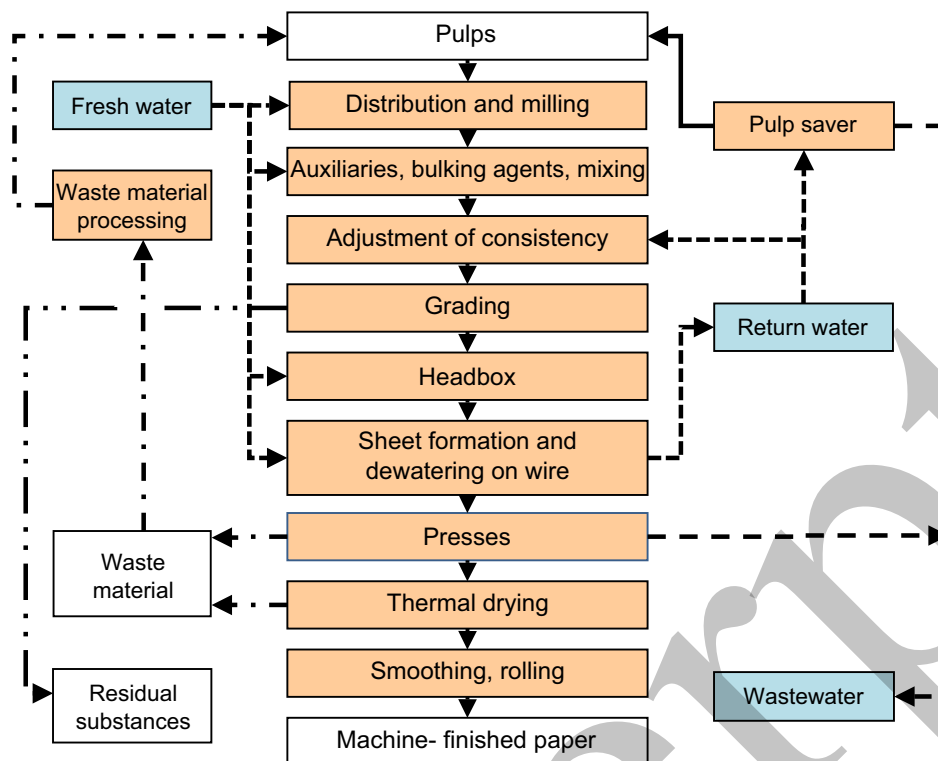


Fig. 3.6: Simplified general paper manufacturing process [11]

3.3.4 Water cycles and in-house measures

Before we take a look at wastewater volume and wastewater purification, we will firstly present the essential features of water cycles in paper manufacturing, together with some in-house optimisations.

3.3.4.1 Types of water cycle

With an eye to economic and ecological constraints, the required amount – and quality – of water has to be provided for every part of the production process. *Figure 3.7* shows how one can make a rough distinction between three cycles: primary, secondary and – if available – tertiary [7].

Primary, secondary and tertiary cycle

- The **primary cycle** is the biggest cycle in terms of volume, and contains the first white water stream. In this cycle, the pulp is collected and the sheet is formed on the wire.
- The **secondary cycle** comprises excess white water from the first stream and also mostly consists of discharges from the wire pit plus the water that has been separated from the vacuum boxes and vacuum pumps. The total volume flow of this cycle is generally passed through a pulp saver. The pulp that has been recovered is transferred to the headbox or the stock preparation facility, while the clear water from the pulp saver is used in a variety of ways: for example, for defibering in the pulper, to regulate the consistency,

for spray pipes in the wire section, as seal water, or to dissolve auxiliary materials. Depending on the pulp saver that is used, several purified water qualities can be available for reuse. The part that is not reused is sent to the wastewater purification plant.

- The **tertiary cycle** is only available in a limited number of mills, and it describes the partial return of purified wastewater to the production process. In the case of certain grades (e. g. corrugated base papers), the entire volume of purified wastewater can be returned to production. Opportunities to use water from the tertiary cycle depend on its quality. The use of wastewater that has been subjected to full biological purification can often be problematic as a result of the calcium carbonate it contains, since this can lead to deposits in the production process and the clogging of nozzles, etc. [7].

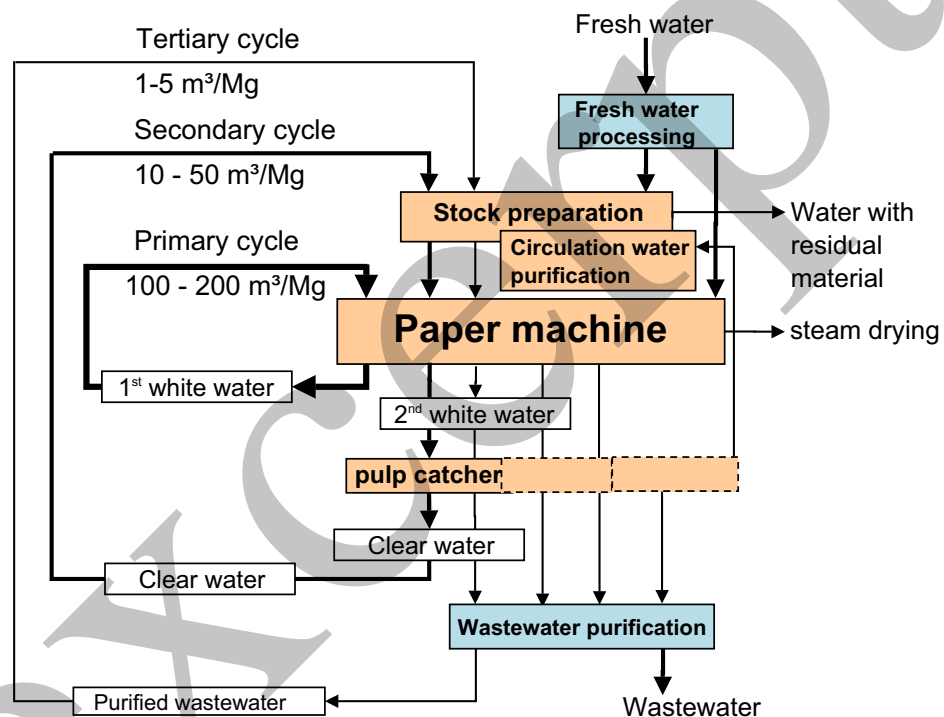


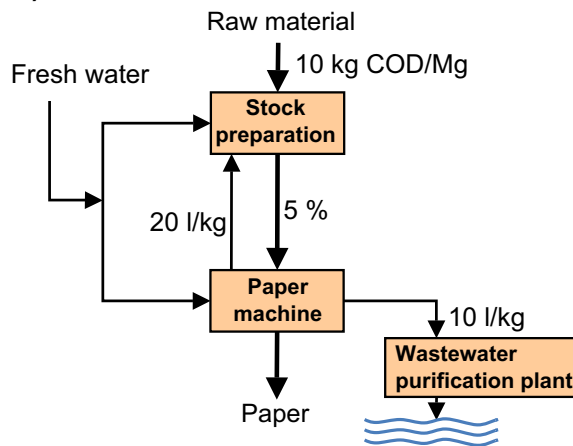
Fig. 3.7: Simplified diagram of water flows in a paper mill (sample figures) [7]

3.3.4.2 Circulation systems and characterisation of water cycles

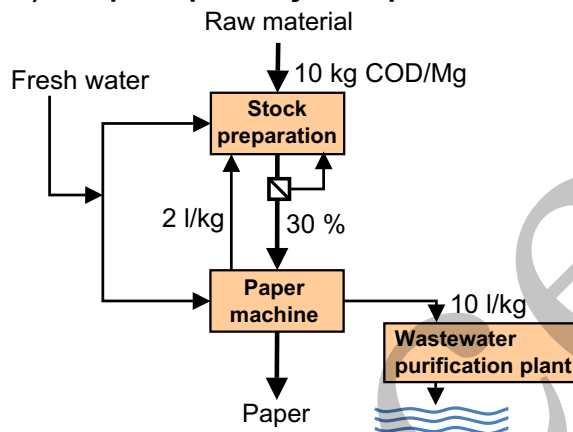
Simple system (A)

Fresh water is potentially used in both stages of the simple system (A) shown in *Figure 3.8*, namely stock preparation and the paper machine. The wastewater is predominantly discharged from the paper machine. Furthermore, water is exchanged in both sub-systems. The volume of water that is returned from the paper machine to the stock preparation facility is determined by the density of the material that is transferred to the paper machine.

A) Fundamental elements of the material / water system



B) The principle of cycle separation



C) The principle of counterflow operation

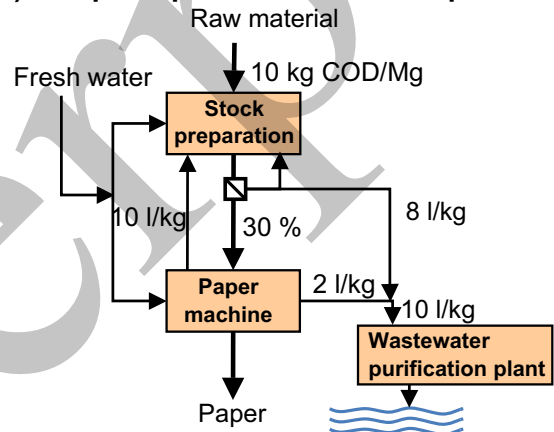


Fig. 3.8: Possible circulation systems [7]

In order to optimise water flows, it is possible to define two important principles: **cycle separation (B)** and **counterflow operation (C)**. The water cycles can to a large extent be kept separate by installing a thickening device (e. g. press). As the mixture becomes thicker and thicker, less water is transferred from the stock preparation facility to the paper machine, which means the extraneous materials contained in the water are retained in the stock preparation facility. However, if wastewater is not discharged from the stock preparation facility (see B), there is no sink for the extraneous materials contained in the wastewater, so no real reduction in the COD of the sub-system (paper machine) occurs.

*Cycle separation (B)
and counterflow
operation (C)*

Counterflow operation extends the principle of closed loop recirculation: a proportion of the highly polluted filtrate that is returned to the stock preparation (SP) facility is discharged into the wastewater treatment plant. In order to offset the discharge from the stock preparation facility, more water is returned from the paper machine to the stock preparation process. This means that water of superior quality is used in the most sensitive part of the paper machine, while wastewater from the most highly polluted sub-system (stock preparation) is discharged. The water and materials flow

in opposite directions, and the COD load in the sub-system (paper machine) is markedly reduced [7].

Figures to measure the efficiency of in-house circulation systems

For an initial analysis with a view to possible optimisation, Hutter [6] suggests simple figures / indices which can be used to describe the efficiency of in-house circulation systems (CS). Two figures ($F_{CS\ 1}$ and $F_{CS\ 2}$) are defined for this purpose, each of which describes the ratio of the COD values at various junctures during production (see *Figure 3.9*):

$$F_{CS\ 1} = \text{COD}_{\text{ww}} / \text{COD}_{\text{white water}}$$

$$F_{CS\ 2} = \text{COD}_{\text{sp}} / \text{COD}_{\text{white water}}$$

The first value ($F_{CS\ 1}$) is the ratio of COD in the wastewater and the white water from the paper machine, and it should be at least 1 or higher; only then can one assume that no fresh water leaves the water cycle without having been used. $F_{CS\ 2}$ describes the ratio of the COD values in the water cycles of the stock preparation facility and paper machine: the COD load in the white water from the paper machine in relation to the COD value in the stock preparation facility should be as small as possible ($F_{CS\ 2} \gg 1$), i. e. the COD is mainly retained in the stock preparation facility and the COD load when forming sheets on the paper machine wire is reduced. A third parameter ($F_{CS\ 1}/F_{CS\ 2} = \text{COD}_{\text{ww}}/\text{COD}_{\text{sp}}$) characterises whether the correct wastewater is discharged from the paper manufacturing plant. If $F_{CS\ 1}/F_{CS\ 2}$ is approximate to 1, this means that the COD value in the wastewater almost matches that of the stock preparation, and a counterflow circuit as shown in *Figure 3.8* (C) is to a large extent achieved.

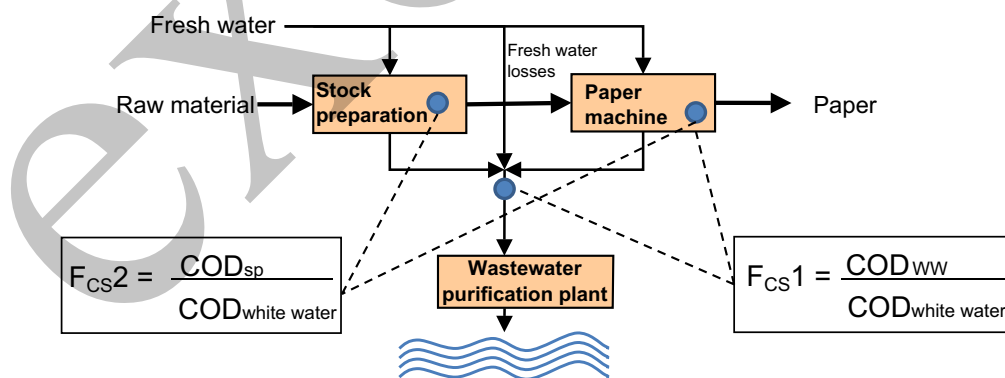


Fig. 3.9: Possible circulation systems [6]

Possible optimisations

The relationships that we have just illustrated apply to simple production facilities with precisely one water cycle for stock preparation and the paper machine. Depending on the range of paper grades produced and the layout of the mill, these relationships can be more complex, and it is possible to make a detailed distinction between a multitude of possible combinations of stock preparation and paper machine. However, this requires a very in-depth analysis of the water cycles as the starting

point for possible optimisations. Zippel [16] provides a detailed description of this, based upon a survey of numerous mills.

3.3.4.3 Optimising the water cycles: in-house measures

In-house measures to optimise water cycles are crucially important in cellulose / pulp production and paper manufacturing. The most important objective is often to further restrict the water cycles with a view to cost savings in relation to direct- or indirect discharge. One further reason for implementing in-house measures is the fact that non-optimised water cycles can adversely affect production and product quality.

It is possible to define the following **objectives when optimising water cycles** [8]:

*Objectives when
optimising water
cycles*

- To reduce wastewater volumes and improve the quality of circulation water, possibly by completely closing the water cycle
- To reduce fluctuations in the volume of water
- To minimise solid losses (valuable raw material is wasted if usable fibres are lost)
- To simultaneously avoid (excessive) salting, limescale deposits, and odours

Research conducted by the *Papiertechnische Stiftung* (PTS) demonstrates that the specific wastewater volume in many production facilities can be further reduced without increasing the level of contamination in white water from the paper machine [8]. For example, this can be achieved by optimising the circulation system as outlined above (separation of water cycles, counterflow operation), so the extraneous materials are systematically discharged at the points where this is possible with the least amounts of water. Some typical limits arise when reducing the specific wastewater volume in the context of optimising water cycles, and they can only be adhered to if a considerable amount of investment is made. Amongst other things, these limits are determined by the following parameters: the quantity of fresh water used as cooling water before it is used in production; the volume of wastewater that accumulates and is discharged with the reject materials; and the maximum concentration of COD and other dissolved extraneous materials (calcium, sulphate, salts) which can be tolerated in the white water for the respective product. The problems presented by salting, odours, and limescale deposits can be exacerbated by water cycles that are to a large extent closed, and this can also lead to operational issues. If the amount of wastewater is to be successfully reduced, one must always take account of the impact on production too.

*Opportunities for
reduction*

In order to further restrict the water cycles beyond these limits or to completely close them, one must then use **circulation water purification processes** which control the extent to which the circulation water is polluted with dissolved extraneous substances (COD, salts, dye, etc.). Depending on the problem, the following processes (individual or combined) can be considered: anaerobic / aerobic biological

*Circulation water
purification*

treatment (COD removal), ultrafiltration, nanofiltration and reverse osmosis, ozonisation, vacuum steam drying, etc.

3.3.5 Volume and composition of residual wastewater, plus discharge conditions

3.3.5.1 Wastewater composition in general

Low levels of contamination in paper mill wastewater

Typical paper mill wastewater – in the form in which it is often encountered – is not very concentrated, not toxic, and readily biodegradable. Higher concentrations of dissolved organic and inorganic substances are inevitably found in the paper industry of Central Europe as a result of the extensive return of production water. This particularly applies to the production programmes and product groups that are suitable for this purpose, namely wood-containing papers and papers made from waste paper. Paper mill wastewater is essentially not very polluted, and this can be explained by the fact that paper manufacture uses raw materials that are insoluble in water, and only a small amount of water-soluble auxiliaries [11].

Organic pollution

The bulk of **organic pollution** stems from the mechanical wood pulp and waste paper pulp production that is integrated into the mills. The organic pollution mainly consists of carbohydrates that are readily biodegradable and lignins that are less readily biodegradable. The average BOD/COD ratio in the case of mechanically pre-purified paper mill wastewater is 0.5. Wastewater from cellulose production manifests a similar composition, although in this case one should expect a higher percentage of persistent lignin compounds (lower BOD/COD ratio) and – with regard to biological purification – a certain toxicity which is caused by the resin acids and other wood and/or bark components.

Sulphate concentrations

The **sulphate concentrations** are typical of various product ranges. Aluminium sulphate is still a widespread auxiliary when manufacturing paper. It is occasionally deployed in subsidiary areas, where it is nevertheless sometimes used in large quantities. One should generally expect sulphate concentrations of up to 600 mg/l in paper mill wastewater, albeit much lower values (< 300 mg/l) in the case of wood-free ranges. When producing paper from waste paper, one can observe sulphate concentrations close to the upper limit of the above-mentioned range (600 mg/l). However, they can also reach > 1,000 mg/l, and are introduced via the waste paper (5–8 kg sulphate per MG of waste paper).

Calcium concentrations

Calcium carbonate is the source of rising **calcium concentrations** in circulation water and wastewater, since it has increasingly been used in recent years as an inexpensive bulking agent or coating pigment. This also increases the percentage of calcium in the waste paper, so this secondary raw material duly introduces additional calcium. Excessive calcium concentrations can lead to operational problems caused by deposits and blockages.

Only small quantities of **nitrogen and phosphorus** are generally present in the wastewater from paper mills, and they must usually be added for biological purification in order to arrive at the stoichiometrically required BOD/N/P ratio.

Surfactants (defoamers, stock deaerators, other tensides) in the wastewater are likelier to occur in higher concentrations with some product ranges, and can adversely affect the operation of wastewater purification plants.

Surfactants

3.3.5.2 Wastewater accumulation: evolution of specific wastewater volume

The in-house measures outlined above have significantly reduced the specific wastewater volume in recent decades. *Figure 3.10* shows the evolution of specific wastewater volumes for all grades of paper from 1974 to 2002. It has only been possible to achieve a modest additional reduction in recent years; any further significant decline in specific water consumption will in future only be achieved via increased expenditure and more sophisticated technology.

Significant reduction in wastewater volume in recent decades

There are of course considerable differences between individual product grades. In particular, wood-free and speciality papers still require high specific water volumes, whereas grades of paper and packaging made from waste paper can achieve very low wastewater volumes (see *Table 3.9*).

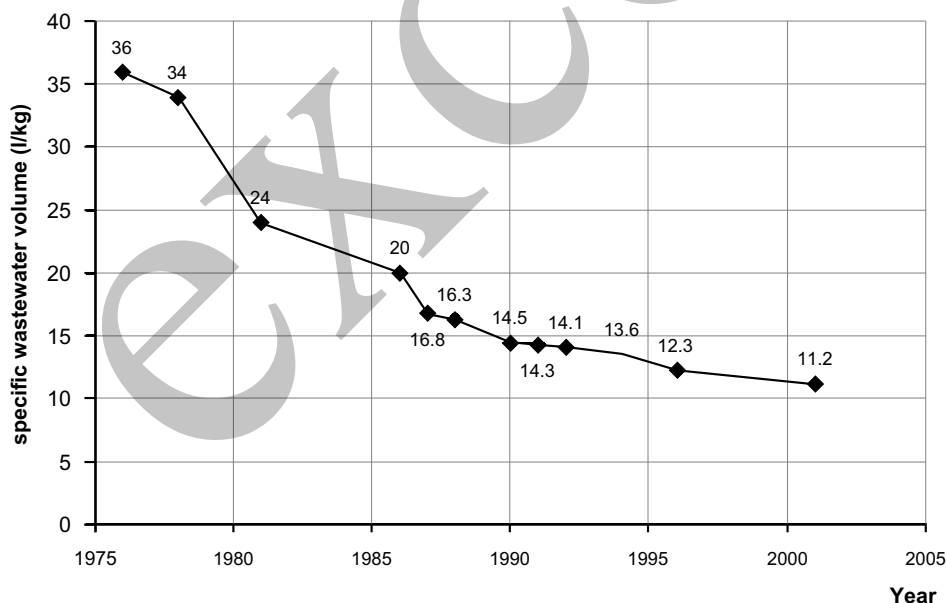


Fig. 3.10: Evolution of specific wastewater volume in the paper industry in Germany [8]

3.3.5.3 Grade-specific wastewater composition

Concentrations and specific wastewater volumes acc. to grades of paper

Table 3.9 shows the mean concentrations and specific water volumes for the essential product groups and certain grades of paper. The data is based upon mechanically pre-purified wastewater.

Increasing specific COD loads for grades that contain waste paper

The specific concentrations, water volumes and loads depend not only on the product being manufactured but also on the pulps used, the way in which the water is circulated, and the paper auxiliaries added, which means that major differences can be encountered within the individual product groups [11]. The specific COD loads for grades that contain waste paper have steadily increased over recent years. Amongst other things, deteriorating waste paper quality and higher product requirements in relation to improved stability / rigidity have necessitated the addition of COD-promoting auxiliaries such as starch.

Table 3.9: Typical ranges for concentrations and specific wastewater volumes according to grades of paper [11]

	Grade of paper	Concentrations				Spec. wastewater volume	
		BOD ₅ (mg/l)		COD (mg/l)		Q (l/kg)	
		from	to	from	to	from	to
Wood-free papers	1.1 Tissue	50	100	95	270	9	25
	1.2 Alpha-cellulose	20	40	50	100	20	70
	2.1 Wood-free printing	65	220	150	400	5	20
	2.2 Wood-free speciality	40	550	90	1,100	15	60
	3.1 Heavily milled	10	30	20	60	100	250
	3.2 Speciality papers	10	40	45	110	50	100
	5. Wood-free coated	170	260	360	540	20	30
Wood-containing papers	6.1 Supercalendered	125	480	450	1,020	13	20
	6.2 Light-weight coated	150	460	430	1.300	12	30
	6.3 Wood-containing printing	220	500	500	1.160	8	30
	6.4 Card < 50 % waste paper	140	200	320	490	15	25
Papers containing waste paper	7.1 Newsprint	460	1270	960	2,400	7	20
	7.2 Corrugated base paper	1,280	2,840	2,190	5,680	0	10
	7.3 Card (waste paper)	530	3,000	1,140	5,500	0	15
	7.4 Recycling paper	250	400	540	790	10	20

3.3.5.4 Discharge conditions

Appendix 19 of the Wastewater Ordinance (*AbwV*) specifies the minimum requirements for the cellulose industry for the discharge of wastewater into surface waters; the requirements for the paper industry are laid out in Appendix 28. *Table 3.10* reproduces the minimum requirements for paper manufacturing.

The requirement for substances removable by filtration no longer applies if the wastewater is biologically purified. An exception can be made for certain areas of production, whereby a production-specific COD load of up to 5 kg/Mg is permitted. Prior to blending with other wastewater at the point of discharge, the wastewater must meet a level of 10 g/Mg (in the random sample) for adsorbable organically bound halogens (AOX), although this is another case where there are exceptions for special grades of paper. The production-specific load values are based upon the mill's underlying gross machine capacity.

Table 3.10: Minimum requirements for the discharge of wastewater from the manufacture of paper and cardboard, Appendix 28 [1]

	Qualified random sample or 2-hour composite sample	
	[mg/l]	[kg/MG]
Substances removable by filtration	50	-
BOD ₅	25	-
Total nitrogen as the sum of ammonia, nitrite and nitrate nitrogen (N _{total})	10	-
P _{total}	2	-
COD	-	3

3.3.6 Wastewater treatment processes

The biological purification of wastewater is 'state of the art' for cellulose and paper manufacturing. The only area where no further treatment is required is wastewater from the production of wood-free uncoated papers, where high specific water consumption is unavoidable; furthermore, the wastewater has low levels of initial pollution, and after chemical / mechanical treatment manifests BOD₅ concentrations of less than 25 mg/l and does not exceed the stipulated specific load for BOD₅ and COD. *Table 3.11* makes it clear that the majority of biologically purified wastewater in the German paper industry is directly discharged into receiving waters.

The majority of biologically purified wastewater in the German paper industry is directly discharged into the receiving water

Table 3.11: Wastewater from the German paper industry based upon production volume in 2001 [3]

Type of purification and discharge	Percentage
Direct discharger with biological purification	74 %
Closed cycle	4 %
Indirect discharger	18 %
Direct discharger with chemical purification	3 %

Possible treatment stages

Wastewater purification facilities in the paper industry are frequently configured as follows, although they may not include every treatment stage:

- Separation of solids, e. g. via sedimentation
- Neutralisation (if required)
- Cooling of wastewater (wastewater temperatures often lie above the maximum discharge temperature, and the temperature must also be lowered to the optimal temperature range in order to carry out the subsequent biological stages)
- Biological stage (single-stage or two-stage concept, either anaerobic / aerobic or aerobic / aerobic)
- A tertiary purification stage (if required in order to satisfy the monitoring values). For example: biofiltration, ozone stage, or chemically supported flotation.

3.3.6.1 Mechanical pre-purification / separation of solids

Principally to separate off solids

Mechanical purification processes are principally used to separate off solids. They can form part of in-house measures to recover recyclable solids (paper fibres), and are also deployed to purify the wastewater that accumulates. In-house measures mainly use filtration, flotation, and to some extent sedimentation; wastewater purification almost exclusively uses sedimentation. Disc filters are mainly used for filtration, but curved screens and drum filters are also deployed. Once it has been filtered, the clarified water manifests a suspended solid content of 10 to 100 mg/l. Flotation is also used instead of filtration for in-house treatment within the cycle. Unlike filtration processes, chemicals are often added to flotation facilities in order to achieve the desired level of solid separation.

Residual wastewater is often heavily polluted with bulking agents and fibres

It is often the case that the residual wastewater from paper production is particularly heavily polluted with bulking agents and fibres which can no longer be recycled because the fibres are too short. In order to avoid a biological facility becoming excessively polluted with solids which for the most part cannot be degraded, the solids must be separated off in advance. Rectangular or circular sedimentation tanks with bottom scrapers are predominantly used to mechanically separate solids in the residual wastewater. To avoid interfering with the sedimentation process, one should strive to achieve a hydraulic load that is as even as possible. A buffer tank should therefore be provided if there are major fluctuations in the wastewater volume.

Sample calculation 3.1 (dissolved air flotation for paper manufacture):

In this example, the intention is to calculate the necessary surface area for dissolved air flotation, with the following parameters:

- Inflow: 2.5 l/s
- Solids loading ($\text{Load}_{\text{Area}} - L_A$): 3 kg/(m²·h)
- Maximum solid content in flotation tank (Dry Matter_{flotation tank} – DM_{ft}): 3 g/l
- Design-related experiments identified that the optimal ratio of Q_{in} to Q_{return} is 5.

Steps toward a solution:

- $DM_{\text{in}} \cdot Q_{\text{in}} \cong DM_{\text{ft}} \cdot (Q_{\text{in}} + Q_{\text{return}})$
- $A_{\text{req}} = DM_{\text{ft}} \cdot (Q_{\text{in}} + Q_{\text{return}}) / L_A$
- $A_{\text{req}} = 3 \text{ kg/m}^3 \cdot (2.5 \cdot 3.6 \text{ m}^3/\text{h} + 1/5 \cdot 2.5 \cdot 3.6 \text{ m}^3/\text{h}) / 3 \text{ kg}/(\text{m}^2 \cdot \text{h}) = 10.8 \text{ m}^2$

3.3.6.2 Biological processes

The use of **two-stage biological wastewater purification processes** can be described as 'state of the art' for the paper and cellulose industry in Central Europe. The final – or only – biological stage is almost invariably an aeration plant. There has been an increasing tendency over recent years to subject partial flows or the total wastewater to various pre-treatment processes prior to joint final purification using the aeration process [11]:

Two-stage biological processes

- Physical / chemical treatment (chemical precipitation)
- Anaerobic biological treatment *or*
- Aerobic biological treatment with film reactors (e. g. moving bed biofilm reactors, trickling filters, etc.)

The combination of processes that is preferred in individual cases depends on the grade-specific composition of the wastewater to be treated. **Table 3.12** provides an overview of the possible combinations, depending on the mills' production schedule. The processes indicated are those that frequently occur, although other processes and combinations of processes which are not explicitly listed can also be deployed.

Combinations of processes

Table 3.12: Selected processes, depending on the origin of the wastewater [5]

Production schedule	Preferred biological process(es)
Sulphate cellulose	Oxygenated cascade aeration Moving bed biofilm reactor + aeration
Sulphite cellulose	Anaerobic reactor + aeration
Wood-free papers BOD < 70 mg/l BOD > 70 mg/l	Biofilter 2-stage biofilter, cascade aeration
Coated papers	Cascade aeration, moving bed biofilm reactor + aeration
Wood-containing papers	Moving bed biofilm reactor + aeration
Papers containing waste paper	Moving bed biofilm reactor + aeration with anaerobic reactor + aeration

Aerobic processes

Activated sludge plants

Activated sludge plants to purify wastewater from the paper industry should be constructed in such a way that a gradient in the sludge loading occurs (plug-flow, cascade plants), thereby avoiding the formation of bulking sludge. The composition of the wastewater means that it is virtually impossible in single-stage, completely mixed systems to control the formation of bulking sludge. In addition to the classic procedures that use activated sludge tanks and final sedimentation, sequencing batch reactors (SBR) and membrane aeration have also been used in recent years, or are being tested.

Moving bed biofilm reactors

Moving bed biofilm reactors (MBBRs) are often used as the first stage in two-stage facilities. They contain plastic support media which act as substrate for the biomass, and which are retained with meshes at the outflows from the reactor. Their specific density of 0.9 to 1.3 g/cm³ means they are kept afloat by the aeration of the reactors. Two-stage facilities with an MBBR as the first stage are operated without intermediate settling.

Anaerobic processes

Advantages

Anaerobic wastewater purification, which has already become popular to treat the vapour condensates from cellulose production, has also recently met with increasing interest in the paper industry. The essential reasons for this are the low energy demand, the option of using biogas, and the minor accumulation of excess sludge. Thanks to the state of development that the various anaerobic processes have reached, anaerobic purification of paper mill wastewater with a COD concentration of 2,000 mg/l can be considered a viable option. Installations are already operating with lower concentrations in the wastewater.

The upflow anaerobic sludge blanket (UASB) process and the resulting types of tall reactor have become popular for the treatment of paper mill wastewater. A sizing parameter of between 6 and 10 kg COD / (m³·d) is usually chosen for the UASB process. The more sophisticated pellet reactors (e. g. internal circulation (IC) reactors or biobed reactors) are operated with volumetric loadings of between 17 and 25 kg/(m³·d). The main emphasis when applying the anaerobic process is corrugated base paper production, since this is where high sulphate concentrations are generally lacking and plant tends to run with low specific water volumes with increased COD concentrations.

*The UASB process
and types of tall
reactor*

Sample calculation 3.2 (IC reactor):

In this example, the intention is to calculate the diameter of a circular IC reactor for the purification of wastewater that accumulates during paper manufacturing.

- $C_{\text{COD, in}} = 2,400 \text{ mg/l}$
- $Q_{\text{in}} = 4,000 \text{ m}^3/\text{d}$
- Possible design parameters for IC reactors: level of water = 20–24 m; volumetric loadings = 22–26 kg COD/(m³·d)

Steps toward a solution:

- \Rightarrow Parameters chosen for reactor: $L_{\text{reactor}} = 24 \text{ kg COD}/(\text{m}^3 \cdot \text{d})$ and $h_{\text{lw}} = 22 \text{ m}$
- COD load: $L_{\text{design, COD}} = C_{\text{COD, in}} \cdot Q_{\text{in}} = 2,400 \text{ g/m}^3 \cdot 4,000 \text{ m}^3/\text{d} = 9,600 \text{ kg/d}$
- Calculate reactor volume required:

$$L_{\text{reactor}} = L_{\text{design, COD}} / V_{\text{IC, total}}$$

$$\Rightarrow V_{\text{IC, total}} = L_{\text{design, COD}} / L_{\text{reactor}} = 9,600 \text{ kg/d} / 24 \text{ kg}/(\text{m}^3 \cdot \text{d}) = 400.0 \text{ m}^3$$
- Calculate area required: $h_{\text{lw}} = 22 \text{ m}$

$$\Rightarrow A_{\text{IC, total}} = V_{\text{IC, total}} / h_{\text{lw}} = 400.0 \text{ m}^3 / 22 \text{ m} = 18.2 \text{ m}^2$$
- \Rightarrow Selected: 2 reactors where $A_{\text{IC}} \geq A_{\text{IC, total}} / 2 = 9.1 \text{ m}^2$
- Calculate diameter: $A_{\text{IC}} = \pi/4 \cdot D^2$

$$\Rightarrow D = (4 \cdot A_{\text{IC}} / \pi)^{1/2} = (4 \cdot 9.1 \text{ m}^2 / \pi)^{1/2} = 3.4 \text{ m}$$

$$\Rightarrow \text{selected: } D = 3.5 \text{ m} \Rightarrow A_{\text{IC, total}} = 19.2 \text{ m}^2 \text{ and } V_{\text{IC, total}} = 423 \text{ m}^3$$

3.3.6.3 Example of two-stage aerobic / aerobic wastewater treatment

We will begin by presenting the treatment of wastewater from a paper mill where two paper machines produce approx. 400,000 Mg per annum of wood-containing, coated rotogravure papers. The aeration facility was initially conceived in 1982 as a one-stage operation (with a second line added in 1988), and was supplemented with an upstream MBBR in 2004. This was brought about by changes to the product mix as well as the installation of a new peroxide groundwood bleaching unit which led to higher specific COD loads in the wastewater. Furthermore, there were occasional operating problems in the old facility caused by high sludge indices, as is often the case with single-stage facilities in the area of paper wastewater purification.

Sizing parameters

The sizing parameters for the expanded facility are indicated in *Table 3.13*.

Table 3.13: Sizing parameters for an aerobic / aerobic wastewater treatment facility

Parameter	Unit	Value
Inflow	m ³ /d	14,400
COD	mg/l	1,300
COD	kg/d	17,000
Solids	mg/l	2,900
Temperature	°C	47

Treatment stages

The wastewater treatment facility with two lines initially comprises neutralisation, two circular primary settlement tanks, and a cooling plant (six heat exchangers and two cooling towers in the relevant cooling water circuit) where the wastewater is cooled to 35 °C. The newly built high-performance MBBRs that are placed upstream of the existing activated sludge tanks (see *Figure 3.11*) each have a volume of 1,137 m³ and are designed for a volumetric loading of 7.5 kg COD/(m³·d). The reactors are filled (to a level of 30 %) with support media to promote the growth of biomass, and they manifest a specific surface area of 380 m²/m³. In order to control the growth of biofilm on the support media, airlift pumps and a spray system to combat foam are installed in the reactors. Aeration and mixing through are assured by perforated pipes. The subsequent activated sludge tanks each have a volume of 2,000 m³ and are equipped with medium-sized bubble compressed air aeration. In the case of average DM contents of 5–7 g/l, the BOD₅ sludge loading in the activated sludge tanks amounts to approx. 0.3 kg BOD₅/(kg DM·d). The two final sedimentation tanks are equipped with suction scrapers, and the excess sludge is dewatered in a belt filter press.

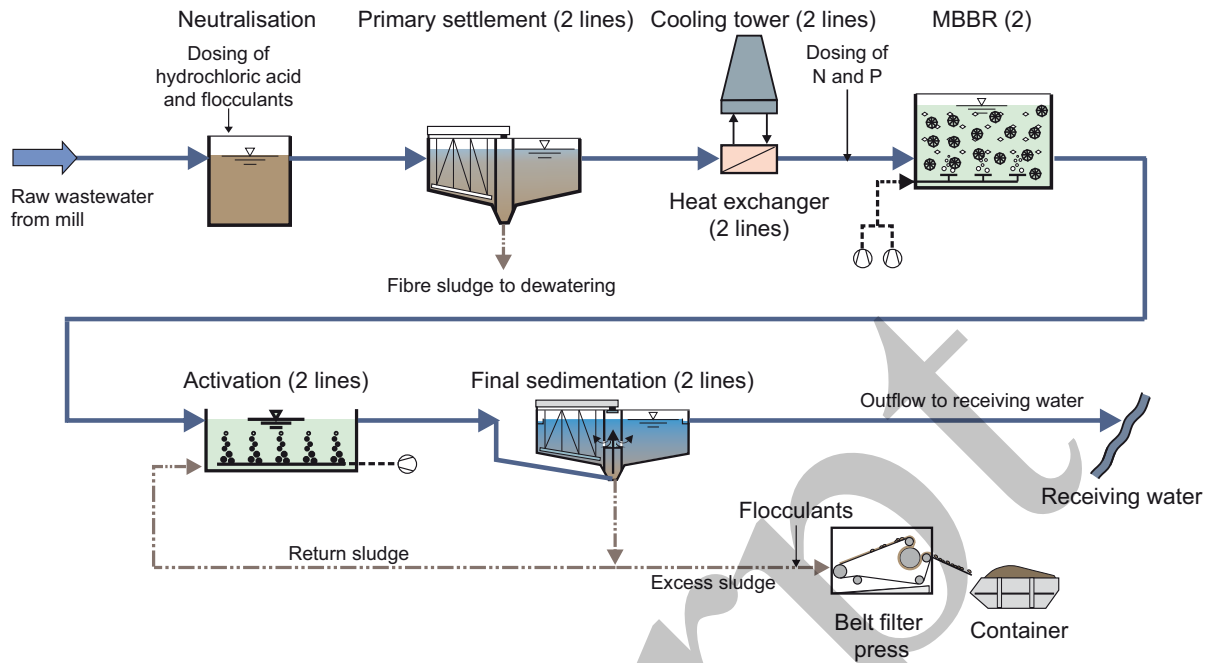


Fig. 3.11: Diagram showing the example of a two-stage aerobic / aerobic wastewater treatment plant (Image: Veolia Wasser GmbH)

Ever since the expanded facility was put into service, it has been possible to demonstrate the long-term operational stability of the chosen plant technology. 40-50 % of the COD load from the inflow is degraded in the new MBBRs. As a result of this, the sludge index in the second aeration stage has improved so that it is consistently below 100 ml/g (indices of up to 700 ml/g were measured before the MBBRs were put into service). Flaking of solids from the final sedimentation tank have no longer been recorded since the plant was rebuilt. With a mean inflow load of 14.2 Mg COD/d (mean inflow concentration = 1,055 mg/l COD), a mean of 166 mg/l COD was measured in the outflow of the final sedimentation tank. The overall level of efficiency for COD degradation comes to approx. 85 %. A COD concentration of 310 mg/l must be adhered to in the outflow. The declared value is fixed at 240 mg/l, and is safely adhered to for the above-mentioned inflow loads.

Operational outcomes

Within the context of managing operations at this facility, one should pay particular attention to effectively controlling the growth on the packing media at the high-load stage. Nutrient dosing should also be continuously monitored and carefully anticipated, and the facility should be run so that it can cope appropriately with peak loads and hold-ups in production.

3.3.6.4 Example of two-stage anaerobic / aerobic wastewater treatment

Sizing parameters

The following example presents the wastewater purification facility for a paper mill that manufactures corrugated base paper and testliners from waste paper; its annual capacity is 400,000 Mg. *Table 3.14* shows the sizing parameters for this facility.

Table 3.14: Sizing parameters for an anaerobic / aerobic wastewater treatment plant

Parameter	Unit	Value
Inflow	m ³ /d	7,416
COD	mg/l	5,394
COD	kg/d	40,000
Solids	mg/l	200
Temperature	°C	35

Treatment stages

Solids are removed as part of the production process, and the wastewater is subsequently fed into the wastewater treatment facility with almost no solids remaining in it. After cooling to approx. 32 °C in an air cooler, the wastewater is initially fed into a combined buffer- and hydrolysis tank (retention time for buffer and hydrolysis: 2 h respectively). As a result of the hydrolysis, three anaerobic reactors are charged. These anaerobic (IC) reactors have a total volume of 1,650 m³, a diameter of 5 m, and a height of 28 m. The reactors are designed for a volumetric loading of 24.2 kg/(m³·d) for 75 % COD degradation. An additional, identically constructed tank serves as a storage tank for the sludge pellets from the reactors, although it can if required be adapted to form a fourth anaerobic reactor. The sulphur is removed from the biogas in a biological desulphurisation facility and the gas is converted into electricity in two CHPs, which greatly improves the overall economic viability of wastewater purification.

In order to make operation of the facility more flexible, the anaerobic stage can to some extent be circumvented, and clarified wastewater from the outflow of the final sedimentation tank can be recirculated into the anaerobic reactors. Anaerobic pre-purification is followed by aerobic purification in two activated sludge tanks with a total volume of 5,000 m³ as well as two final sedimentation tanks with suction scrapers. The activated sludge tanks are equipped with injector aerators, and some of the outflow from the final sedimentation tank can be recirculated into paper production.

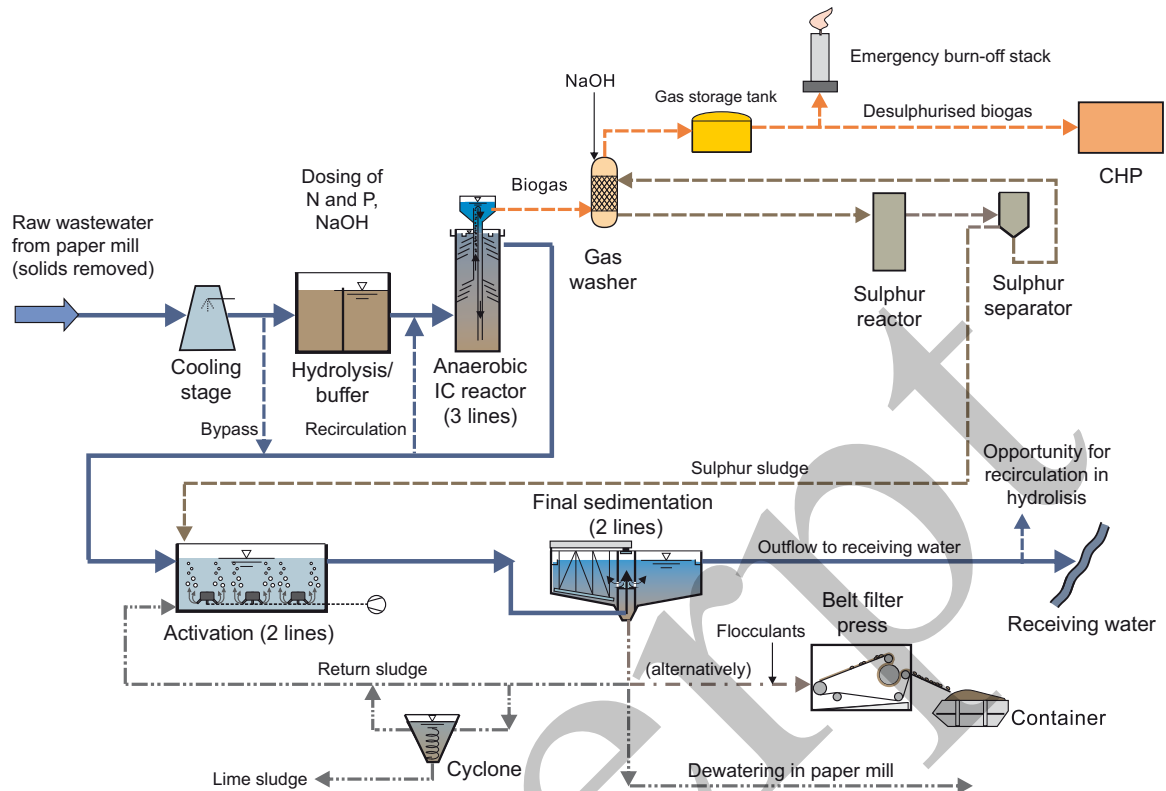


Fig. 3.12: Diagram showing the example of a two-stage anaerobic / aerobic wastewater treatment plant (Image: Veolia Wasser GmbH)

The facility has been in service since March 2005. Approx. 80 % of the COD inflow load is degraded during the anaerobic stage. COD concentrations < 180 mg/l are generally achieved in the outflow from the final sedimentation tanks. The COD level of efficiency for the entire facility is thus approx. 97 %. The operating parameters for the anaerobic stage should be set so that lime precipitation is broadly avoided and one achieves an even pellet bed in the reactors with a high organic dry matter content.

After the wastewater purification plant had become operational, it was initially possible to observe noticeable lime precipitation which adversely affected biological degradation and throughflow in the reactors. This problem was solved by optimising the water cycles in the production of paper. One special feature of this wastewater purification facility is the use of a cyclone to separate lime from the return sludge. This device discharges calcariferous sludge from the system so that the inorganic part in the activated sludge can be kept to a minimum value.

Operational outcomes

The option of using biogas for energy means that, viewed overall, a facility comprising a preliminary anaerobic stage and a second aerobic stage can constitute a meaningful and economically viable way of purifying wastewater. This mainly applies to more concentrated wastewater, as is present in this example of a mill that processes waste paper.

EXCERPT

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