

**Water Use and
Wastewater Treatment
in Papermills**

Christian H. Möbius

First Edition 2006

The history of life on earth has been a history of interaction between living things and their surroundings.

Rachel Carson, *Silent Spring* (1962), Boston / New York 1994

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Preface

Water is a valuable and ever more estimated natural resource. For pulp and paper industry, it is one of the essential means of production and has been needed in tremendous amounts relatively to the amount of products in former times. In densely populated highly industrialized regions like Central Europe, the industry soon learned to decrease the specific amount of water needed for production since the amount of products was increased. One of the purposes of this book is to summarize the experiences of the industry and the methods developed in the course of this process.

Most of the water needed for production ends as wastewater (only few of it is evaporated drying the product). Wastewater treatment in the pulp and paper industry requires some special care besides the since the days of W. P. DUNBAR¹ well-known standard rules (much improved and extended since those days). These special requirements and techniques of wastewater treatment for the pulp and paper industry are not so well documented as for municipal effluents. Therefore, this book may give some help for all those who have to deal every day with the special problems in this field as well as for those who only need some basic information.

The author worked in the field of environmental protection and especially water and wastewater in pulp and paper industry since the 1970s in applied research and development as well as consultancy. He tried to summarize the results and experiences in the field in his German language book “Abwasser der Papier- und

¹ William Philipp Dunbar, 1863 - 1922, born in the USA, studied medicine and worked in Germany. He published his book “Leitfaden für die Abwasserreinigungsfrage” in 1907 (English version London 1908).

Zellstoffindustrie”, regularly updated since 1994². Now this book tries to give the facts that are internationally relevant in English language, focussing, however, on the field of paper industry only, since the special requirements of pulp industry are reported far better in Northern Europe and North America. However, most of the informations on wastewater treatment are relevant for pulp industry as well.

Literature references were selected without any desire for completeness as a way to find further information on items only mentioned shortly. They are set between square clips and in capital letters.

Symbols, definitions, abbreviations and calculation formulae follow whenever possible the IWA³ system, see [HENZE et al. 1995] and [IWA 2000].

Regarding the spelling of words, it is tried to keep as near as possible to the British way (for instance fibre instead of fiber, as it is spelled in the American way).

Internet references often are subject to changes, but all references have been checked prior to publication.

Augsburg, October 2006

² see www.cm-consult.de

³ International Water Association, www.iwahq.org.uk

Abbreviations and Dimensions

Sign	explanation	usual dimension
A	area (index giving the allocation, like A_{sc} for the area of the secondary clarifier)	m^2
AOX	adsorbable organic halogen compounds	$\mu g/l$
B_A	specific surface solids loading	$kg/(m^2h)$
B_d	load per day (second index giving the parameter, e.g. for BOD $B_{d,BOD}$)	kg/d
B_V	specific volume loading (of a bioreactor, e.g. for BOD $B_{V,BOD}$)	$kg/(m^3d)$
B_X	specific sludge loading in bioreactor related to biomass, also called F/M, for BOD $B_{X,BOD}$)	$kg/(kgd)$
BAT	best available technique	
BOD	biochemical oxygen demand (in 5 days: BOD_5)	mg/l
c	concentration (index giving the parameter)	mg/l
COD	chemical oxygen demand	mg/l
Delta, Δ	difference of two values	
E_B	specific energy for biodegradation	kWh/kg
E_V	specific energy for aeration	$kWh/(m^3d)$
ES	excess sludge	
ES_B	excess sludge per BOD elimination	kg/kg
ES_V	excess sludge per aeration volume	$kg/(m^3d)$
eta, η	elimination efficiency	%
HRT	hydraulic retention time in a reactor	h

LOI	loss on ignition	
MLSS	mixed liquor suspended solids (biomass in activated sludge plant)	
mv	mean value (arithmetical, statistics), average	
Q_h	flow per hour	m^3/h
Q_d	flow per day	m^3/d
q_A	specific surface volume loading	$m^3/(m^2h)$ or m/h
q_l	weir overflow rate	$m^3/(mh)$
q_{sv}	specific surface sludge volume loading	$l/(m^2h)$
quot	quotient BOD/COD (with index for in, out or elimination)	
quot _{el}	elimination quotient (Δ BOD / Δ COD)	
R_v	volumetric recycle ratio, e.g. for return sludge	%
s	standard deviation of a grab sample for n-1	
SS	suspended solids	mg/l
S_v	sludge volume (settled volume in 30 minutes, diluted)	ml/l
SVI	sludge volume index	ml/g
T	temperature	°C
TKN	Total KJELDAHL Nitrogen as sum of ammonia nitrogen and organic bound nitrogen	
V	volume of a reactor	m^3
wwtp	wastewater treatment plant	
X_{ss}	concentration of biomass in reactor (in activated sludge plant MLSS)	
Θ_x	sludge age (activated sludge)	d

Calculation Formulae

Specific Load

specific volume loading B_V [kg/(m³d)]

$$B_V = \frac{B_d}{V_a}$$

example: specific BOD volume loading in aeration $B_{V,BOD}$

B_d = load of parameter per day

V_a = Volume of aeration tank

specific sludge loading B_X [kg/(kg*d)]

$$B_X = \frac{B_d}{X_{SS} * V_a} = \frac{B_V}{X_{SS}}$$

example: specific BOD sludge loading in aeration $B_{X,BOD}$

X_{SS} = concentration of biomass in reactor

specific surface solids loading B_A [kg/(m²*h)]

$$B_A = \frac{Q_h * X_{SS}}{A} = q_A * X_{SS}$$

specific surface volume loading q_A [m³/m²h]

$$q_A = \frac{Q_h}{A}$$

specific surface sludge volume loading q_{SV} [l/(m²*h)]

$$q_{SV} = S_V * q_A$$

S_V = sludge volume (settled volume in 30 minutes, diluted)

weir overflow rate q_l [m³/(m*h)]

$$q_l = \frac{Q_h}{l_w}$$

l_w = length of weir

Elimination

elimination quotient $quot_{el}$ (dimensionless)

$$quot_{el} = \frac{BOD_{in} - BOD_{out}}{COD_{in} - COD_{out}} = \frac{\Delta BOD}{\Delta COD}$$

elimination efficiency η [%]

$$\eta = 100 * \left(\frac{c_1 - c_2}{c_1} \right) = 100 - \left(\frac{100 * c_2}{c_1} \right)$$

Energy

specific energy for aeration E_V [kWh/(m³*d)]

$$E_V = \frac{E_d}{V_a}$$

E_d = aeration energy per day

specific energy for biodegradation E_B [kWh/kg]

$$E_B = \frac{N_V}{B_V * 0,01\eta} = \frac{E_d}{B_{d,BOD} * 0,01\eta}$$

Sludge

sludge age Θ_x [d] (calculation from measured values in activated sludge plant)

$$\Theta_x = \frac{X_{SS} * V_a}{Q_{d,ES} + Q_d * (c_{SS2} - c_{SS1})}$$

ES = excess sludge

c_{SS} = concentration of suspended solids (in and out)

sludge age Θ_x [d] (theoretical calculation for activated sludge plant)

$$\Theta_x = \frac{X_{SS} * V_a}{B_{d,BOD} * E_{SB}}$$

sludge volume index SVI [ml/g]

$$SVI = \frac{S_V}{X_{SS}}$$

specific excess sludge per aeration volume ES_V [kg/(m³*d)]

$$ES_V = \frac{Q_{d, ES} * X_{SS}}{V_a}$$

specific excess sludge per BOD elimination ES_B [kg/kg]

$$ES_B = \frac{Q_{d, ES} * X_{SS}}{B_{d, BOD} * 0,01\eta} = \frac{ES_V}{B_V * 0,01\eta}$$

volumetric recycle ratio R_V [%]

$$R_V = \frac{Q_{total} - Q_{effluent}}{Q_{effluent}} * 100 = \frac{Q_{recycle}}{Q_{effluent}} * 100$$

example: return sludge flow ratio

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1. Introduction

Paper industry today is an environmentally friendly industry with rather low emissions usually having no relevant toxicity. The raw materials used – fibres and fillers – are insoluble in water. The water used for the production of paper, carton and cardboard (summarized under "paper" here) always extracts soluble substances contained in the fibres, though. Chemical additives (mostly soluble in water) are used only in small quantities.

The European pulp and paper industry has invested substantially in environmental improvements. The result has been the decoupling of environmental impacts from production growth. While production and some physical parameters (primary energy consumption, electricity consumption, water consumption) have increased since 1990 (production by 150%, for example) the environmental impact measured in emissions (CO_2 , BOD, COD, AOX, SO_2 and NO_x) has decreased. **Figure 1** gives the absolute emission levels relatively to the values of 1990 (data collected by the national associations and aggregated by CEPI; at national level, some figures have been estimated) [CEPI (2005)].

Trying to establish an ecological balance sheet [GORE (2000), CRAWFORD-BROWN (2001)), KREBS (2001), DOUGLAS AND POLSON (2004)] you have to take into consideration all the input and output aspects as given in **fig. 2**. The results differ very much depending on the type of integrated fibre production (chemical pulp, mechanical pulp, secondary fibres) and the type of paper production, as partly will be shown in this book (only for the water part of the balance).

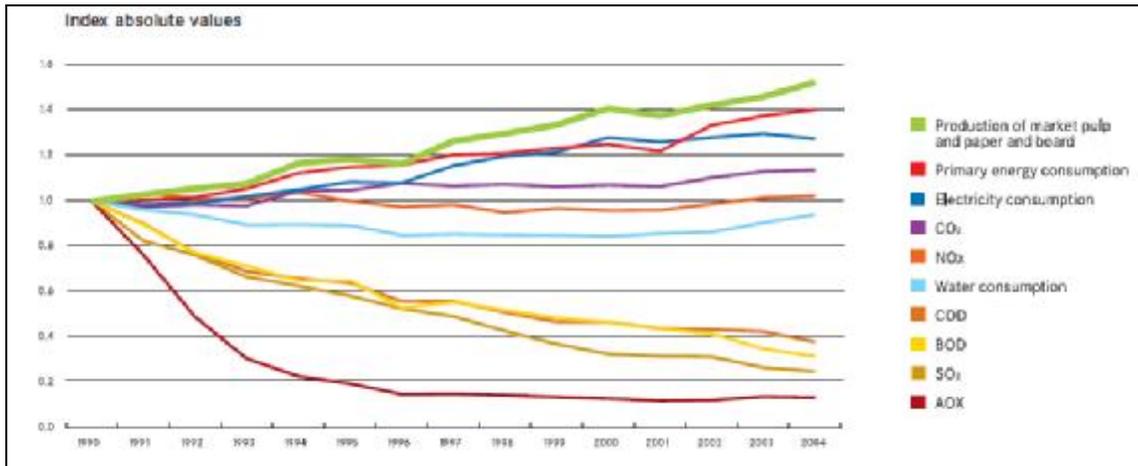


Figure 1: Production and emission levels of European pulp and paper industry since 1990 [CEPI 2005]

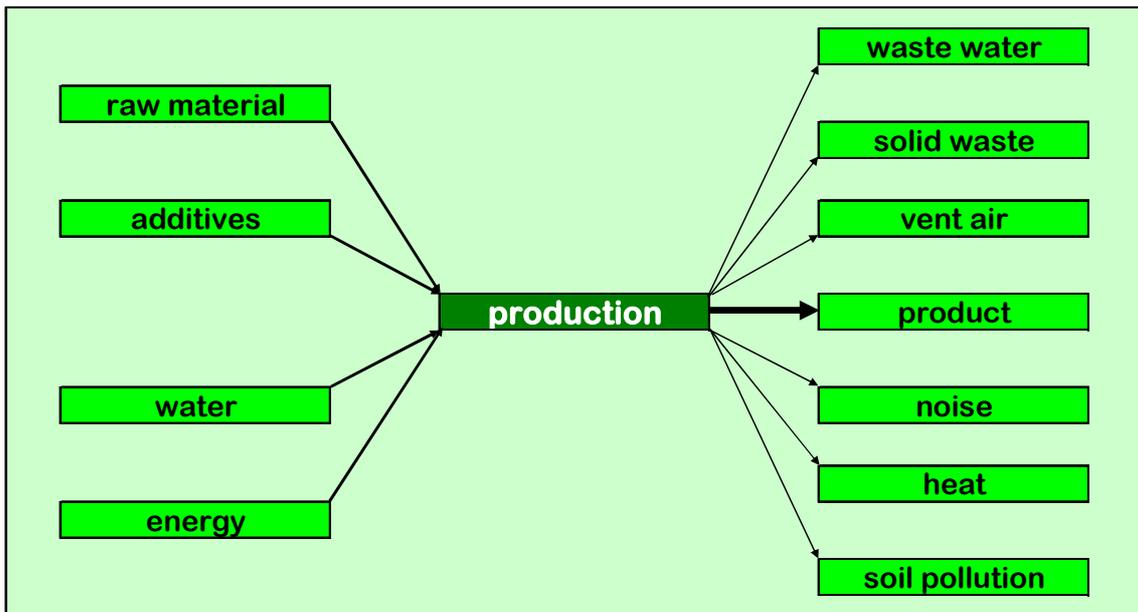


Figure 2: input output scheme for paper production

The comparative assessment of the environmental influences of products in the type of a cradle to grave consideration is difficult. Among other things energy consumption, transport and material or energetic usability of the solid wastes (so called residual substances) also have to be taken into account for all products of the

production chain. The point in which the consideration is broken off is usually arbitrary and depending mainly on the available time and the available (financial) resources. Wherever such eco-balances of environmental impact studies were presented until now, they have always been attacked with more or less correct arguments. However, the attackers generally themselves consider only selected aspects, mostly due to economic interests.

Therefore, the scientific esteem of those balances is – mainly without justification – not very high, but it seems necessary to improve the methods and input data to get truly reliable results.

Regarding ecological as well as economical optimization, which is a crucial demand today, the input side of the scheme is as relevant as the output or ecological impact. Paper industry generally has an advantage compared to other industrial producers since the raw materials used are renewable resources. Therefore, pulp and paper industry has the best prerequisites to be really sustainable. Quoting CEPI sustainability report 2005: *“The paper industry is keen to be among the best performers in terms of sustainability. We recognise that the only way to gauge progress and drive continuous improvement is through measurement and action.”* [CEPI (2005)]

More than 95% of the substances used in paper production are water insoluble fibres and fillers, the fibre sources being either waste paper or plant, mainly wood. Both are sustainable sources, plant as renewable resources (growing again) and obviously waste paper due to the ecological advantage of reuse. For the European Union the recycling rate was 54.6 % in 2004, the forecast for 2005 being 55.7 % [CEPI (2005)]. CEPI signed a Recycling Declaration in August 2006 stating the aim of a rate of 66 % for 2010. within the paper industry in the EU.

Waste paper often is regarded as the “a priori most environmentally favourable raw material”. This is true only in part, since the effort to gain secondary fibre useful for high quality paper grades has to be considered (both regarding environmental impact and costs) and it has to be seen that the use of wood isn't "consumption" but for the care of the woods is imperative in densely populated areas (being neutral regarding CO₂ production as well).

In the past, the product mentioned on the output side here usually was not taken into account for ecological considerations. But any anthropogenous material that is dismissed into the ambient environment of course has an ecological impact, which still has to be quantified better.

Water is needed for the paper production unavoidably, today in relatively small quantities, specific to the produced paper, compared with former times. Quantity and type of the emitted wastewater whose treatment is main object of this book are dependent on the specific amount of water used for the production.

Solid wastes (production residues, residual substances) arise as in the case of almost every production also at the pulp and paper production. By development of improved and new procedures, they can be avoided partly but never completely. A considerable part of the wastes is recycled, recovered, used as additive for different processes or thermally used for energy production.

For the question of the emissions of harmful substances into the air, the following has to be noticed:

Many papermills are running their own power stations since apart from electric power also steam is needed for the paper production. Many of these have a capacity below 50 MW. Normally the electric power produced is only part of the amount needed, while the steam is produced in the necessary amount for the mill.

Drying the mechanically dewatered paper (after the press section of the paper machine) with a water content of about 45 to 55 % in the machine produces a mixture of air and steam with low content of organic substances.

Bad odour sometimes emitted by papermills is arising from different sources. One possible source is the raw material, another may be the circulating water in the mill or the effluent treatment plant, when anoxic or anaerobic decomposition of organic substances takes place. This, however, can and must be avoided (also for reasons of the product quality).

Noise emission is a substantial environmental influence of the paper production. It can be decreased technically with in principle well-known, but very costly means to an acceptable measure.

Paper production is emitting thermal energy, which mainly is led away with the wastewater and the vent air. The low temperature of this emission aggravates an economic use so much that this is carried out only in exceptions to this day although technical possibilities for energy recovery are known. The warming of receiving waters by papermill wastewater is increasingly considered as a problem, especially when the quality of the natural water bodies had been increased by extensive wastewater treatment efforts of the mills (and other users as well).

Pollution of soil today can be and has to be avoided completely, except at accidents.

2. EU Regulations

The most relevant regulation applying directly to the operation of industrial plant in the European Union is the Directive for Integrated Pollution and Prevention Control (IPPC), adopted in 1996, addressing pollution from large industrial installations [EC (1996)].

The system applies the principle, that environmental influences are judged no longer separated to the media air, water, ground but that the evaluation (appropriately also the requests) and the avoidance measures are seen in an integrated approach, regarding the influence to all the environmental media. Simultaneously – it probably would not be meaningful otherwise – not single plants of a site but the site altogether is judged.

The guideline aims at the “categories of industrial activities referred to in article 1” (which are listed in the Appendix I) to achieve an integrated avoidance and reduction of the pollution of environment by coordination of the authorities’ decisions on issues regarding air, water and ground in order to achieve a high protection standard for the ambient environment altogether.

With the implementation of this directive in national laws in the EU member states the application of the best available techniques to avoid environmental pollution became the permission prerequisite for industrial plants as a core element in Europe. The best available technique (BAT) is described for the respective key industries in the Best Available Technique Reference Documents (BREF), for the pulp and paper industry in [BREF (2001)] with about 510 pages.

With the BREFs, a guideline for approval procedures is created. They do not represent a legal instrument at approval procedures

for new plants and at essential changes; however, the consideration of the leaflets is obliging for the authorities.

If the BAT are not used, be it for costs or competition reasons, this must be explained and justified precisely by the applicant. For existing plants, transition terms shall be made possible.

In the BREF pulp and paper manufacture, integrated processes are described separately. So even in so called non integrated mills (no production of chemical pulp on the site) the data for the generally integrated processing of mechanical fibres (chapter 4) and secondary or recycled fibres (chapter 5) are given separately, whereas the papermaking and “related processes” are given in the final chapter 6 (chapter 7 are conclusions and recommendations).

The chapters 2 and 3 give information for chemical pulping processes (kraft in chapter 2, sulphite in chapter 3), as well for separate pulp mills as for pulp production integrated in papermills. Chapter 1 gives general information.

Detailed information on the different types of production and the resp. BAT values are given in the BREF in the chapters mentioned. It has to be kept in mind (and is explained in the BREF in annexes II to IV) that in the EU member states very different ways of legislative regulations regarding emissions and consequently different ways of monitoring are applied. Therefore, in most cases it is not possible to compare national standards with the BAT values in a proper way. For instance German Standards (so called minimum requirements) allow a discharge of up to 5 kg/t COD related to an almost maximum level (their level is not statistically defined, but it is about 95th percentile) and to a maximum production capacity of absolutely dry paper for integrated production of recycled fibre papers with deinking. The BAT (see table 2) allows

up to 4 kg/t as yearly average related to the actual production, which is far more than the German Standard, but cannot really be compared on a general basis. Comparison is only possible for a certain mill, when enough data for valid statistics are available.

To give an overview of the BREF data, some summarizing tables are given here (tables 1, 2, and 3). The specific emission levels refer to yearly average values related to actual production.

For integrated mechanical pulp and papermills, the emission levels refer to both pulping and papermaking and are related to kg pollutant per ton of paper produced. The wastewater flow is based on the assumption that cooling water and other clean waters are discharged separately.

Table 1: Emission values for integrated mechanical pulping plant applying BAT

	Flow m ³ /t	COD kg/t	BOD kg/t	TSS kg/t	AOX kg/t	Total N kg/t	Total P kg/t
Integrated mechanical pulp & paper mills (such as newsprint, LWC and SC paper mills)	12-20	2.0-5.0	0.2-0.5	0.2-0.5	< 0.01	0.04-0.1	0.004-0.01

The values in table 2 refer to integrated mills i.e. recovered paper processing and papermaking is carried out at the same site.

Table 2: Emission values for integrated recycled fibre processing plant applying BAT

	Flow m ³ /t	COD kg/t	BOD kg/t	TSS kg/t	Total N kg/t	Total P kg/t	AOX kg/t
Integrated RCF paper mills without de-inking (e.g. wellenstoff, testliner, white topline, cartonboard etc.)	< 7	0.5-1.5	<0.05-0.15	0.05-0.15	0.02-0.05	0.002-0.005	<0.005
RCF paper mills with de-inking (e.g. newsprint, printing & writing paper etc.)	8 - 15	2-4	<0.05-0.2	0.1-0.3	0.05-0.1	0.005-0.01	<0.005
RCF based tissue mills	8-25	2.0-4.0	<0.05-0.5	0.1-0.4	0.05-0.25	0.005-0.015	<0.005

In table 3 the reference data for different types of non integrated mills are given.

Table 3: Emission values for non-integrated papermills applying BAT

Parameters	Units	Uncoated fine paper	Coated fine paper	Tissue
BOD ₅	kg/t of paper	0.15-0.25	0.15-0.25	0.15-0.4
COD	kg/t of paper	0.5-2	0.5-1.5	0.4-1.5
TSS	kg/t of paper	0.2-0.4	0.2-0.4	0.2-0.4
AOX	kg/t of paper	< 0.005	< 0.005	< 0.01
Total P	kg/t of paper	0.003-0.01	0.003-0.01	0.003-0.015
Total N	kg/t of paper	0.05-0.2	0.05-0.2	0.05-0.25
Flow	m ³ /t of paper	10-15	10-15	10-25

In some of the EU member states (for instance Germany, The Netherlands) levies for discharge of wastewater have to be paid. In some places (for instance in some of the German Federal States) a tax for water use has to be paid. However, both do not apply on EU level.

Core of the EU regulations for protection of surface and groundwater certainly today is the Water Framework Directive WFD [EC (2000)]. Many of the older regulations (like different directives on surface water quality for certain uses⁴, on discharge of dangerous substances⁵, and especially the directives for protection of surface water and groundwater⁶, see complete listing in⁷) are already or will be substituted by this regulation.

In December 2007, the following will be repealed (see⁸):

- Surface Water Abstraction Directive – 75/440/EEC
- Exchange of Information on Surface Water Decision – 77/795/EEC
- Surface Water Abstraction Measurement / Analysis Directive – 79/869/EEC

⁴ Council Directive 75/440/EEC of 16 June 1975 concerning the quality required of surface water intended for the abstraction of drinking water in the Member States (OJ L 194 25.07.1975 p. 26); Council Directive 76/160/EEC of 8 December 1975 concerning the quality of bathing water (OJ L 031 05.02.1976 p. 1); Council Directive 78/659/EEC of 18 July 1978 on the quality of fresh waters needing protection or improvement in order to support fish life (OJ L 222 , 14/08/1978)

⁵ Council Directive 76/464/EEC of 4 May 1976 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community (OJ L 129 18.05.1976 p. 23)

⁶ Council Directive 76/464/EEC of 4 May 1976 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community (OJ L 129 18.05.1976 p. 23); Council Directive 80/68/EEC of 17 December 1979 on the protection of groundwater against pollution caused by certain dangerous substances (OJ L 020 26.01.1980 p. 43)

⁷ <http://europa.eu.int/eur-lex/lex/en/repert/1510.htm#15102020> under 15.10.20.20 Water protection and management

⁸ <http://www.environment-agency.gov.uk/business/444217/444663/955573/955741/957258/?version=1&lang=e>

In December 2013, the following will be repealed:

- Freshwater Fish Directive – 78/659/EEC
- Shellfish Waters Directive – 79/923/EEC
- Groundwater Directive – 80/68/EEC
- Dangerous Substances Directive – 76/464/EEC

The EU Water Framework Directive focuses on integrated river basin management for Europe. It establishes the aim to reach until 2015 a good quality (at least grade II according to new EU standards) for most of the surface waters in the EU member states.

The WFD as it was decided in 2000 had a long history starting in 1995. All interested parties, such as local and regional authorities, water users and non-governmental organisations (NGOs) have been included in the discussions leading to the actual directive.

The best model for a single system of water management is management by river basin - the natural geographical and hydrological unit - instead of management according to administrative or political boundaries. This has been adopted by the WFD. Besides general protection of the aquatic ecology, different special aims have to be met only in certain surface water bodies: specific protection of unique and valuable habitats, protection of drinking water resources, and protection of bathing water. Therefore, a very differentiated but nevertheless integrated approach has to be taken.

Regarding surface water – which only applies here – a general requirement for ecological protection, and a general minimum chemical standard, was introduced to cover all surface waters. These are the two elements "good ecological status" and "good chemical status". Good ecological status is defined in Annex V of the WFD, in terms of the quality of the biological community, the

hydrological characteristics and the chemical characteristics. Whereas the good ecological status in a certain degree depends on the local situation of the water body, the good chemical status is defined in terms of compliance with all the quality standards established for chemical substances at European level. The Directive also provides a mechanism for renewing these standards and establishing new ones by means of a prioritisation mechanism for hazardous chemicals. This will ensure at least a minimum chemical quality, particularly in relation to very toxic substances, everywhere in the Community.

The WFD for the first time at EU level formalises the combined approach, meaning that besides controlling and improving the quality of the water body by ecological measures the necessary steps to decrease emission levels at point sources in order to meet the quality requirements for the receiving water body are to be taken. Therefore, the WFD, in the first step only giving instructions for action to governments and authorities, may lead to certain emission levels for point sources going further than existing regulations and being effective even when BAT rules, as explained before, are already met.

This will be the way by which WFD applies directly to papermills in Europe. When we take a very near look on the situation, it seems that, generally, the chemical standards will not be the problem for papermills, but in some sites, the ecological status, especially the hydrological characteristics of the water body, might be a problem causing orders for the mills.

The Water Framework Directive sets out clear deadlines for each of the requirements, which add up to an ambitious overall timetable. The key milestones are listed in **table 4**:

Table 4: Timetable for implementation of WFD

Year	Issue	Reference
2000	Directive entered into force	Art. 25
2003	Transposition in national legislation	Art. 23
	Identification of River Basin Districts and Authorities	Art. 3
2004	Characterisation of river basin: pressures, impacts and economic analysis	Art. 5
2006	Establishment of monitoring network	Art. 8
	Start public consultation (at the latest)	Art. 14
2008	Present draft river basin management plan	Art. 13
2009	Finalise river basin management plan including programme of measures	Art. 13 & 11
2010	Introduce pricing policies	Art. 9
2012	Make operational programmes of measures	Art. 11
2015	Meet environmental objectives	Art. 4
2021	First management cycle ends	Art. 4 & 13
2027	Second management cycle ends, final deadline for meeting objectives	Art. 4 & 13

3. Protection of Surface Waters

Cleaning of wastewater always aims at the protection of the receiving water. The ecological quality of the water body is quantified with different assessment systems. To meet certain quality standards it is necessary to apply the best possible measures to avoid emissions in the production process as well as the relevant treatment measures for the wastewater. Equally important is taking the best generally accepted measures for improving the morphological structure of the water body.

Discussing the question, how surface waters are to be protected against pollution requires some definitions in order to speak the same language. The terms are used here in the following sense (source partially in ⁹):

- *Pollution*: Unreasonable interference with the beneficial uses of the resource.
- *Point Source Pollution*: Pollution discharged or emitted from a stationary location or fixed facility.
- *Water Quality Criteria*: Scientific information about concentrations of specific chemicals in water, which protect aquatic life and human health.
- *Surface Water Protection*: Suitable application of narrative standards and numeric criteria to avoid pollution of the surface waters.

Both the main EU regulation systems explained in chapter 2 apply equally to the goal of protection of the surface waters (being

⁹ B.E.MILLER, Utah State University, Dept. ASTE, Lecture Water Pollution, Waterquality5260.ppt, <http://www.aste.usu.edu/miller/ASTE5260/lectures.htm>

generally the receiving water for directly discharging industrial plant):

- IPPC (see p. 27) requiring best available technique for operation of the production plant as well as for the effluent treatment, and
- WFD (see p. 31) describing the requested good ecological status of the water body and giving the instrument to authorities to impose conditions for the discharge of wastewater surpassing the BAT values given in the respective BREF (see p. 27).

In this situation, the WFD itself does not give enough information. The WFD Implementation Guidance Documents¹⁰ have to be used to find out which demands a certain industrial site has to expect.

4 of these documents are of special interest here:

- Identification of Water Bodies [EC (2003a)],
- Identification and Designation of Heavily Modified and Artificial Water Bodies [EC (2003b)],
- Rivers and lakes – Typology, reference conditions and classification systems [EC (2003c)], and
- Overall approach to the classification of ecological status and ecological potential [EC (2003d)].

This work has to be done by the administration, but the industry looks for early information. The following may help to that.

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http://forum.europa.eu.int/Public/irc/env/wfd/library?l=/framework_directive/guidance_documents&vm=detailed&sb=Title

In the WFD, community legislators have purposely abandoned the notion that national boundaries apply to water management scenarios. Instead, the directive supports the goal of transborder management of **river basin** districts. The various river basin districts are divided into clearly delineated surface water bodies for purposes of water resource management. The WFD defines a surface water body as a “discrete and significant element of surface water such as a lake, a reservoir, a stream, river or canal, part of a stream, river or canal, a transitional water or a stretch of coastal water” [EC (2003a)]. The way this works is explained in **figure 3**:

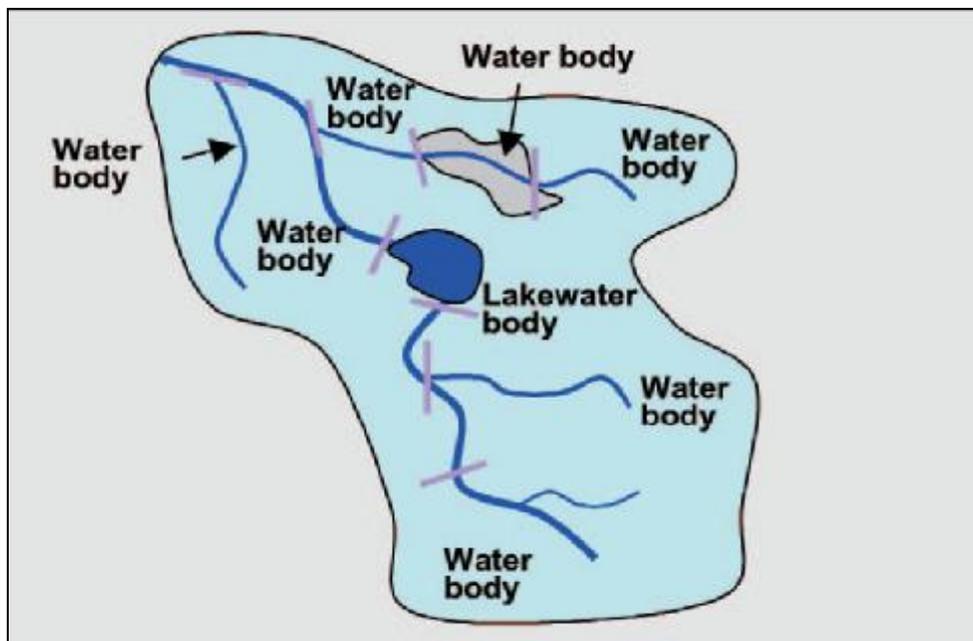


Figure 3: Schematic drawing of water body delineation
[BORCHARDT, BOSENIUS, DÖRR (2005)]

The designation of heavily modified water bodies (HMWB) might get special relevance to papermills, where heavy modifying of water bodies for withdrawal (abstraction) of freshwater or for production of electric power has a long tradition. However, the des-

ignation of HMWB is only possible in very special cases, as can be seen in [EC (2003b)].

The classification of water bodies [EC (2003c)] of course is decisive for the question, which measures have to be taken to improve the quality, if necessary. This might have severe implications for a mill discharging wastewater to this water body.

Since the new ecological classification system of the WFD [EC (2003d)] will replace all the differing systems in the EU member states, it has to be described here more intensely .

Like many other classification systems, WFD defines 5 quality stages (**figure 4**). One of the ways to define the grade is to calculate an ecological quality ratio (EQR) considering previous exploitations, as is shown in the figure.

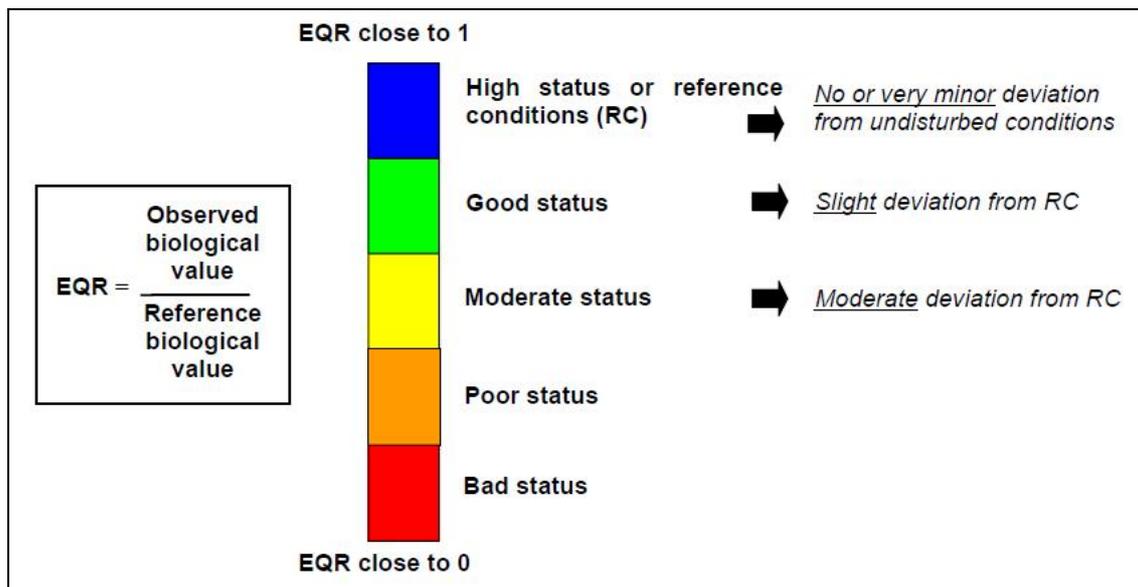


Figure 4: Basic principles for classification of ecological status based on Ecological Quality Ratios [EC (2003c)]

The quality system considers biological, chemical and hydrological (structural or morphological) quality parameters. The different

elements have to be combined according **figure 5** (examples of how indicative parameters may be combined to estimate the condition of the biological quality elements; the one-out all-out principle has to be used on the quality element level as indicated with the phytobenthos example).

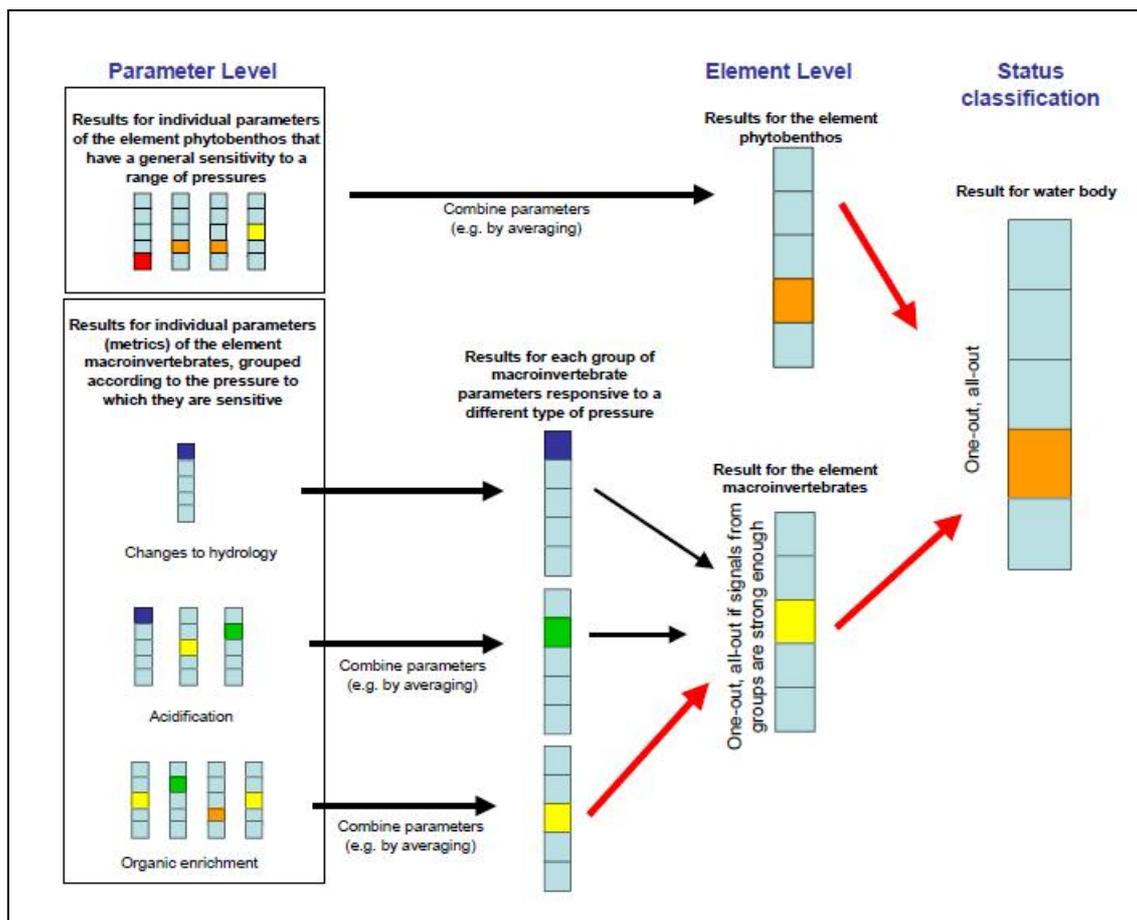


Figure 5: Examples for combination of quality parameters [EC (2003d)]

Figure 6 represents a generalised view of the WFD's classification scheme. The number of quality elements (QEs) relevant in princi-

ple in classification will vary. In shorthand, like explained in fig. 5, classification is based on a one-out all-out system.

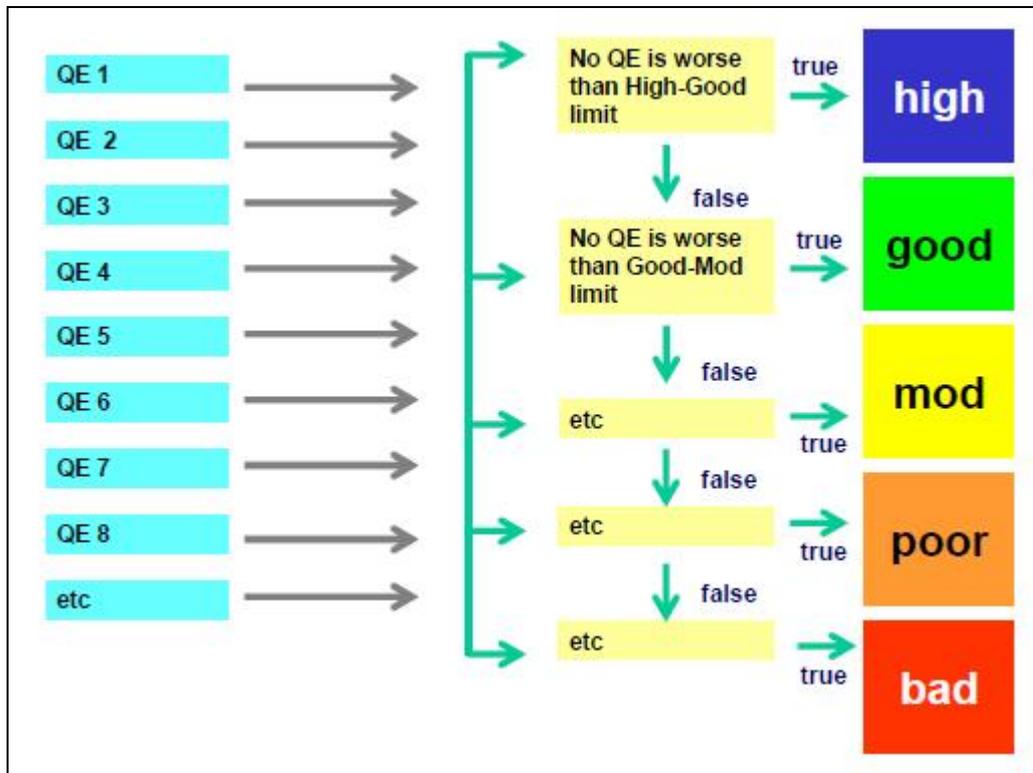


Figure 6: Representation of the WFD's classification scheme for ecological status [EC (2003d)]

Not yet finally decided (state August 2006) are the relevant criteria for the chemical status¹¹. A list of data to be controlled and the accompanying environmental quality standards (EQS) still are not fixed. But since the EU member states had to prepare a preliminary validation of the water bodies and subsequently the river basins till the end of 2004 (see table 4, p. 34) they had to establish

¹¹ see proposal of the European Commission COM (2006) 397 final of 17 July 2006 (2006/0129 (COD)); http://ec.europa.eu/environment/water/water-dangersub/surface_water.htm

preliminary criteria for the chemical status, which are likely to meet the final list rather well.

Article 10 of the WFD provides that for all discharges to water bodies – either point or diffuse sources – until 2012 emission limits have to be established. So if the authorities realize in case of a papermill discharge that it endangers the quality aim for the receiving water recognizably by the concentration of one (or several) of the listed substances or substance groups they will be forced to impose emission limits for these substances, even if the mill already operates according BAT.

The list of priority substances to be considered as part of the EQS has been published already in 2001 [EU (2000)], but this list does not contain concentrations as basis for EQS. After checking this list (and putting in relation to the EQS expected), it has to be concluded for the paper industry that generally no effects on emission limits are to be expected because the concentrations of the priority substances emitted by papermills are rather low¹².

So for papermills it may be stated quite safely, that the consequence of the high EU standards for protection of surface waters – which are expected to be an example for future standards world wide – mainly will be the question of structural (hydrological, morphological) deficits in their receiving waters caused by weirs or channels¹³. This presupposes that the mill operates according to BAT in production and effluent treatment, so that biological deficits in the receiving water are not to be expected generally.

¹² KERSTEN, A.; HAMM, U.; SCHABEL, S.; ÖLLER, H.-J.; Analyse von Papierfabrikations-abwässern vor dem Hintergrund verschärfter EU-Anforderungen, ipw - Das Papier (2006) Nr. 6, T79-T88

¹³ C.H. MÖBIUS, Auswirkungen der EU-Wasserrahmenrichtlinie auf Papierfabriken, in: I. Demel und H.-J. Öller (Hrsg.), PTS-Wasser- und Umwelttechnik-Symposium, München: PTS 2005

4. Water Use

In paper production, water serves as a means for suspension as well as for transport of fibres and fillers, as solvent for chemical additives and – this is probably the most important function, if a ranking is sensible at all - as a medium to build hydrogen bridge bonds between the fibres which is the most essential component of the strength of the product. Therefore, paper in the sense familiar to us cannot be produced without water. For the conditioning of the fibres and the formation of the fibre fleece on the wires between 250 and 1000 l of water per kg of product are required, depending on type of product. However, the largest portion of this water can be used again so that the specific water use is substantially lower as is presented later.

In this process, wastewater is only expelled as excess from the internal water circuit. Therefore, it has substantially the same concentrations of organics and inorganics (salts, electrolytes) as the circulating whitewater itself. This is marked by the load of soluble material brought into the system with fibres and additives (and therefore typical for a certain type of product) in combination with the production specific amount of fresh water used.

Smaller part streams of less concentrated waters going to the effluent, like washing and sealing waters, are the reason for a lower concentration in the wastewater compared to the white water. Dividing for instance the COD in the wastewater by the COD in the whitewater results in values between 0.4 and 0.8 for this reason. This ratio in a certain sense is a measure for the intensity of the fresh water use. When it is low, a high proportion of fresh water does not have intense contact with the stock and therefore is rather clean when discharged.

Clean fresh water in relatively small amounts is needed for certain points of production (cooling water not regarded), for instance dilution of some chemical additives. Additional fresh water, normally much more, is needed for the dilution of the white-water to lower concentrations of organics (only in special types of production inorganics as well) to values, which are acceptable for the type of production. Only about 1.0 to 1.5 l/kg are evaporated in the drying section, the rest of the fresh water added has to be expelled as wastewater.

Fresh water used for the production and wastewater discharged in paper industry generally are quantified by specific values, related to the absolutely dry bulk production of paper (bulk machine production BMP as is measured on the pope roller).

BMP depends on the type of production, the state of technique applied and the necessity to lower fresh water consumption and / or wastewater discharge and therefore vary in a wide range.

An example for the development in this respect in EU pulp and paper industry is given in fig. 1 (see p. 22). What has been achieved in paper industry in a densely populated highly industrialized country (Germany) is shown as an example in **figure 7**.

Differences in the demand for different types of product are marked by different demands on the purity of the white water. Typical values for specific amount of wastewater depending on the type of product in Germany are given in **table 5** (higher values can be justified in special situations due to technical reasons, lower values are possible taking special measures). In other countries, depending on the local situation, much higher values are typical, but not necessarily technically required.

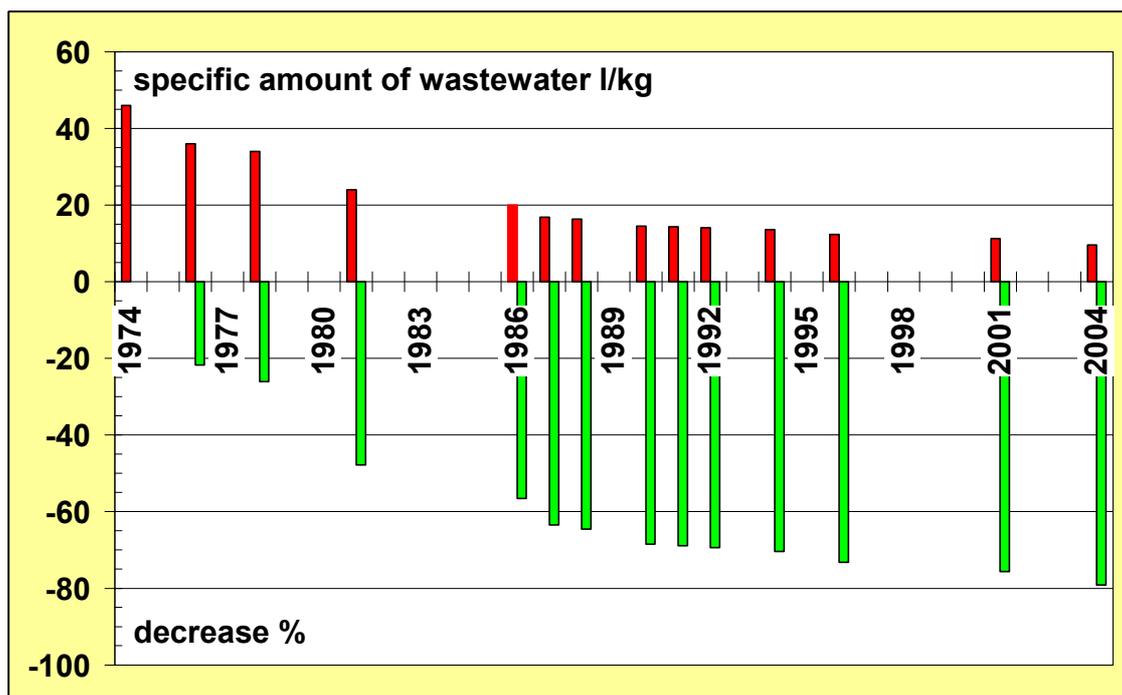


Figure 7: Development of the average specific amount of wastewater in the German paper industry¹⁴

Table 5: Typical ranges of specific amount of wastewater in papermaking in Germany

Program	from	to	
Woodfree uncoated paper	5	40	l/kg
Woodfree special paper	10	80	l/kg
Coated paper	5	20	l/kg
Printing paper (mechan. and secondary fibres)	5	20	l/kg
Packaging paper (secondary fibres)	2	10	l/kg

¹⁴ JUNG, H.; DEMEL, I.; GÖTZ, B.; Wasser und Abwassersituation in der deutschen Papierindustrie - Ergebnisse der Wasserumfrage 2004. Wochenblatt für Papierfabrikation 134, (2006), No. 9, p 478-481

Reducing the specific amount of wastewater in a papermill means intensifying the recirculation of whitewater in the mill up to totally closing the circuit (effluent free papermill, only evaporated water is substituted by fresh water).

The reduced fresh water input in the papermill without application of internal measures to decrease concentrations (see [HELBLE AND MÖBIUS (2001)]) has effects on the production conditions and on the product. In the circulating whitewater are to be expected:

- higher concentrations of inorganic substances,
- higher concentrations of organic substances,
- higher temperatures.

In general, the decrease of fresh water used is not favourable for the production conditions, however the rise of temperature has also positive effects in most cases.

The dependence of conditions in the circulating whitewater of the specific amount of wastewater is shown in **figure 8**. This figure gives concentrations as well as effluent load. In the case studied here (mechanical fibre containing printing grades) the specific amount of wastewater originally was around 19 l/kg and was decreased as far as it seemed possible, which in this case was around 14 l/kg. This limit was set by increased problems with the functionality of chemical additives and problems with product quality. That is an example for a product specific limit of increasing whitewater recirculation.

In case of a totally closed water circuit with no effluent discharged of course, no load is discharged as well. This, however, normally is not possible without taking special measures against the problems mentioned above. Nevertheless, it is interesting even in terms of economics to decrease the effluent load as far as possible by decreasing the specific wastewater amount (fig. 8).

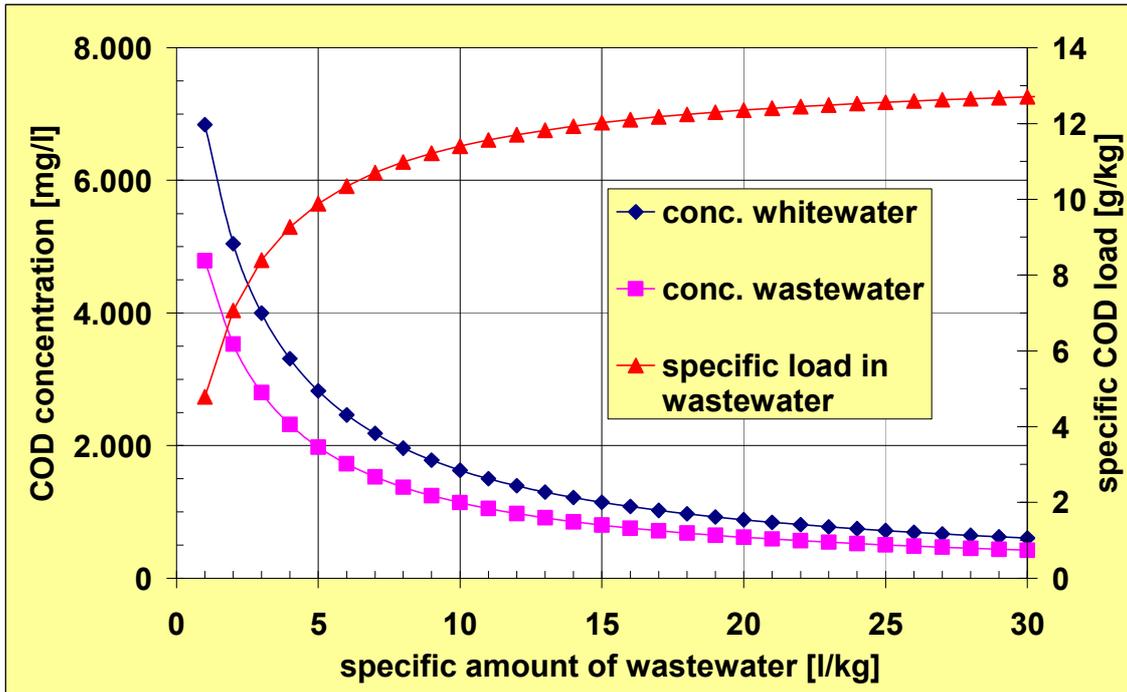


Figure 8: Interdependence of COD load and concentration in the wastewater as well as COD concentration in the circulating whitewater of the specific amount of wastewater in a production plant for printing papers

In case of rather low specific use of fresh water, generally increased growth of microorganisms is to be stated. Part of these microorganisms consume the dissolved oxygen in the whitewater for metabolism. Since in most parts of the stock and water system the oxygen input is low, the dissolved oxygen is exhausted fast. Optionally anaerobic microorganisms increase under the resulting anoxic to anaerobic conditions quickly. The metabolic products of these microorganisms lead to the following secondary observations:

- Smell of hydrogen sulphide H_2S , resp. sulphides in the whitewater,
- Smell of organic acids, especially volatile organic acids in the whitewater,

- Drop of pH value.

This again leads to a change in composition of the organic substances, resulting in an increase of the BOD to COD ratio. **Figure 9** gives an example for this as a possibility to monitor the development in an actual case.

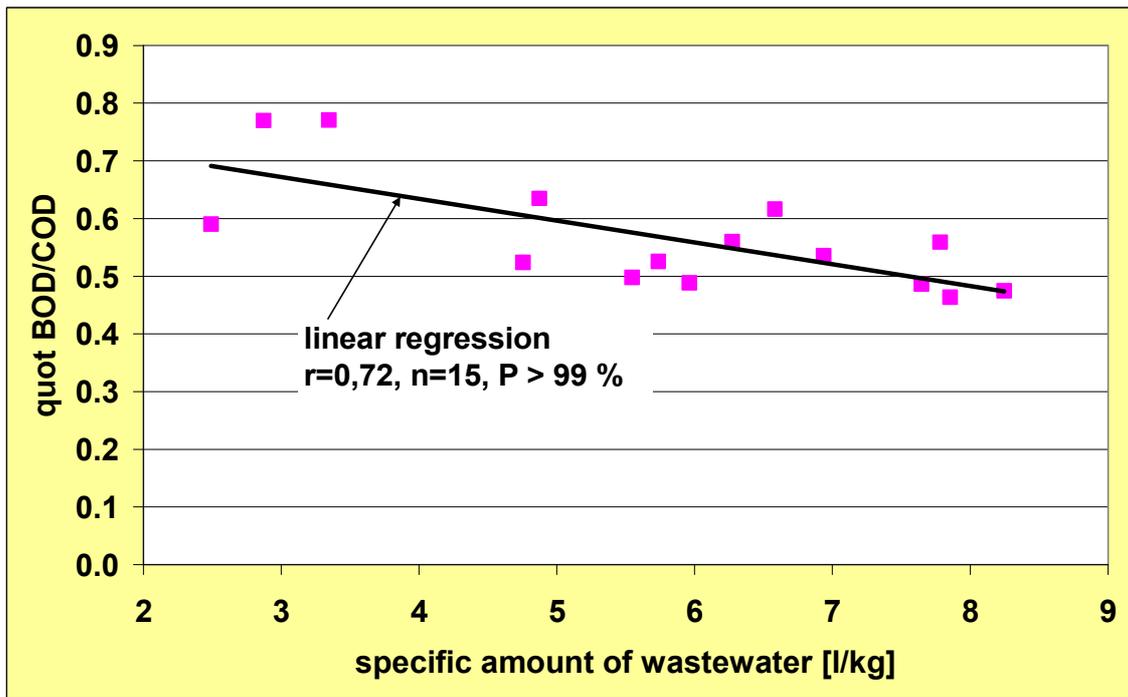


Figure 9: Connection between the ratio BOD/COD in the wastewater after mechanical treatment and the specific amount of wastewater for a papermill using secondary fibre in a practical example

The optimum specific amount of fresh water used has to be found for any type of production and even for any mill system. Certain

functional relations characterizing the stock-water-system in a mill may assist in finding this optimum value¹⁵.

When the specific amount of wastewater is decreased below about 20 l/kg first influences on production efficiency and product quality may be observed. Going further down below 10 l/kg these observations generally result in more or less severe problems, which for some types of product and production systems will be crucial and lead to the conclusion, that the optimum value for specific wastewater will be between for instance 10 and 14 l/kg (most printing grades containing mechanical and / or secondary fibres). For other product types, mainly packaging paper with high content of secondary fibres, specific amounts of wastewater below 10 l/kg, down to about 4 l/kg, or even having a closed circuit, will be possible without special measures in the whitewater cycle.

The problems to be observed (and monitored) are different for general types of paper production.

For **graphic papers** the main problems arise from the content of anionic dissolved and colloidal substances, so called "anionic trash", in the whitewater (main origin are mechanical and secondary fibres)¹⁶. They interfere with several functions of chemical

¹⁵ KAPPEN, J.: Kennwerte als Werkzeuge zur Minimierung des Wasserbedarfs bei der Papiererzeugung - ein Beitrag zum prozessintegrierten Umweltschutz. Dissertation München 2001. (= Ber. aus Wassergüte- und Abfallwirtschaft TU München Nr. 166)

¹⁶ <http://www4.ncsu.edu/~hubbe/DCS.htm>: „Anionic trash" is one of the popular names used to describe a wide range of anionic dissolved polymeric and colloidal materials. Another common name is "DCS" for "dissolved and colloidal substances." Many such substances come from the wood and get released during pulping. Some key components include fatty acid salts, resin acid salts, hemicellulose and its oxidation by-products, lignin derivatives from kraft pulping, and dispersants or anionic latex and dispersants from coated broke. Various types of bleaching agents tend to oxidize hemicellulose and extractives, further increasing the anionic charge of the dissolved and colloidal fraction of the pulp slurry. Pulp washing of thickening stages after pulping and after major bleaching

additives, the interference can only be partly compensated by other additives. An example for the interference with filler retention is shown in **figure 10**.

These substances can be detected with a polymer titration using a Streaming Current Detector (SCD). The solubility – and by that the concentration in solution – of the anionic trash is mainly influenced by production and conditioning process, temperature, pH value, dwell time, and stock consistency. With decreasing specific fresh water, the anionic substance concentration rises parallel to the increase of organic matter in the system. This has influence on

- productivity,
- efficiency of chemical additives,
- paper quality,
- wastewater composition.

stages are intended to keep this material from going to the paper machine, but it is common for such devices to be working beyond their rated capacity. Anionic colloids and dissolved polymeric materials interfere with the performance of cationic retention aids, cationic dry-strength agents such as cationic starch, and wet-strength resins. Also they can play a role in deposit problems.

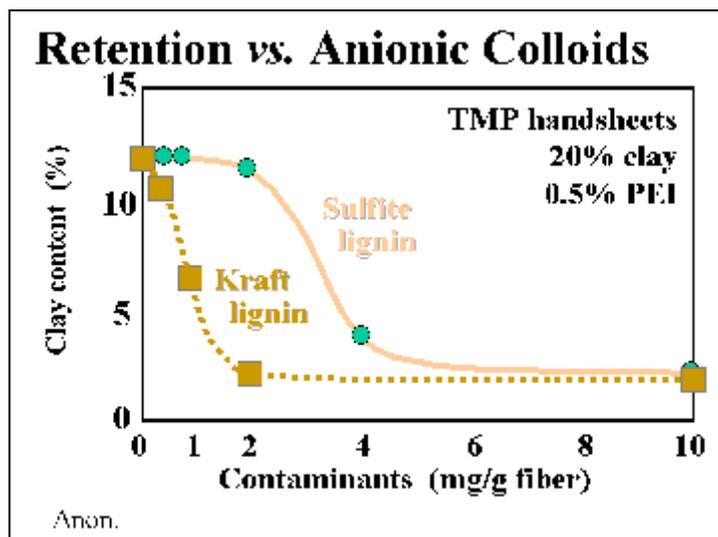


Figure 10: Examples showing how two types of anionic colloidal materials can influence the retention of clay¹⁶

The colour of the circulating whitewater gets darker with a very low amount of specific fresh water. This can be a limiting factor particularly for the production of white papers.

Both these effects are not of high relevance for the production of **packaging paper** in general, especially when they are produced with a high proportion of secondary fibre (in Central Europe normally 100 %). For this type of production, the general decrease of productivity due to unfavourable whitewater conditions arising with specific freshwater below about 5 l/kg is crucial. Limiting factor in these cases is the overall hydraulic retention time in the system, which should be below about 10 hrs. This avoids problems resulting from anaerobic (or anoxic) decomposition, such as corrosion and difficult cleaning of the whitewater in savealls.

An example for an optimized system for production of graphic papers containing mechanical and / or secondary fibre is given in **figure 11**:

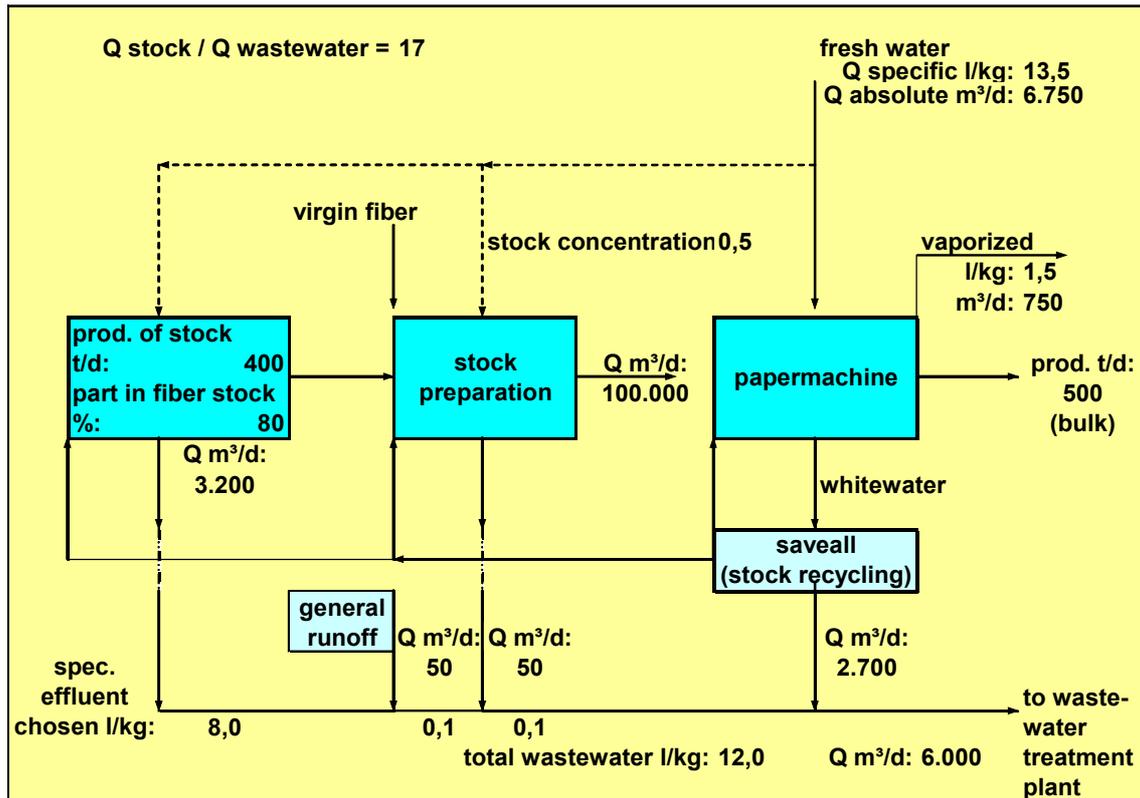


Figure 11: Example for water circuits in a system producing graphic papers [HELBLE AND MÖBIUS (2001)]

Internal treatment systems for the whitewater, exceeding the usual mechanical cleaning in savealls (so called kidney systems), which are technically known but not really well developed, as well as recirculation of externally treated effluent to the production make it possible to achieve low fresh water use of about 2 to 4 l/kg or even totally closed circuits for almost every type of production (see [HELBLE AND MÖBIUS (2001)]). This in certain cases may be an economic alternative to the conventional systems discussed above.

With the fibres (especially of integrated production) and the chemical additives, certain loads of organic and inorganic substances are brought into the production system. Composition of the whitewater is further influenced by the conditions of the system (fig. 9, p. 48). The concentration of whitewater and wastewater, however, is decided by the specific freshwater use. Composition and concentration of the wastewater are decisive for the use of methods of wastewater treatment. Therefore, here some basic information to these questions is given (see [MÖBIUS AND CORDESTOLLE (1994)]).

According to a survey made in German papermills effluent after mechanical treatment in the early 1990's (basically being still representative) the results given in **table 6** have been found for a set of paper products. A diagram presentation of the data for COD concentration ranges is given in **figure 12**. **Figure 13** shows the information for the ratio BOD/COD. All data are given for the wastewater after mechanical treatment.

Table 6: Effluent data for a set of paper products

main type of pulp	type of product	mean value of ratio			typical conc. ranges mg/l				ww specific	
		BOD/COD	BOD/TOC	TOC/COD	BOD		COD		l/kg	
					low	high	low	high	low	high
chemical pulp	soft tissue	0.39	1.76	0.24	50	100	95	270	9	25
	decorative sheet	0.46		0.37	20	40	50	100	20	70
	woodfree printing	0.45	1.42	0.35	65	220	150	400	5	20
	woodfree special	0.49			40	550	90	1,100	15	60
	low freeness	0.45	1.34	0.24	10	30	20	60	100	250
	specialty papers	0.34			10	40	45	110	50	100
	woodfree coated	0.46	1.66	0.32	170	260	360	540	20	30
mechanical pulp	super calandered	0.38	1.26	0.34	125	480	450	1,020	13	20
	leight weight coated	0.38	1.12	0.29	150	460	430	1,300	12	30
	mechanical printing	0.39	1.57	0.29	200	500	500	1,160	8	30
	carton board mp	0.43			140	200	320	490	15	25
secondary fibre	newsprint paper	0.48	1.52	0.33	460	1,270	960	2,400	7	20
	corrugated board	0.53	2.06	0.27	1,280	2,840	2,190	5,680	0	10
	carton board sf	0.48	1.32	0.33	530	3,000	1,140	5,500	0	15
	recycling paper	0.51			250	400	540	790	10	20

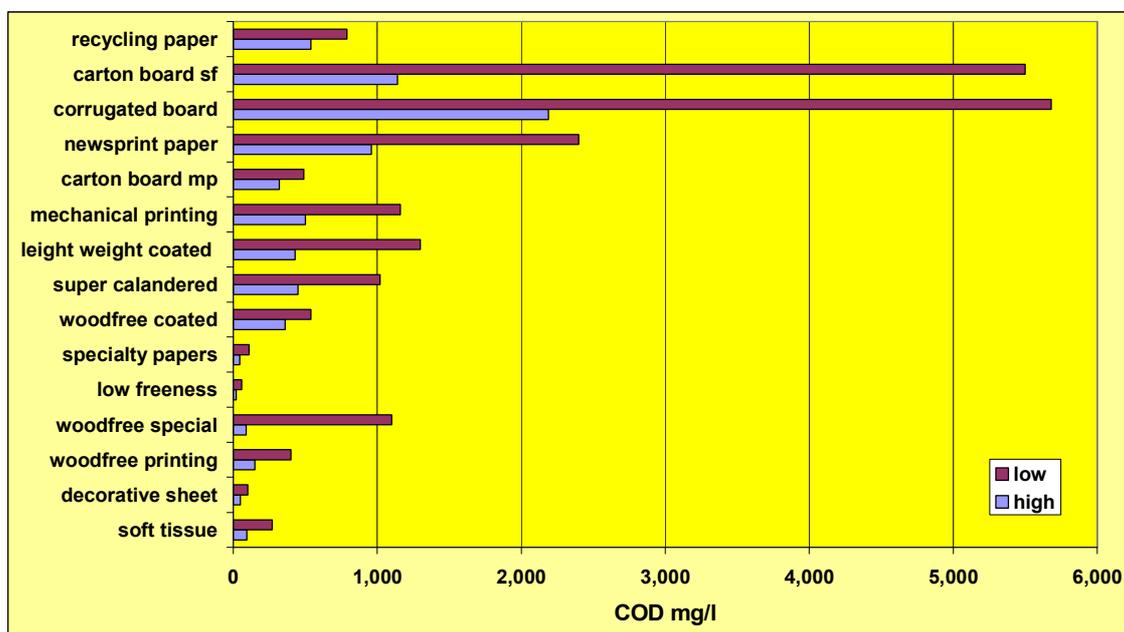


Figure 12: COD concentration ranges in papermill effluents (see tab. 6)

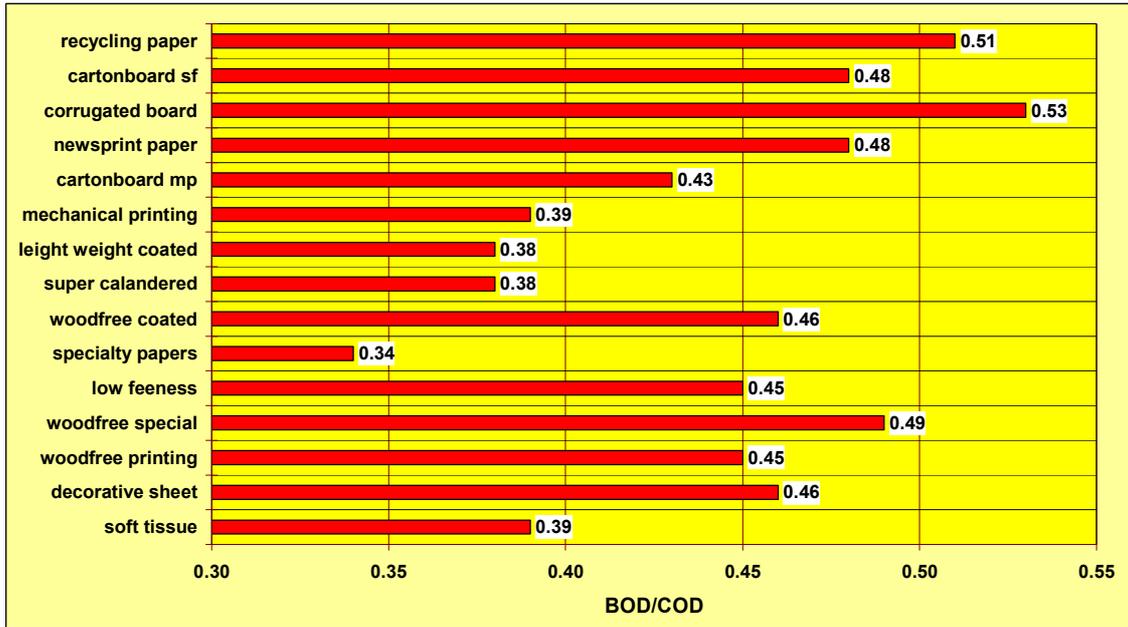


Figure 13: Average ratios BOD/COD in papermill effluents (see tab. 6)

5. Wastewater Treatment

5.1 General remarks

Biological treatment of production effluent is state of the art for paper industry (as well as for production of chemical pulp). Generally, the biotreatment stage is subsequent to a mechanical or chemical-mechanical treatment stage, which eliminates the suspended solids in order to protect the biological reactors. This can be done by sedimentation, flotation or filtration. The choice of the type of process depends on the type of solids to be eliminated and on the conditions of the site.

Only in case of some woodfree paper types produced with a high specific freshwater use, the BOD concentrations are so low that a biological treatment is difficult, rather ineffective and often not required by legal standards.

The biotreatment can be achieved by a public treatment plant (indirect discharge), but normally it is done by the mill itself (direct discharge). The situation in Germany in 2004 gives an example for the distribution of the treatment methods (**figure 14**).

The composition of the papermill effluent generally requires the addition of nitrogen and phosphorus for every type of biological treatment as nutrients necessary for the growth of microorganisms.

Independent of the general elimination of organic matter by the treatment, biotreatment is helpful or necessary for protection of the receiving water, since it eliminates the substances causing oxygen consumption in the water. This protects organisms in the water needing a higher oxygen concentration for living and re-

production, by this helping to reach a higher ecological status as far as biological parameters are concerned¹⁷.

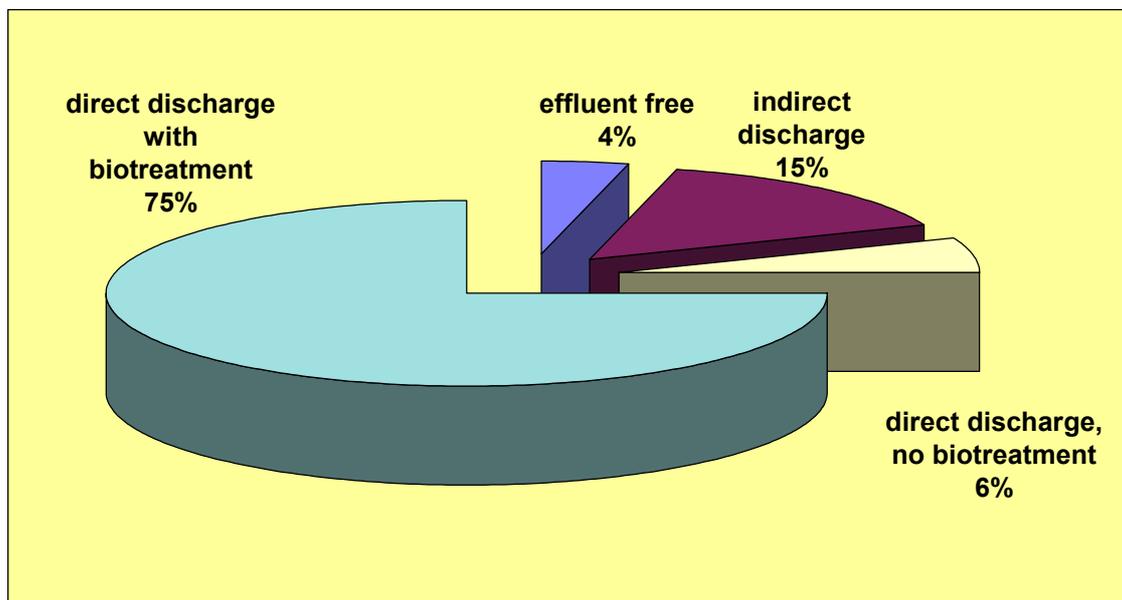


Figure 14: Wastewater treatment in German paper industry related to the production in 2004¹⁴

For understanding the elimination of organics in bioreactors in terms of the generally used parameters BOD and COD, it is necessary to understand the exact meaning of these terms. Both are quantifying certain effects (oxygen consumption caused by bacterial activity in case of BOD, chromate reduction caused by chemical oxidation in case of COD), which are used like amounts of substances (concentration, load). Therefore, when we say a water sample has 100 mg/l BOD, we describe that the organic matter in the water needs 100 mg oxygen per litre to be biochemically de-

¹⁷ see <http://www.freshwaterecology.info/>, an information page of the EU funded research project Euro-limpacs, designed to assess the effects of future global change on Europe's freshwater ecosystems (<http://www.eurolimpacs.ucl.ac.uk/>)

graded (which is exactly the meaning of BOD – biochemical oxygen demand).

By definition, biochemical processes in an aerobic bioreactor will only eliminate oxygen consuming substances, quantified as BOD. However, with every BOD elimination a certain COD elimination is coupled. Every organic substance has a certain ratio of BOD to COD. So if this substance is eliminated by biodegradation, the BOD will be eliminated (almost) completely, but COD will be eliminated in the ratio inherent to the substance as well (and will be eliminated completely only when the substance is completely biodegradable, otherwise in spite complete elimination of BOD a rest of COD will remain). Example: When 1 g of a completely biodegradable substance with a BOD to COD ratio of 0.6 is decomposed, 600 mg of BOD and 1000 mg of COD are eliminated. Carbohydrates, representing the most of the biodegradable matter in papermill wastewaters, have a BOD to COD ratio of 0.6 to 0.65, which allows a prediction of the achievable COD elimination by biodegradation. A smaller part of the ingredients of the papermill effluents is less to almost non-biodegradable (in this case $BOD/COD < 0.1$). This part remains almost untouched in a bioreactor. Depending of the type of process, however, part of this is eliminated as well – for instance by adsorption –, which has to be considered making a prediction of the COD elimination.

This may be explained further by **figure 15**, in which the hardly biodegradable portion of course is the remaining amount of substance (indicated as COD) after biotreatment.

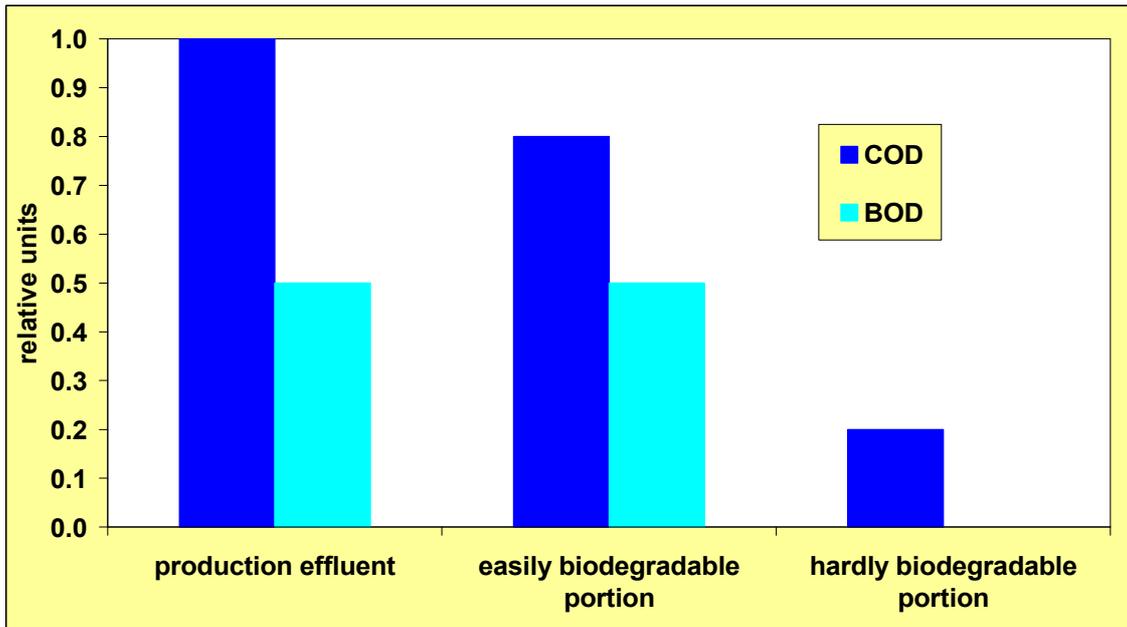


Figure 15: Exemplary presentation of BOD and COD elimination in biological treatment of a typical papermill wastewater

For a prognostic calculation of remaining COD after biotreatment of papermill wastewater, the following method may be used:

COD elimination efficiency

$$\eta_{\text{COD}} = \eta_{\text{BOD}} * \text{quot}_{\text{in}} / \text{quot}_{\text{el}}$$

with $\text{quot}_{\text{in}} = \text{BOD}_{\text{in}} / \text{COD}_{\text{in}}$,

and with

$$\text{quot}_{\text{el}} = \frac{\text{BOD}_{\text{in}} - \text{BOD}_{\text{out}}}{\text{COD}_{\text{in}} - \text{COD}_{\text{out}}} = \frac{\Delta \text{BOD}}{\Delta \text{COD}}$$

quot_{el} is dependent on the type of effluent and the type of treatment system and has to be chosen according experience. It does not exactly represent the biodegradation, but the total elimination in the bioreactor.

This method for prognosis of COD after biotreatment only works with average values of a valid and statistically sufficient set of data, at least 20 daily values (consistent 2 hrs or 24 hrs samples), and the result is only an average value again. The experience to fix $quot_{el}$ so far is limited to activated sludge treatment plant. It may be extended to multistage wastewater treatment plant (wwtp) with activated sludge reactor as final stage using sufficient practical experience.

Table 7 gives some examples for the COD calculation following this method for different types of papermill wastewater and a treatment using BAT.

Table 7: Examples for prognostic calculations of remaining COD after biotreatment of papermill wastewater

case	A	B	C	D	E
Inflow biostage					
COD mg/l mv	120	350	1,200	3,000	5,000
BOD ₅ mg/l mv	40	150	550	1,450	2,500
after biotreatment					
BOD ₅ mg/l mv	10	10	10	10	10
calculated data					
$quot_{in}$	0.33	0.43	0.46	0.48	0.50
η BOD %	75.0	93.3	98.2	99.3	99.6
chosen: $quot_{el}$	0.43	0.49	0.51	0.52	0.54
COD in treated effluent mg/l mv	51	63	138	248	389
η COD %	57.7	81.9	88.5	91.7	92.2

For biodegradation of organic substance, the microorganisms need nitrogen and phosphorus as nutrients and also some trace elements in form of biological available compounds. The biodegradation produces energy, CO₂ and water, and additional biomass (protein). For the biomass production, the nutrients are needed. In the aerobic process about half of the degraded organic substance is changed to protein – the rest ends as CO₂ and water. In the anaerobic process only about 5 % of the degraded organic

substance are used to produce excess biomass, products of the biodegradation are mainly methane and besides CO₂ and water. That is the reason why aerobic degradation needs much more nutrients than anaerobic degradation.

Whereas trace elements seem to be sufficient available in papermill wastewaters, phosphorus and in most cases as well nitrogen are insufficient and have to be added. This is quite different to municipal wastewaters and most effluents of food processing industry, where nutrients are available in excess.

Even when high concentrations of carbohydrates as biodegradable organic substance are present, papermill wastewaters contain normally only small quantities of nitrogen and phosphorus.

The required nutrient ratio is determined empirically and related to BOD. The required ratio normally is indicated as BOD₅ : N : P = 100 : 5 : 1 for aerobic degradation. In praxis generally a ratio of 100 : 4 : 0.8 down to 100 : 3 : 0.5 prove sufficient to get a good biomass growth and good degradation efficiency.

The required additional nutrients generally are added as a solution of technical urea and technical phosphoric acid. Nevertheless, other salts of ammonia and phosphorus, for instance diammoniumhydrogenphosphate, can be used as well.

To find the optimum dosage in many cases it is sufficient to analyse nitrogen compounds and ortho phosphate in the treated effluent¹⁸, but to be sure, the content of nitrogen and phosphorus in the biomass itself should be checked¹⁹.

¹⁸ In principle a small excess of ammonia would be sufficient, but if nitrification - the biological oxidation of ammonia to nitrate - is to be expected the nitrate has to be checked too.

¹⁹ Generally it is stated that TKN should be more than 5 % and P should be more than 1 % of the dry biomass with a LOI of around 30 to 40 %.

5.2 Types of Reactors

The two main types of bioreactors used in effluent treatment of paper industry are anaerobic and aerobic reactors.

5.2.1. Anaerobic Process

The anaerobic process only works when oxygen is completely excluded. The microbiological pathways of the anaerobic degradation in general are shown in **figure 16**.

All the main features of the process can be derived from these pathways. The main advantage of the anaerobic process is the production of excess energy (energy is required for pumping the water and energy rich biogas is produced). A further advantage is the low specific amount of excess biomass (only about 5 % of the degraded organics are changed to biomass).

However, there are some severe drawbacks: The process only works *economical* when the organic substrate concentration is high enough, given as COD for instance more than 1.000 to 2.000 mg/l depending on the conditions. If the ratio of COD to SO_4 is too low, the process will not work properly due to the sulphate reduction.

The methanogenous bacteria (final step of the process) are reproducing slowly and are very sensitive to different deviations from preferred conditions, for instance pH (7.0 is preferred), and temperature (38 °C preferred in the mesophilic process). They are much more sensitive to certain toxic substances than other groups of bacteria.

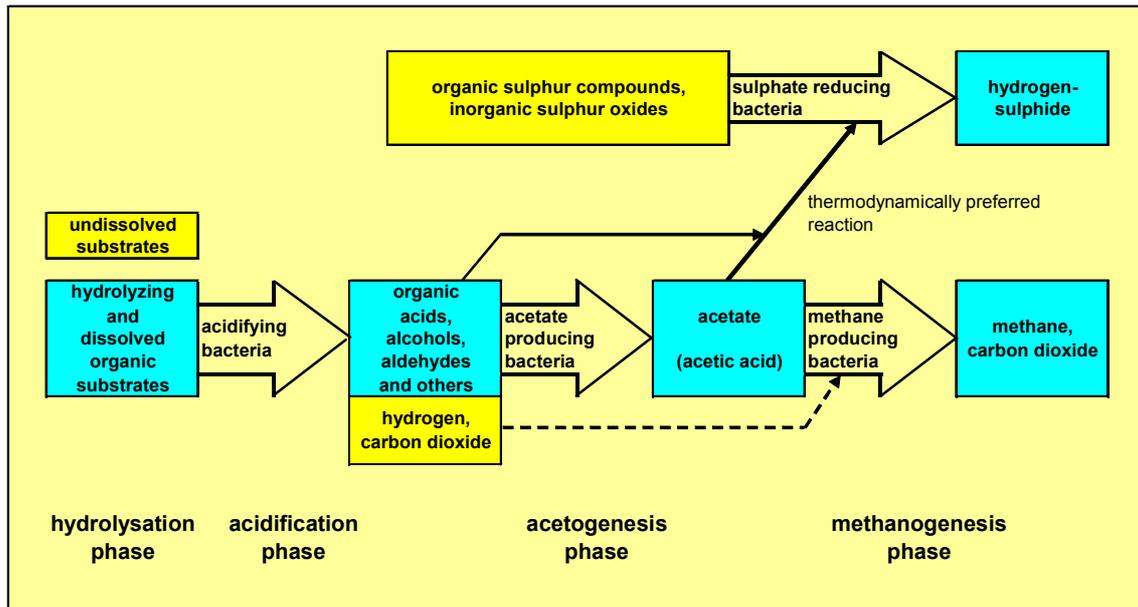


Figure 16: Microbiological pathways of anaerobic degradation²⁰

Several different types of reactors for anaerobic degradation of papermill effluents with their normally relatively low substrate concentration and comparatively high sulphate concentration have been developed [LETTINGA et al. (1983); LETTINGA (1995)]. Today the preferred type of reactor is the so-called tower reactor basing on the upflow anaerobic sludge blanket (UASB) process [LETTINGA et al. (1980); HULSHOFF POL et al. (2004)]. Main examples for this type are the IC reactor and the BIOBED reactor (see **figures 17, 18**).

²⁰ SEYFRIED, C.F., H. SIXT, Behandlung organisch verschmutzter Abwässer mit anaeroben Verfahren zur Minimierung des Energieaufwandes, Gewässerschutz-Wasser-Abwasser (Aachen) 45, (1981), S. 109 - 134

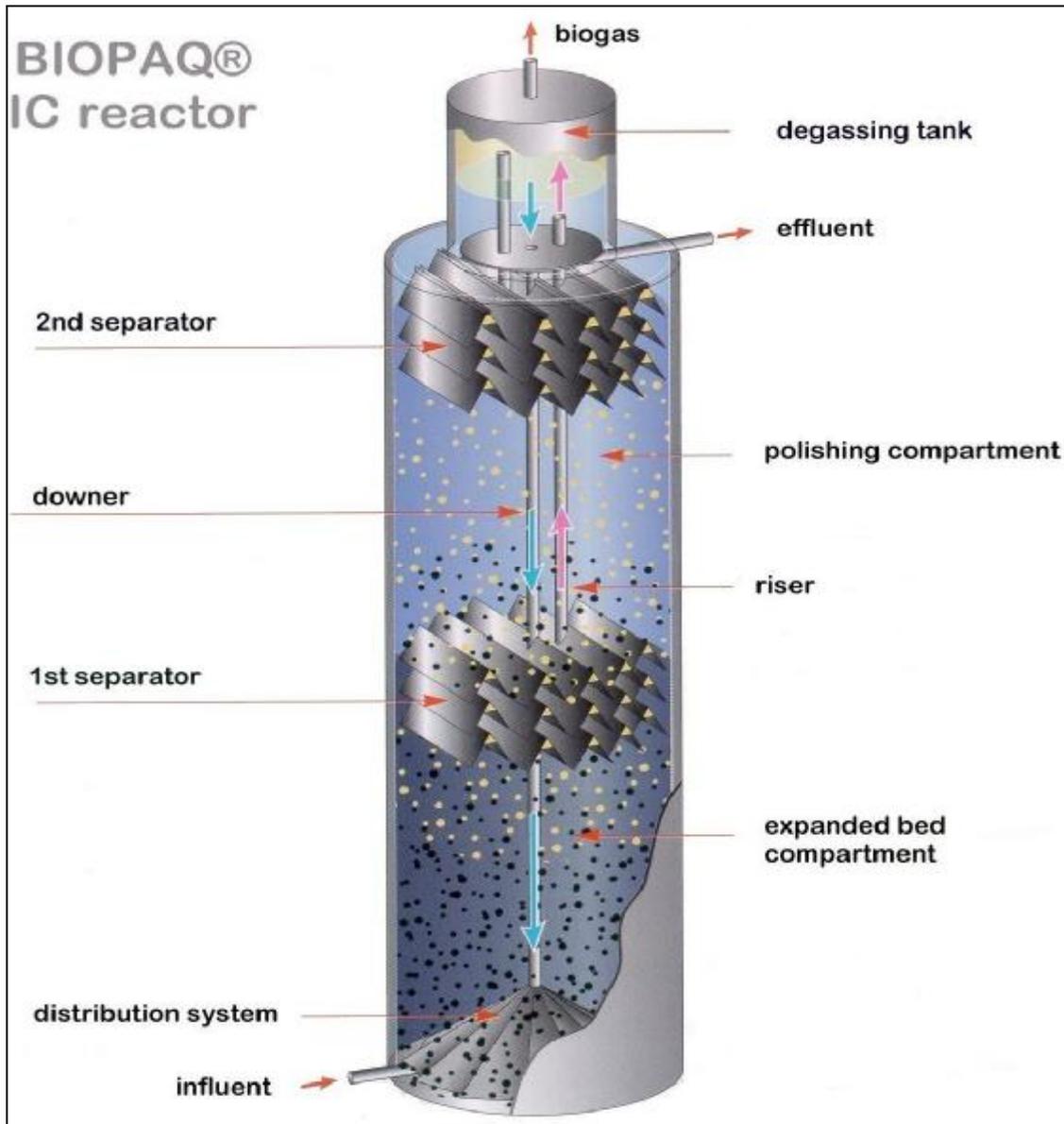


Figure 17: Preferred types of anaerobic reactors for treatment of papermill wastewater: IC reactor (© Paques)

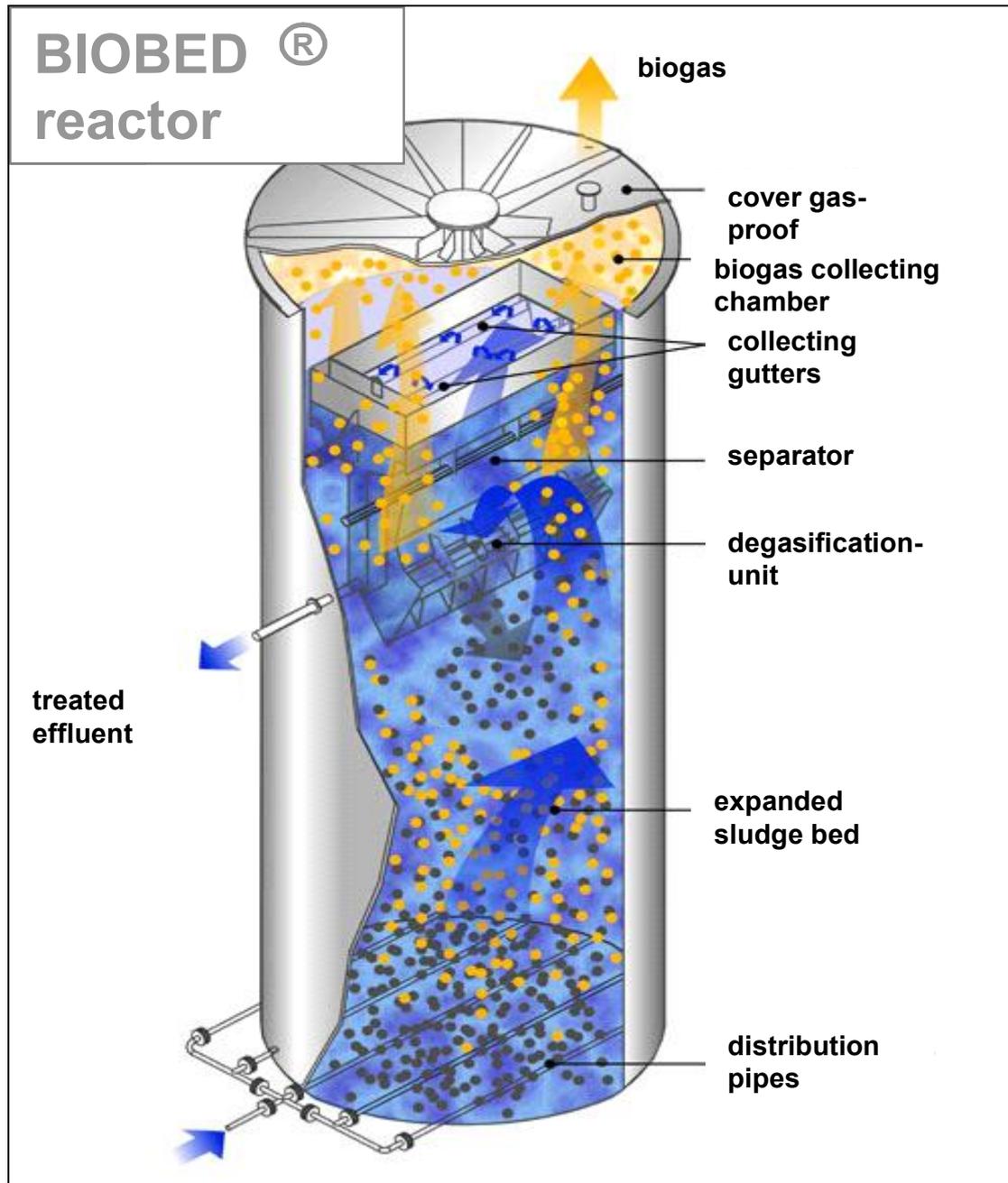


Figure 18: Preferred types of anaerobic reactors for treatment of papermill wastewater: biobed reactor

(© VA Tech)

Sulphate reduction (see fig. 16) causes several problems, one of them is the potential inhibition of methanogenesis by high concentrations of sulphide, see [KOSTER, RINZEMA, DE VEGT, LETTINGA

(1986)]. Others are loss of energy in biogas, loss of methanogenic bacteria, and insufficient granulation of biomass. Several proposals have been made to avoid the sulphate reduction²¹ or eliminate the produced sulphide²² (which only avoids part of the problems). In actual practice, the problem of sulphate reduction is not solved up to now.

Due to products of anaerobic (and anoxic) metabolism, the effluent of an anaerobic reactor never has a sufficient quality for direct discharge, if complete biodegradation (BOD₅ average below 20 mg/l) is requested. Therefore, generally the anaerobic reactor is used as a first biological stage, followed by an aerobic stage, mostly an activated sludge reactor.

Even when no direct discharge is intended, but a discharge to a public sewer or the reuse of the anaerobic treated effluent in the production, a further oxidative treatment is required to eliminate or at least oxidize the metabolic products. This may be a simple oxidation with air in some cases. To eliminate sulphide 3-valent iron salts can be added, forming insoluble Fe₂S₃ (which is black).

5.2.2. Aerobic Process

In natural surface waters as well as in technical treatment plants the aerobic degradation – that is the process, which needs oxygen – is the most widely used. The activated sludge treatment, a degradation process for organic substances using oxygen consuming

²¹ WEHENKEL, S. and R. DIEKMANN: Selektive Hemmung von sulfatreduzierenden Bakterien durch den Einsatz von Molybdat, *Korrespondenz Abwasser* **40**, (1993), Nr. 9, S. 1457 - 1460

²² BUISMAN, C.J.N.; LETTINGA, G.: Sulphide removal from anaerobic waste treatment effluent of a papermill, *Water Research*, **24** (1990), No 3, p. 313-319.

bacteria and protozoa, has been in technical use for effluent treatment since more than 100 years¹. In surface waters, biodegradable organic substances are degraded by a similar biocenosis with much lesser biomass concentration.

Besides the activated sludge treatment, which still is the main treatment process for papermill wastewaters, some biofilm processes are in use, mainly to mention:

- the suspended carrier process (moving bed biofilm reactor MBBR), primarily used as high loaded first stage in combined processes, and
- the wastewater biofilter for effluent with low BOD concentration, used as a secondary stage following primary elimination of suspended solids or as a tertiary stage following another bioreactor.

Other processes, which are still in use, but not so widely spread, are the sequencing batch reactor²³ (which can be used instead of the activated sludge treatment) and the trickling filter²⁴ (above all used as high loaded first stage). These will not be discussed further here.

In pulp and paper producing countries, which are not as densely populated as Central Europe, like northern European countries and Canada, aerobic biological treatment systems with long retention times and subsequently large area required, like aerated lagoons and extended aeration activated sludge treatment, are still in use. However, these systems probably will be no longer state of the art in some years due to relatively high cost and large area need. Therefore, these systems are not discussed here.

²³ http://www.epa.gov/owm/mtb/sbr_new.pdf

²⁴ http://www.epa.gov/owm/mtb/trickling_filter.pdf

The basic principle of the **activated sludge process** can be seen in **figure 19**.

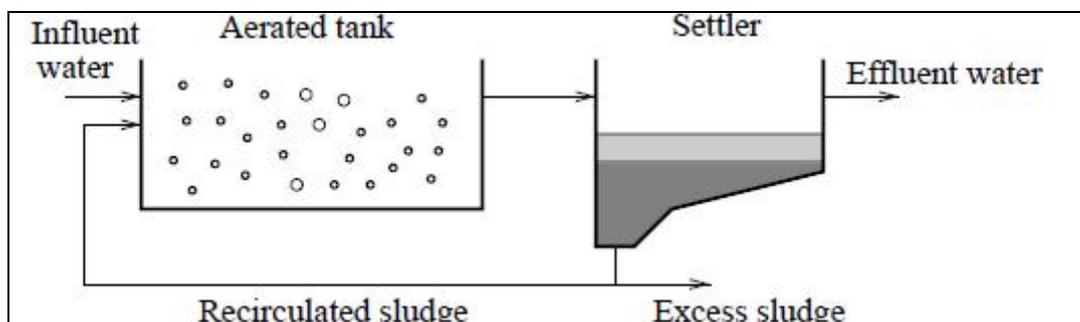


Figure 19: Basic principle of the activated sludge process²⁵

Only by recycling the biomass settled in the secondary clarifier (or retained by another process like flotation or filtration, for instance in the MBR, see p. 73) to the aeration tank (activated sludge reactor) the necessary biomass concentration in the aeration can be kept and the effluent is clean enough for discharge in due retention time. So it easily can be realized that this step is crucial to the whole process.

Several different types of activated sludge reactors have been designed. In order to get the required elimination of organics and to keep good settling conditions for the biomass, oxygen concentration and the specific BOD to mass load in the reactor have to be kept in a certain range, which of course basically is depending on the type of reactor.

The composition of the papermill wastewaters, particularly the high quota of carbohydrates (which are the main biodegradable organics in papermill wastewaters), causes a strong inclination

²⁵ C.-F. Lindberg, Control and estimation strategies applied to the activated sludge process, Dissertation Uppsala University, Uppsala 1997, ISBN 91-506-1202-6;
<http://scholar.google.de/url?sa=U&q=http://www.syscon.uu.se/Research/cfl/phd.pdf>

for development of so called bulking sludge. Bulking can hardly be avoided in completely mixed aeration tanks. This is one reason why a high loaded first stage is preferred, or at least a cascade reactor (alternatively a plug flow reactor or selector) is used.

Bulking sludge is defined by a high proportion of filamentous bacteria, shown in **figure 20** in comparison to the preferred floc forming bacteria, leading to a poor settling quality indicated by a high sludge volume index SVI. In case of bulking sludge the SVI, characterizing the settleability in the secondary clarifier, is more than 200 ml/g, in papermill plant mostly more than 300 ml/g, and so the separation in the clarifier will be poor, meaning a high proportion of biomass will be lost with the effluent.

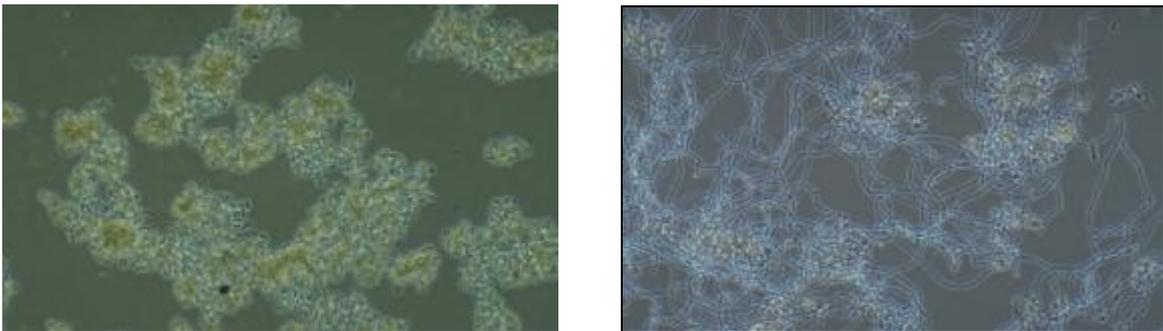


Figure 20: Floc forming (left) versus filamentous bacteria
in aerobic activated sludge bioreactor

The **suspended carrier process** is characterized by the biomass carrier, which allows operating the reactor with a high concentration of biomass. The carrier is retained in the reactor by a sieve in the outlet (see **figure 21**). Only the excess suspended biomass is leaving the reactor with the (partly) biodegraded wastewater. The typical carrier used today is shown in **figure 22**. Different types have been used in the last years – with more or less success – and others (hopefully better and less expensive) may be used in fu-

ture. Regarding the relevance of the type of carriers, see [ODEGAARD, GISVOLD AND STRICKLAND (2000)].

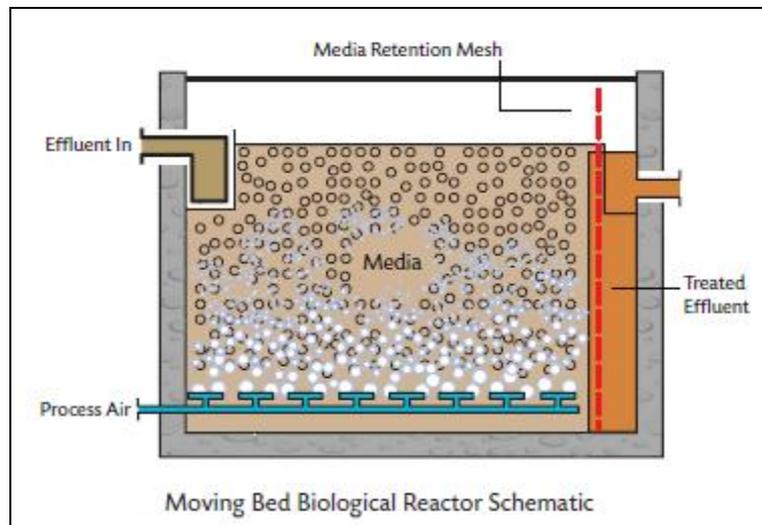


Figure 21: Principle of the suspended carrier reactor²⁶

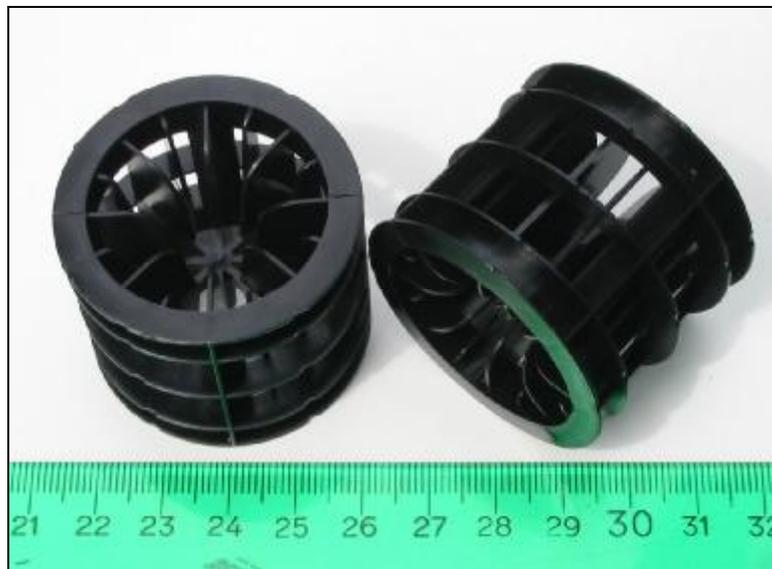


Figure 22: Typical biomass carrier in suspended carrier reactor © CM Consult

²⁶ www.bnm.ie/downloads/MBBR.pdf

For low BOD concentrations, another type of biofilm reactor is widely used in papermill wastewater treatment: the **wastewater biofilter**. The typical reactor type is a biological submerged filter containing a fixed, dense granular bed with influent wastewater flowing in an upward direction. The system normally uses as filter medium (biomass carrier) granulated burned clay (lightweight expanded clay aggregate), that serves as a biological contactor as well as a filter, eliminating the need for separate clarification and by this saving space²⁷. The system is shown schematically in **figures 23 and 24**. Recently process air is blown in via special nozzles in the strainer plate of the filter.

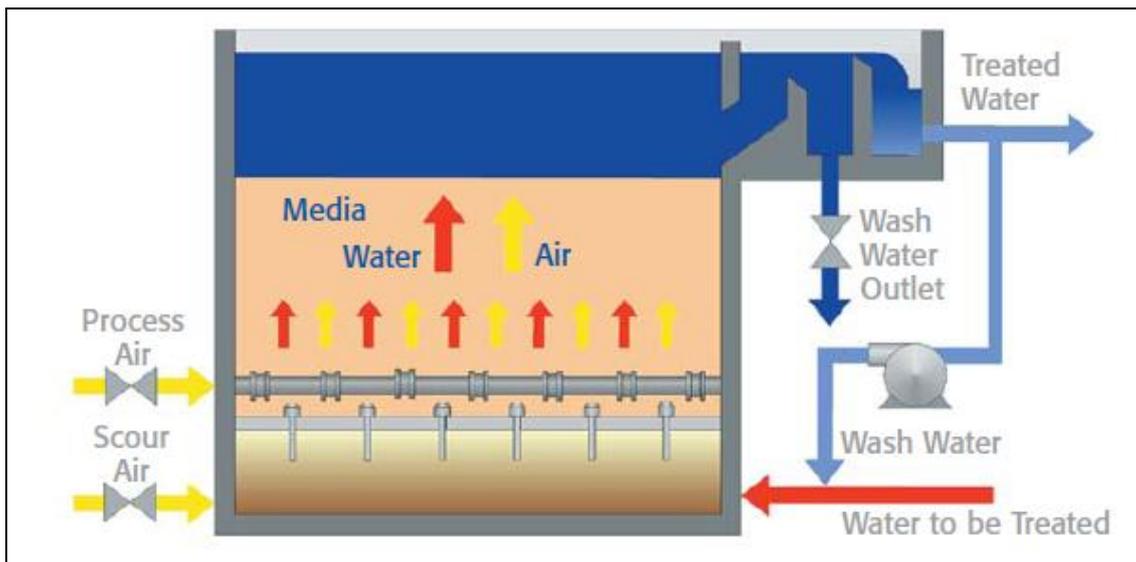


Figure 23: System of wastewater biofilter schematically
(© Infilco Degrémont²⁷)

²⁷ http://www.infilcodegrement.com/biofiltration_1.html

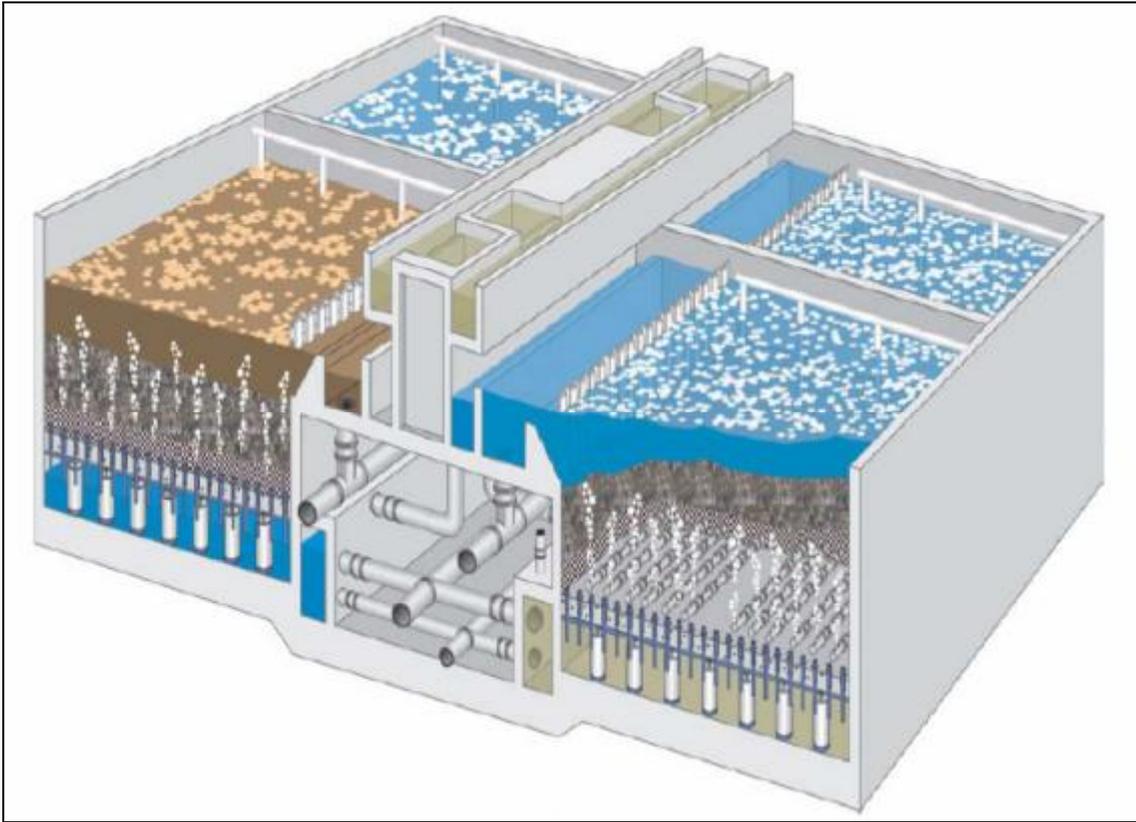


Figure 24: System of wastewater biofilter in operation
(© Infilco Degrémont²⁷)

The wastewater biofilter is used as a secondary stage following primary elimination of suspended solids or as a tertiary stage following another bioreactor or (for instance) an advanced oxidation step like ozonation [MÖBIUS (1999a)].

A rather new variant of the activated sludge process is the **membrane bioreactor (MBR)**. In this process, the secondary clarifier is replaced by membranes. Generally, microfiltration or ultrafiltration membranes are used, but sometimes, in order to get a higher effluent quality, nanofiltration membranes (the latter normally as a further membrane filtration step after a microfiltration unit). This has the advantage that the biomass concentration in the aeration tank can be kept substantially higher than in conven-

tional activated sludge reactors (usually 10 to 15 g/l versus around 3 g/l conventional). By this for keeping a certain specific BOD to mass load the reactor needs less volume, and the area required for the complete plant is much smaller. Due to the membrane separation the effluent of the system is almost free of suspended solids and can have – dependent on the type of membrane used – a much better quality than the outflow of a conventional activated sludge system in terms of SS and microorganism content. Therefore, the effluent is highly qualified for reuse. The system is not disturbed by the usual problems causing bad settleability of the biosludge like bulking or floating.

The membrane module can be placed inside or outside the aeration tank (either as crossflow membranes outside or as dead end resp. submerged filtration inside or outside in a separate tank, see **figure 25**). The transmembrane flux for the submerged membranes is chosen between 10 and 20 l/m²h, with a tendency to lower rates between 10 and 12 l/m²h. The type of aerators must be able to suspend a high biomass concentration of typically up to 15 g/l.

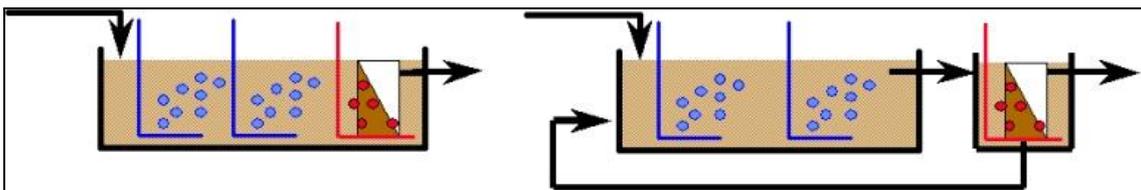


Figure 25: Different modes for installation of membrane modules in MBR²⁸

Different pore sizes can be used. However, system suppliers tend to offer ultrafiltration membranes with pore size < 0.05 µm. While microfiltration membranes (having bigger pores) would be less

²⁸ http://www.iwar.bauing.tu-darmstadt.de/personen/krause/membran_e.html

costly, they tend to blocking and fouling even more, so that the flux after some time might even be lower than using ultrafiltration membranes. So the relatively high flux reported in rather short time pilot tests using microfiltration membranes should not be a basis for design of plants. The flux in plant design nowadays is tending to 10 l/m²h in the average for submerged membranes.

A significant drawback for the use of MBR processes in papermill wastewater treatment are the substantially higher costs (in a modelled calculation suspended carrier plus activated sludge vs. MBR installation plus 30 % and total annual cost plus 67 % for MBR)²⁹. Therefore, only in cases where the advantages outline the higher costs the MBR will be used.

5.3 Combined Processes

Several reasons may be mentioned for the fact that in treatment of papermill effluents generally two stage bioreactors are preferred. The combined processes help to diminish the effects of big short time changes of concentrations, they help to avoid disastrous effects of shock loads of organics and especially of toxic substances, and they help to avoid floating biosludge on the final clarifier. But the main task of first stage high loaded reactors followed by activated sludge treatment is to avoid bulking sludge and generally to keep SVI low (that means below 150 ml/g) in order to achieve low SS in the effluent of the final clarifier and to establish a stable process in the reactor.

²⁹ C.H. MÖBIUS UND A. HELBLE, Membranbioreaktoren im Vergleich zu konventionell aeroben Abwasserreinigungsanlagen für Papierfabriks-Abwässer, Vortrag ZELLCHEMING-Hauptversammlung 29.06.2006, Wiesbaden

Three examples for complete plants for treatment of papermill wastewater are given to show the practical aspects of the combination of reactors as described in chapter 5.2: the anaerobic-aerobic system (**figure 26**), the aerobic high load followed by aerobic low load combination (**figure 27**) and the two stage wastewater biofilter (**figure 28**), which itself sometimes is combined with one of the afore mentioned process combinations as a final step, but then usually as a one stage filter.

In all the examples the pretreatment steps before the bioreactors are the same: a screen system to eliminate coarse solids (for instance plastic particles usually present in waste paper processing mills), a neutralization tank (depending on the pH range in untreated wastewater, not always necessary), a primary settler (may be a flotation or filtration unit as well), a hydraulic buffer tank (always filled partly, so that a concentration equalization is achieved as well), and a cooling stage (depending on effluent temperature and the discharge temperature requested not always necessary). The hydraulic buffer may be situated in front of the primary treatment as well.

The high loaded biostages are chosen according to the descriptions in chapter 5.2: an anaerobic granulated sludge tower reactor and an aerobic two stage suspended carrier reactor. The resp. low loaded aerobic stage in both examples is an activated sludge plant. For low concentrated wastewater, a two stage biofilter is shown (secondary and tertiary biofilter in combination).

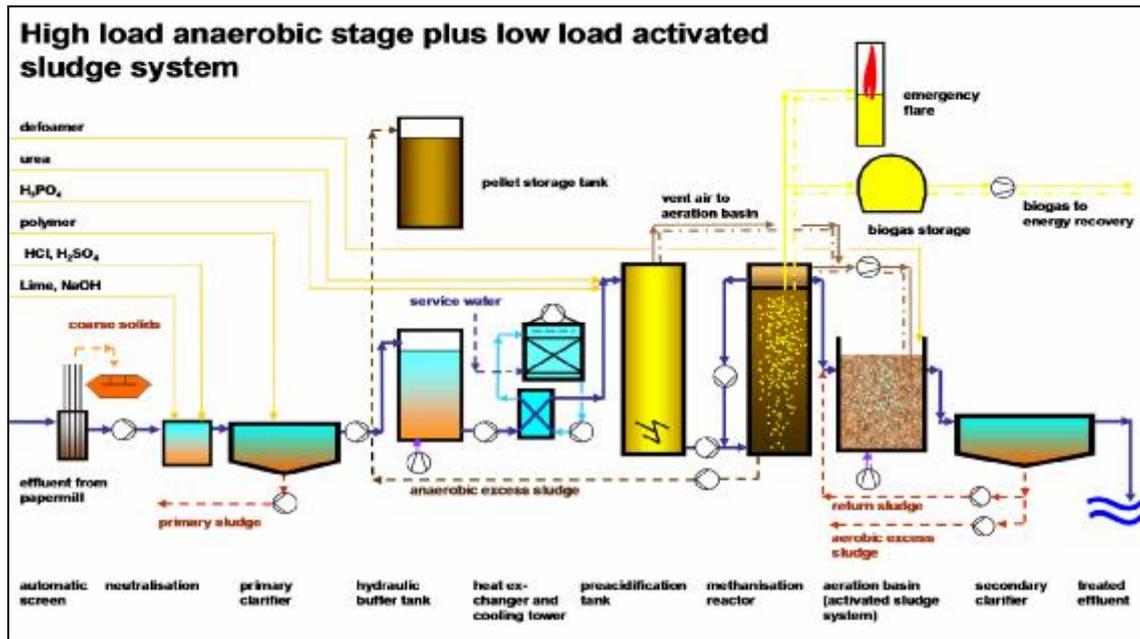


Figure 26: High load anaerobic tower reactor plus low load activated sludge system (© CM Consult)

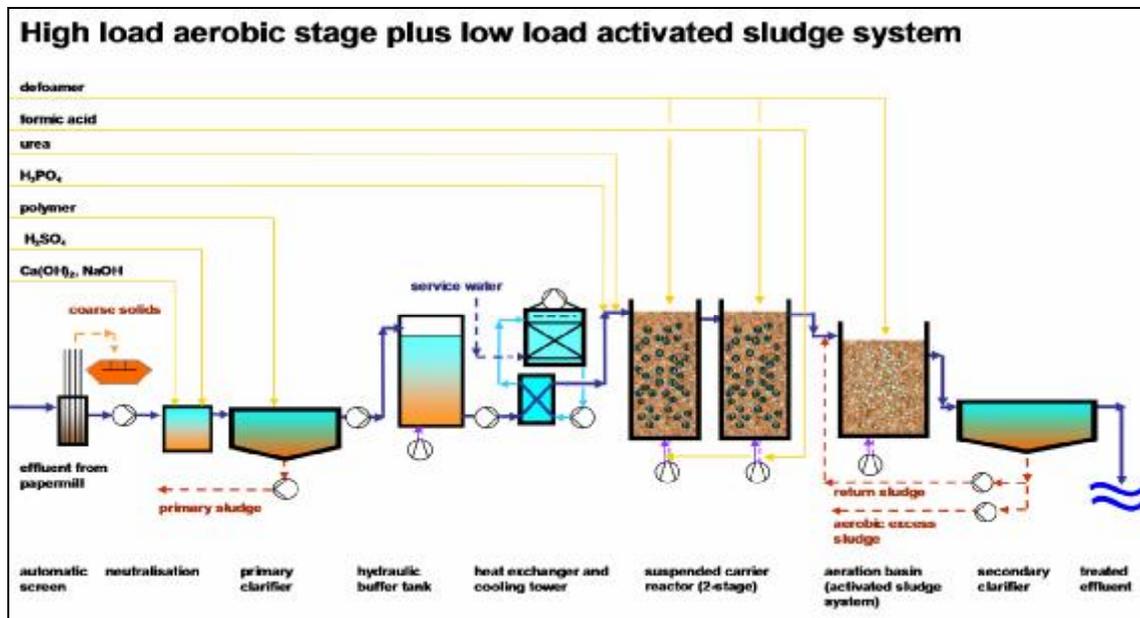


Figure 27: High load aerobic two stage suspended carrier reactor plus low load activated sludge system (© CM Consult)

examined in sufficient extent (because the production plant has to be set up first or the treatment has to be chosen for a planned change of production), information from chapter 4 together with specific experience of experts will help to determine the required data.

The use of statistically evaluated data for dimensioning of wastewater treatment plants is necessary (see annex, p. 97). It must be known on which statistical definition the dimensioning rules used are based. The reason is that the statistical spread in quantity and composition of the wastewaters is very different at different production plants and changing with the type of product (unlike in municipal wastewater treatment plants). A medium load that has proved well in one case can be unfit for another one because of larger fluctuations. Dimensioning using „maximum values" actually makes no sense because these values are always fixed arbitrarily (scientifically a maximum value can never be fixed for a production effluent). As a basis of quality and functional guarantees, maximum values are useless (maybe helpful only for the supplier), since the risk to loose guarantee is intolerable, if not the maximum values for the untreated water are fixed extremely high.

The following procedure has proven helpful in practice and is the basis for all dimensioning rules given in this book:

The load used for dimensioning of bioreactors – BOD for aerobic, COD for anaerobic reactors – always refers to the 24 hr day (B_d). More short-term load fluctuations are not relevant for the aerobic reactors discussed here and their use is not helpful for anaerobic reactors – which are more sensible for short-term shock loads – as well.

In order to take into account the statistical fluctuations of loads, and make different plants comparable, the 80th or 85th percentile of the data set is used as dimensioning value (in practice taken as mean value plus standard deviation $mv+s$ of the data set used, see annex, p. 97).

Some project engineers use 95th percentile ($mv+2s$), however this gives according to practical experience in papermills more safety reserve than required (causing unnecessary cost), when the same dimensioning rules are used as for $mv+s$ values.

Using COD load for dimensioning of aerobic plants is only acceptable, when the dimensioning values are recalculated using the specific BOD/COD ratio of the relevant untreated effluent (which may be different from those of municipal sewage).

In principle, the hydraulic dimensioning of the plants has to use the hydraulic peak load. This is described as a short time value and met sufficiently well by use of the maximum hourly wastewater quantity Q_h . Usually, this is difficult to find with sufficient assurance. Therefore, it is acceptable to calculate $Q_{h,max}$ by multiplying $Q_d/24$ with a proper factor, generally 1.6 to 2 before a hydraulic buffer and 1.3 following a hydraulic buffer. The factor itself is dependent of the statistical quality of Q_d , which well may be a mean value of yearly data.

The following data are used in dimensioning wastewater treatment plants for papermill effluent. The relevant values for certain types of reactors are given in the following sub-chapters. For detailed engineering of treatment plants, additional data may be required, which are not discussed here. For calculation of the design parameters see “Calculation Formulae” on page 11.

- Specific volume loading B_V [$kg/(m^3d)$]: For aerobic reactors preferred $B_{V,BOD}$, for anaerobic reactors $B_{V,COD}$.

- Specific sludge loading B_X [kg/(kgd)]: For aeration tank in activated sludge treatment preferred $B_{X,BOD}$.
- Specific solids volume loading $B_{V,SS}$ [kg/(m³d)]: For Biofilters.
- Specific surface solids loading B_A [kg/(m²h)]: Primarily used for dimensioning of flotation units.
- Specific surface volume loading q_A [m³/(m²h)] (same as upflow velocity m/h): For clarifiers, flotation units and biofilters.
- Specific surface sludge volume loading q_{SV} [l/(m²h)]: For secondary clarifiers, depending of MLSS and SVI of the biomass.
- Weir overflow rate q_l [m³/(m²*h)]: For clarifiers, strictly limited only for secondary clarifiers.
- Hydraulic retention time HRT [h]: For most types of bioreactors a certain minimum HRT is required for the degradation process. For film reactors a very low HRT may cause a wash out of biomass.

Remark: Generally, the MLSS or TS is used to characterize the biomass in an activated sludge reactor. However, in order to get a value nearer to the relevant active biomass, sometimes the organic matter oTS, meaning the TS without the burning residue (ash) is used. Since usually the loss on ignition (LOI) of the biosludge in papermill activated sludge plant is between 65 and 75 %, the relevant dimensioning and operation rules may be (and in fact are) adjusted to this range. Therefore, if the LOI in a special mill differs very much from this range (for instance LOI below 50 %) the given standard rules have to be corrected to oTS using an average LOI of 70 % for the conversion. The reason why we do not refer generally to the oTS is, that this would pretend a higher accuracy of the rules than they really have.

5.4.2. High loaded bioreactors

Anaerobic reactors are dimensioned always using COD volume load (instead of the preferable BOD load for aerobic reactors). The granular sludge tower reactors described in chapter 5.2.1 normally are built about 20 m high with a COD volume load $B_{V,COD}$ of 16 to 22 kg/m³d. The elimination efficiency depends strongly on the wastewater composition and may be expected generally between about 60 and 75 % COD.

Hydraulic retention time (HRT) shall not be too low, but the modern reactors described here do allow a shorter retention time than older reactor types (like UASB or even worse contact reactors). But still the HRT is limiting the use of the anaerobic process economically, since for a low concentrated wastewater the acceptable volume load will be lower in order to achieve the necessary HRT. General HRT limits cannot be given, since they depend strongly on the type of wastewater and the construction of the reactor.

Upflow velocity will play a role in the granular tower reactors, but this strongly depends on the type of separating system.

Suspended carrier reactors as high loaded first biostage for treatment of papermill wastewaters are designed with a BOD volume load $B_{V,BOD}$ of 4 to 6 kg/m³d expecting a BOD elimination of about 50 %. When they are designed as two stage reactors with a similar specific BOD load, the achieved BOD elimination will be higher (60 to 70 %).

When the hydraulic retention time HRT is too short, the elimination efficiency will decrease due to a wash out of biomass. The limit depends on the type of carrier, generally it is expected at between 1.5 and 2 hrs.

The reactor must have a good aeration system, which is necessary to keep the carriers suspended. The aeration capacity must be sufficient to avoid settling of the carriers when they are loaded. Generally, the reactors are operated with 3 to 4 mg/l of dissolved oxygen. The suspension of the carriers will be improved by certain supporting dimensions of the reaction vessel, for instance a cylindrical tower with at least 12 m height and a diameter of about 6 m.

5.4.3. Activated Sludge Treatment

A low loaded activated sludge stage is operated with a BOD sludge load $B_{X,BOD}$ of about 0.12 to 0.16 kg/kgd. With a typical biomass concentration of 3 to 5 g/l, this means a BOD volume load $B_{V,BOD}$ of 0.4 to 0.8 kg/m³d. The oxygen concentration in the aeration tank shall be kept between 2.5 and 3.5 mg/l.

Normally the aeration is responsible for mixing the reactor as well as to achieve the required oxygen input. Different types of aerators are in use (e.g. fine bubble, coarse bubble, surface aerators, ejector aerators, jet aerators, slot injectors³⁰). They have to be chosen regarding the size and depth of the aeration tank.

The secondary clarifier belonging to the activated sludge stage (if not a flotation, filtration or membrane filtration unit for solids separation is chosen) needs a surface large enough to avoid loss of biomass (spoilage of the quality of the clear water and decreasing the efficiency of the bioreactor). The upflow velocity (equal to specific surface volume loading q_A) of course must be substan-

³⁰ <http://www.hait.ac.il/jse/inpress/1040715.pdf>; <http://www.en-found.com/ic9.htm>;
http://www.idswater.com/Common/exhib_94/Brochure_KlaSlotInjector.pdf

tially below the settling velocity of the biomass, which means below about 0.5 m for a good settling biomass. The sludge volume surface loading q_{SV} in papermill plants shall be below 300 l/m²h. For both values, only the wastewater inflow (roughly equal to outflow) is taken into calculation, not the amount of return sludge, since this is drawn from the bottom of the tank.

Instead of a conventional sludge scraper, a suction scraper should be used (avoiding long retention time of the sludge in the settler).

Several different types of activated sludge reactors have been designed. In order to get the required elimination of organics and to keep good settling conditions for the biomass oxygen concentration and the specific BOD to mass load in the reactor have to be kept in a certain range, depending on the type of reactor as well (see chapter 5.2.2).

Some of the conditions for different process and reactor types are given (as an example) in **table 8**:

Table 8: Conditions for operation of different types of activated sludge reactors

type or stage	B_x kg/kg*d	SVI ml/g	O_2 mg/l
1 stage completely mixed tank AS reactor	0,25 - 0,30	300	2,0 - 3,5
AS cascade reactor in 1st cascade tank	1,20 - 2,00	100	0,4 - 0,8
AS cascade reactor in final cascade tank	0,10 - 0,20	150	2,5 - 3,5
2 stage AS reactor stage 1	1,40 - 2,00	100	0,4 - 0,8
2 stage AS reactor stage 2	0,12 - 0,22	200	2,5 - 3,5

The amount of return sludge Q_r in the system is a critical value for the stability of the process. If it is not high enough, biomass will accumulate in the final clarifier and so be lost for the process. We calculate Q_r from the ratio R_v related to the amount of effluent Q passing the reactor:

$$R_v = Q_r : Q * 100 [\%].$$

The necessary R_v for a stable process (stationary state) depends on the ratio of X_u to X_{SS} (MLSS), which is lower, when SVI is high. Assuming a given stationary state, R_v required is calculated as

$$R_v = X_{SS} / (X_u - X_{SS}),$$

provided

$$X_u - [X_{SS} (1 + R_v) / R_v] \leq 0.5$$

(this is a prerequisite for the stationary state).

Therefore, when high SVI has to be expected (200 to 300 ml/g) the installation has to provide the possibility to run high amounts of

return sludge, meaning 200 to 300 %. Generally, a papermill wwtp with low risk of bulking sludge (two stage plant with high loaded first stage) should be able to run return sludge up to 200 %.

5.4.4. Biofilters

Biofilters are designed using BOD volume load $B_{X,BOD}$ (generally between 6 and 8 kg/m³d), upflow velocity q_A (up to about 10 m/h) and solids volume loading $B_{V,SS}$ (total suspended solids mass as a sum of inert solids going to the filters and excess biomass produced by BOD elimination, depending on other factors and commanding the backwash intervals). If the solids loading is high, the intervals of backwash are short. Generally, this interval should be 24 hrs in single stage filters or second stage of a two stage filter and at least 12 hrs in the first stage of a two stage filter.

The biofilter is operated with a low hydraulic retention time of about 0.5 hrs (which obviously is no problem for the degradation) and a hydraulic surface load q_A of around 6 m/h (up to 10 m/h). The typical depth of the filter bed is 3 m (up to 4 m, but it should not be less than 3 m).

During the backwash time, which takes including the following filtration start until effluent is clear enough about 1 hr, no effluent from the filter may be discharged. Therefore a hydraulic retention tank or (preferred) several, at least 2, filters are needed. The loads (BOD volume load, hydraulic surface load, solids volume load) have to be calculated for the filters in operation during backwash of 1 filter element. Most plants have 4 to 6 filter elements running parallel, so that only part of the time 1 element is in backwash mode.

6. Advanced Effluent Treatment

With the processes described in chapters 3 to 5 in suitable combination of different types of reactors, adequate dimensioning and proper operation provided, always an effluent quality according the state of the art or best available technique (BAT) can be achieved for papermill wastewaters. In special local situations, however, it can be required for protection of the receiving water to clean the wastewater furthermore. For papermills generally this concerns the remaining COD concentration (that is the persistent substances), which has to be decreased by procedures of advanced treatment.

Generally speaking, advanced treatment processes of the kind required here may be optionally applied either before or after biological effluent treatment. For all processes that have proven operational in pulp and papermills, it may safely be stated that – unless partial flows can be successfully treated – physical and physico-chemical treatment stages inserted after the biological treatment are most economical and effective. Only these are discussed here, therefore.

The following processes are used as tertiary stages for advanced treatment of papermill wastewaters:

- a) tertiary wastewater biofilters,
- b) membrane processes (ultrafiltration, nanofiltration, reverse osmosis),
- c) evaporation,
- d) precipitation and coagulation,
- e) advanced oxidation processes (AOP).

Sandfilters and polishing ponds following the secondary treatment are not considered to be advanced treatment, since they only have a substantial additional treatment function when the secondary stage does not work properly.

With **tertiary biofilters** between 14 and 33% COD elimination is obtained, depending on the composition of the treated wastewater, related to the effluent quality of the secondary stage as 100 % [MÖBIUS (1999a)]. The interdependency of the ratio BOD/COD before biofilter treatment and the COD elimination in the biofilter is given in **figure 29**:

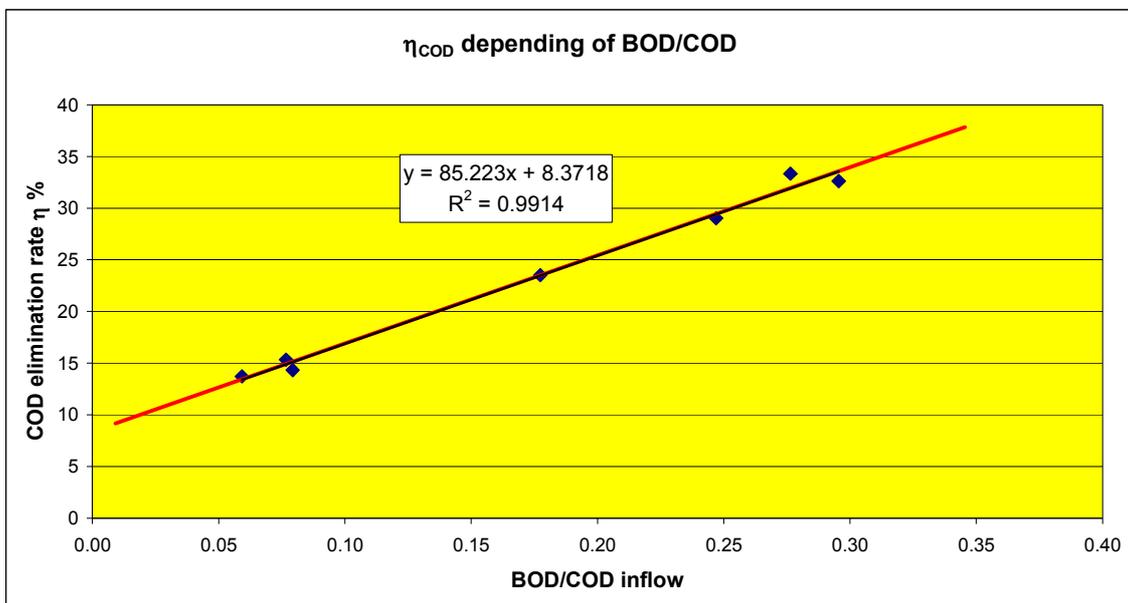


Figure 29: COD elimination in tertiary biofilters related to the effluent quality of the secondary stage as 100 % [MÖBIUS (1999a)]

Membrane processes as well as **evaporation** (followed by condensation) of the effluent are technical possibilities of the advanced treatment which, until now, could not gain acceptance for different reasons. The high operation costs and energy required are a disadvantage of both types of processes. Fouling, blocking and

ageing problems of the membranes, which are not solved yet satisfactorily, are a drawback for the membrane processes.

A completely unsolved problem in papermills (generally not so in pulp mills) is the question what to do with the concentrated extracts of evaporation or the concentrate of membrane processes.

Similar and higher elimination rates as using tertiary biofilters are achieved with a **precipitation and flocculation** using salts of trivalent metals, e.g. iron or aluminium salts, in the tertiary step. Since considerable lots of predominantly inorganic sludge are produced and have to be removed, however, this procedure is not considered having a promising future, although it is not very expensive, as long as sludge disposal costs are low.

A process which has achieved high reputation whenever the elimination achieved in the tertiary biofilter is not sufficient is the **advanced oxidation process (AOP)**, which is operated in the type of ozonation with subsequent treatment in a tertiary biofilter in two Central European papermills (Germany and Austria) with good and stable results^{31,32}.

Processes for oxidative destruction of non-biodegradable substances in wastewater of the pulp and paper industry are using oxidants (partly in combination with catalysts) or high-energy radiation including ultra violet light. Advanced oxidation treatment here is defined as a combination of chemical and biochemical oxidation [MÖBIUS AND CORDES-TOLLE (1997)], where the biodegradable compounds formed in the oxidation step (which should

³¹ SCHMIDT, T.; DEMEL, I.; LANGE, S., Weitergehende Abwasserreinigung von Papierfabriksabwässern mit Ozon: Konzeption und erste Betriebserfahrungen. ipw Das Papier, - (2001), No 2, p. T30-T34.

³² KAINDL, N., Weitergehende Abwasserreinigung mittels Ozonung und nachfolgender Biofiltration. ipw Das Papier, - (2006), No 1, p. T1-T6.

be operated as a partial oxidation) are degraded in a further biostage.

Advanced oxidation treatment is applied to a completely biodegraded effluent. The process applied so far in paper industry has been developed in the 1990s [MÖBIUS AND CORDES-TOLLE (1997), ÖLLER et al. (1997), MÖBIUS (1999b), MÖBIUS AND HELBLE (2004)]. It is a combination of ozonation with following biodegradation in a biofilm reactor. This combination is ecologically preferable and allows economic optimization. High elimination rates of persistent COD, AOX and colour are achieved.

The combination of ozone plus wastewater biofilters makes use of the effect of partial oxidation in which with reduced use of expensive chemical oxidants persistent COD becomes biodegradable. A far-reaching elimination of AOX, colour and other disturbing substances like complexing agents (EDTA and DTPA, for instance) is achieved simultaneously.

The partially oxidized compounds, now biodegradable, are eliminated in the following bioreactor. Due to the relatively low concentrations of biodegradable compounds following the partial oxidation, for the subsequent biotreatment only biofilm reactors can be used. The tertiary biofilters [MÖBIUS (1999a)] used in these applications today are the only biofilm systems tested for this purpose and so far appear to be the best suited type of reactor. The combination has to be optimized technically and economically to achieve best possible results with minimum costs.

A schematic presentation of this process is given in **figure 30**.

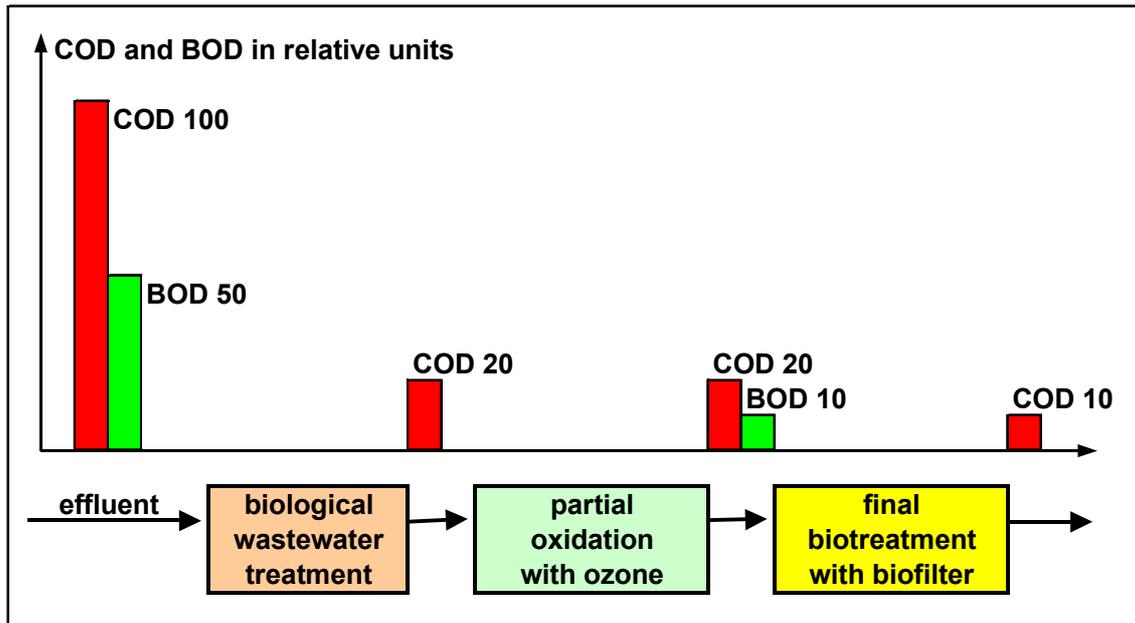


Figure 30: Schematic presentation of the process of chemical-biochemical oxidation of papermill wastewater

The efficiency of the process depends on the optimum ozone dosage in order to achieve maximum BOD/COD ratio or, with other words, best possible biodegradability (see **figure 31**). Once this is achieved, maximum COD elimination in the subsequent biofilm reactor will result [MÖBIUS (1999a, b)].

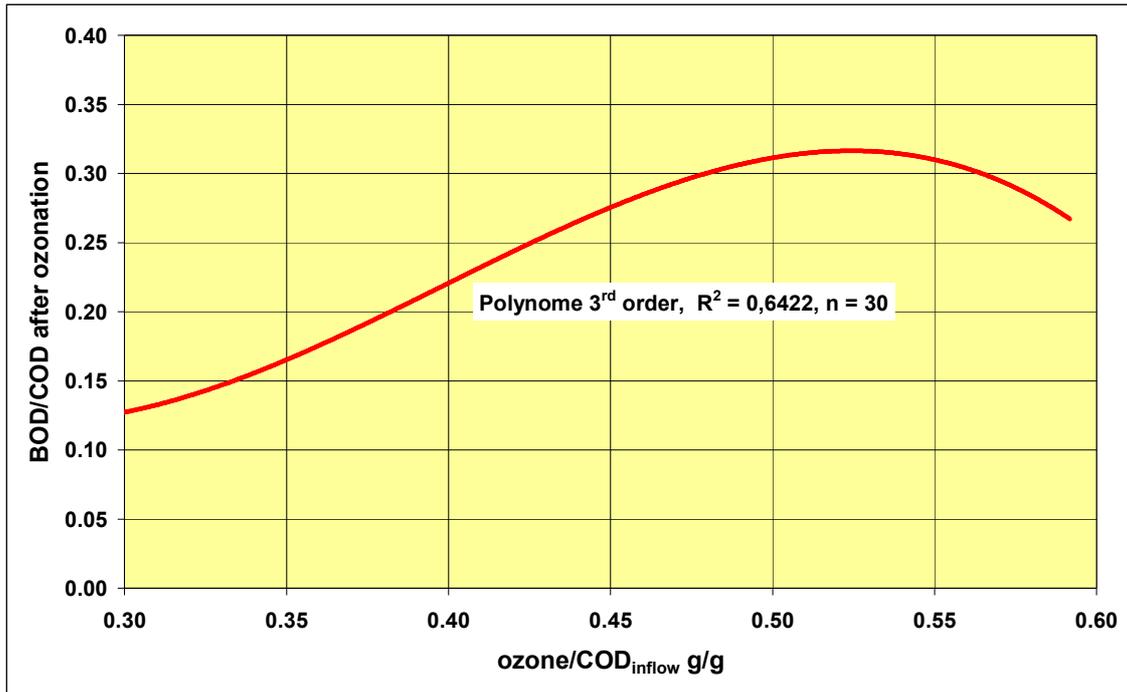


Figure 31: Optimization of ozone input to achieve maximum biodegradability

Depending on the type of production, the advanced oxidation process may be sufficient even for extensive recycling of treated wastewater to the production process, up to 80 %. Only for certain types of specialty paper production requiring very low electrolyte concentration in the product the possibility for recycling treated effluent to the production following the chemical-biochemical oxidation process may be limited down to about 30 % without a further elimination of electrolytes.

Generally with systems like these elimination rates of up to 60 % COD, 70 % AOX and 85 % colour (with respect to the typical lignin compound brown colour, not necessarily valid for soluble dyes) are obtained related to the biological treated effluent, using specific ozone input – depending of the ozonation system – of 0.4 to 1.0 g ozone per g COD eliminated in the combined process. For

papermill application, final optimisation and results should be evaluated in either laboratory batch or pilot test. Higher specific ozone input is due to equipment or technology that is not state of the art.

Operation costs of a plant like this will be 0.8 to 1.4 € per kg of COD eliminated, depending on size and technical standard of the plant. This means in typical cases of papermill wastewater operation costs for the advanced treatment stage of 0.05 to 0.2 € per m³ of wastewater (elimination of 50 to 200 mg/l COD in tertiary treatment). For a typical specific wastewater amount of 10 m³/t, this would mean 0.5 to 2 € per ton of paper produced. In a recently accomplished plant in Austria operation cost (without capital cost) are reported as 1.3 €/kg COD resp. 0.55 €/t of paper³².

When the COD elimination obtained at optimum ozone input is insufficient to meet effluent quality requirements, a two stage system of ozonation plus biofilter is more efficient in terms of operation costs than a single stage system using ozone above the optimum.

In pilot tests with a rather difficult to treat effluent (following activated sludge treatment) with a two stage system COD elimination of 86 % with a specific ozone input of 0.64 g ozone per g COD eliminated in the combined process have been obtained, as is shown in **figure 32**. Colour reduction was 98 %, starting with a dark brown effluent after activated sludge treatment. AOX elimination was more than 80 %. All these data are average values of the final test run.

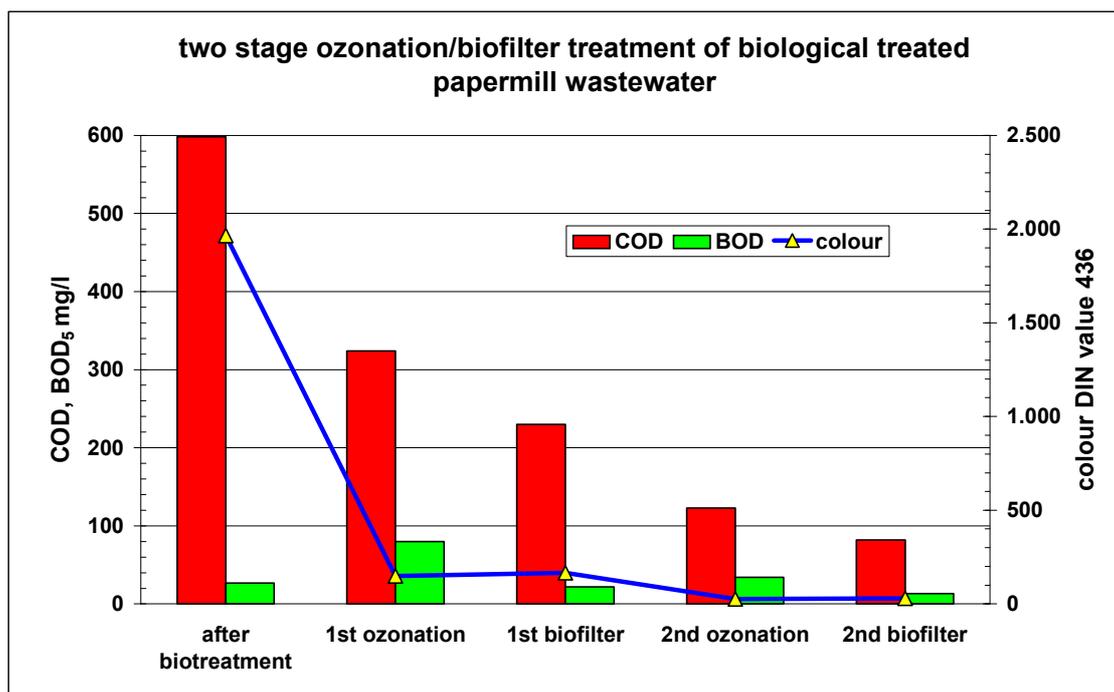


Figure 32: Results of two stage pilot plant tests with papermill wastewater after activated sludge treatment.

Finally, it may be concluded that an advanced oxidation process (AOP) is a highly qualified way of advanced treatment for pulp and papermill effluent wherever elimination of COD and / or AOX above the limits of conventional biotreatment is required. The natural brown colour of these wastewaters, generally increased after bio-treatment, is reduced very efficiently by oxidation as well.

Today the only technically developed process of advanced oxidation for biological treated pulp and papermill wastewater is ozonation followed by a wastewater biofiltration. Oxidation of un-

treated papermill wastewater generally is economically not feasible³³.

This type of AOP is able to eliminate COD with 60 % (single stage) up to 85 % (two stage) with a specific ozone consumption of 0.4 to 1.0 g ozone per g COD eliminated, depending on the ozonation system. Operation costs of a plant like this will be 0.05 to 0.2 € per m³ of effluent treated, depending of the type of wastewater as well as the size and technical standard of the plant. For elimination rates of more than 50 to 60 % COD the two-stage system will be more economic than the single stage system.

Since this type of advanced oxidation wastewater treatment using ozone is still at the beginning of the development (start up of the first technical plant in a papermill was in 1999), we may look forward to even higher efficiencies at less cost in the near future.

³³ An example for an exception is the ozonation of a whitewater with very low BOD concentration in order to eliminate soluble dyes for recycling of the treated water (no biotreatment involved)

Annex:

Some simple remarks on statistics

In the typical careful operation of a papermill wastewater treatment plant (wwtp), numerous data (normally up to 365 per annum for certain parameters at several sampling points) are recorded. They require a statistical (and preferably also graphic) evaluation – more specifically we talk of descriptive statistics. Without this evaluation the data, registered with high costs, are valid for control and operation of the plant, but they cannot be used for further evaluation and handling of problems. So the statistical and graphic evaluation suits the purpose of the operator, but in many cases is also required for the authorities.

Quantity and composition of papermill wastewaters are subject to inevitable deviations, whose kind and size are characteristic for the individual case. The fluctuations have to be considered for the design of a wwtp as well as in defining operational data for the reactors, like for instance B_x . Calculations using average loads as well as such using „maximum“ loads both are not pertinent for the operator of the wwtp. The reason is that the medium load does not consider the specific fluctuations of the untreated wastewater (forcing unnecessary additions to the values fixed for design and operation). On the other hand, “maximum” values in fact are not defined scientifically and therefore are always fixed arbitrarily. An exception is the amount of effluent, for which an admissible maximum value has to be fixed (normally corresponding with the allowed maximum discharge flow).

In this book according to a standard widespread in the industry, the following statistical values are used:

md = median of the available data or 50th percentile, mv = arithmetical mean value or average, s = standard deviation of a grab sample calculated for n-1, v = coefficient of variation or relative standard deviation, min = minimum (resp. lowest measured) value, max = maximum (resp. highest measured) value, mv+s corresponds nearly to 80th percentile (80% of the values are to be expected below this value) or exactly 83.5th percentile, mv+2s corresponds to 95th percentile, accordingly are to be understood mv-s as 20th percentile and mv-2s as 5th percentile, n = number of data evaluated or number of values in the grab sample.

The reading of a standard textbook of mathematical statistics is to be recommended basically, although this can lead to some confusion. Here a simplified description with some typical examples is given.

The statistical dimensions applied here are based on the Normal Distribution or so called Gaussian Distribution³⁴. Their application assumes that the evaluated measured values comply with the following conditions:

- The data have to be recorded continuously (e.g., daily sampling or measurements with a constant frequency per week).
- All values must have been determined using the same method (kind of sampling, sample preparation, analytical procedure).
- The number of the evaluated data must be high enough (if this is doubted it shall be controlled by statistical methods; generally a set of at least 50 values is good enough for our purposes).

³⁴ German mathematician CARL FRIEDRICH GAUSS (1777 - 1855)

In practice, normal distribution often does not apply to the data set when wastewater data are to be analyzed (cf. **figure 33**, see also fig. 34). In this case, plotting a density function by applying the classes of measured data on the abscissa (x axis) against the relative frequency in % on the ordinate (y axis) results in a curve whose maximum lies not in the middle of the whole distribution, but is shifted either to the left ("positive skew") or to the right ("negative skew "). Effluent concentrations of wwtp often show a positive skew. However, generally the type of statistics based on the Gaussian Distribution is good enough for the purpose (i.e. the deviation from the normal distribution is not big enough to require a non Gaussian type of statistics). For an analysis of this kind, it is important not to choose the classes too small and the number of values has to be big enough.

For further explanation of these statements see in **figure 34** the same data set (COD concentrations in wwtp effluent for a complete calendar year) and in **table 9** the statistical data of these values.

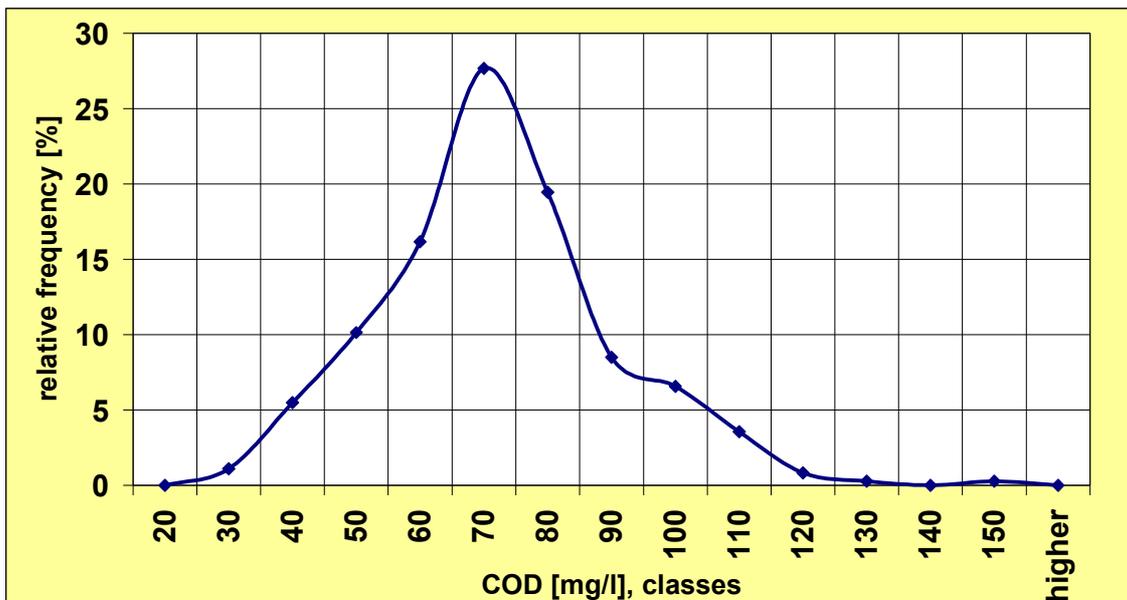


Figure 33: Distribution function of the COD values in the effluent of a wwtp (daily 2 hrs samples for 1 year, n = 366)

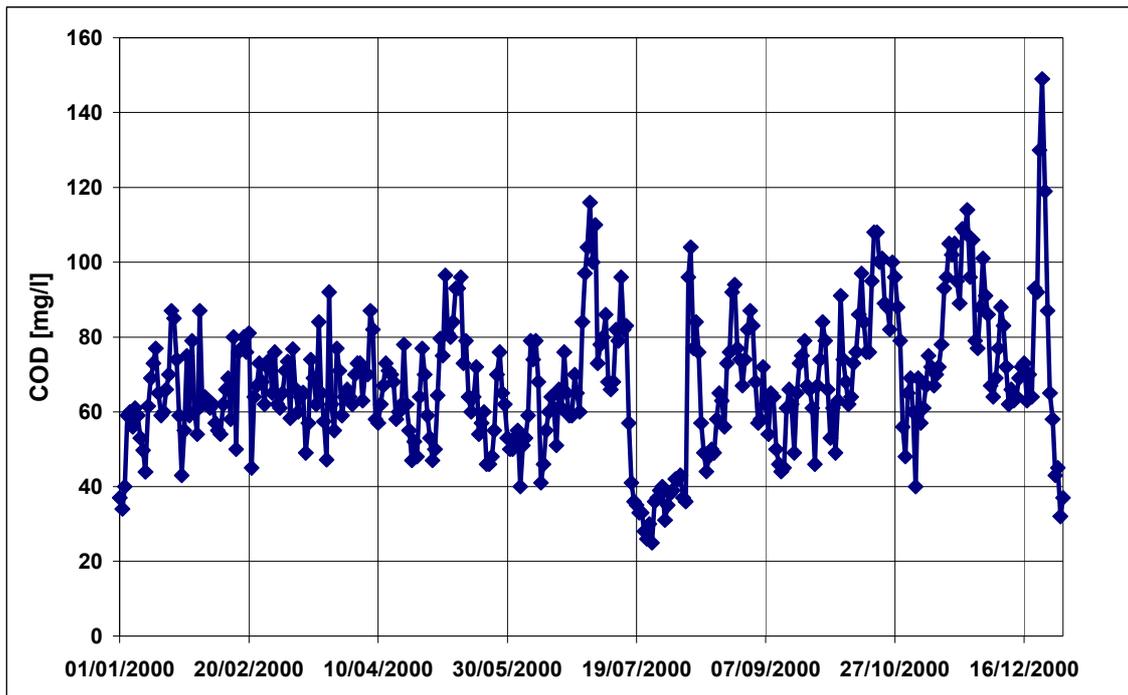


Figure 34: COD concentrations in the effluent of a wwtp for 1 year (same set of data than in fig. 33)

Table 9: Statistical evaluation of the data shown in fig. 34

statistic parameter	COD mg/l
md	573
mv	564
s	190
v %	33.6
min	115
max	1,261
mv+s	754
mv+2s	944
mv-s	375
mv-2s	185
n	366

A further practical example is given in **figure 35**. Here the hourly distribution of the amount of wastewater is plotted for 1 day. The daily flow equalling the maximum allowed amount of effluent is

assumed to be 10,000 m³/d. The two plotted sets of data are calculated for assumed coefficients of variation of 15 resp. 30 %. It shall be pointed out that the hourly flow rate is almost never above the mv+2s or below the mv-2s line (1.3 and 0.7 for v 15 % resp. 1.6 and 0.4 for v 30 %).

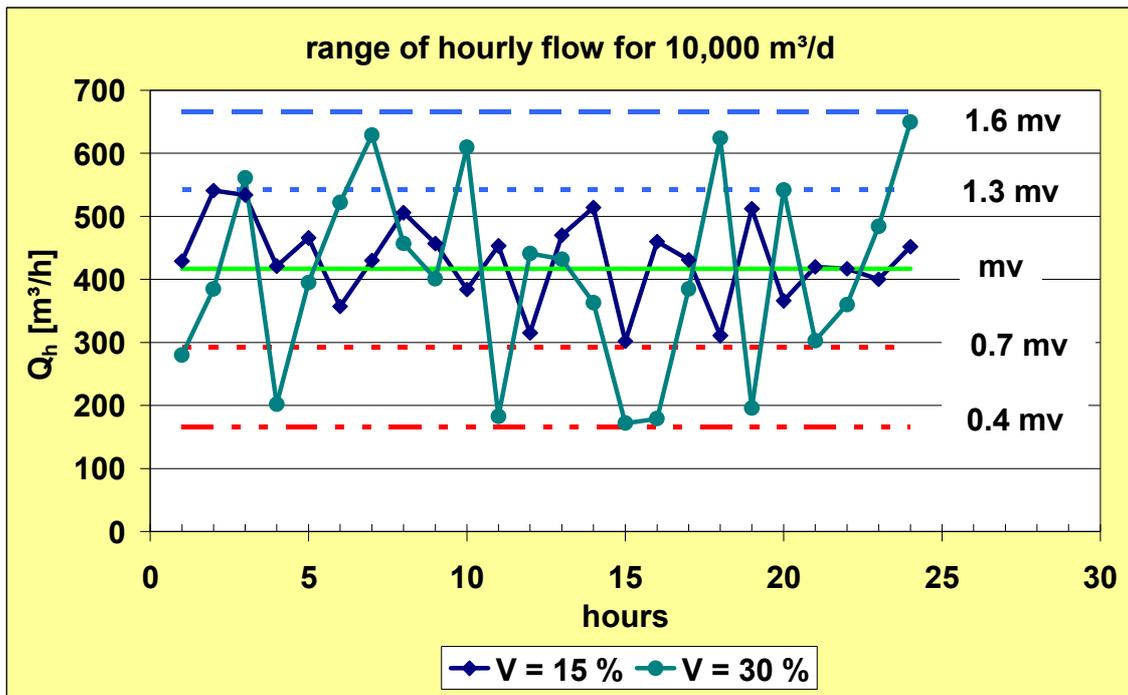


Figure 35: variations of hourly flow for the same amount of effluent per day and different coefficients of variation

For hydraulic dimensioning of reactors in wwtp the maximum short time flow is relevant. Normally the hourly amount of effluent is used, taking the 95th percentile as a „statistical maximum value" instead of the real maximum, which can never be known for sure. In the example given in fig. 35 (Q_d 10,000 m³/d) with an average flow of 417 m³/h the statistical maximum is, depending on the coefficient of variation, either 542 m³/h for v 15 % or 667 m³/h for v 30 %. The bigger v would be typical for a plant with little hydraulic buffering in a papermill.

Since the calculation of the data plotted assumed the maximum amount permitted as the real daily effluent, which in fact normally will not be reached, the assumption of 95th percentile resp. mv+2s as dimensioning value is justified.

So the relevant short time effluent flow in this example can be calculated from the daily flow using

$$Q_{h,max} = (Q_d / 24) * f, \text{ or}$$

$$Q_{h,max} = Q_{h,mv} * f,$$

with $f = 1.3$ for $v = 15\%$ and $f = 1.6$ for $v = 30\%$.

On the other hand, for calculation of bioreactors in the wwtp according to organic load the daily values are relevant. In this case, the 80th (resp. 85th) percentile or mv+s has proven as a sufficient dimensioning value, when the dimensioning rules are adequate to this approach.

For defining the relevant 80th percentile load, it is necessary to evaluate a set of load data statistically. The calculation from the statistically evaluated flow rates and the inflow concentrations generally is not precise enough. When the statistical evaluation of the loads is not applicable assumptions are to be used, like for example $c_{BOD,mv} = 300 \text{ mg/l}$, $Q_{d,mv} = 6,000 \text{ m}^3/\text{d}$, so $B_{d,BOD,mv} = 0.3 * 6,000 = 1,800 \text{ kg/d}$, $v = 30\%$, so $B_{d,BOD,mv+s} = 1,800 * 1.3 = 2,340 \text{ kg/d}$.

An example for the fluctuation of the treated effluent values in one year gives **figure 36** (effluent COD wwtp, daily 2 hrs mixed samples, $n = 366$, $mv = 68 \text{ mg/l}$, $v = 27\%$). Further information can be found in the BREF pulp and paper [BREF (2001)] in annex IV, Examples for Variations of Emissions.

This plot can be used for assumptions regarding the probability that a certain value will be exceeded.

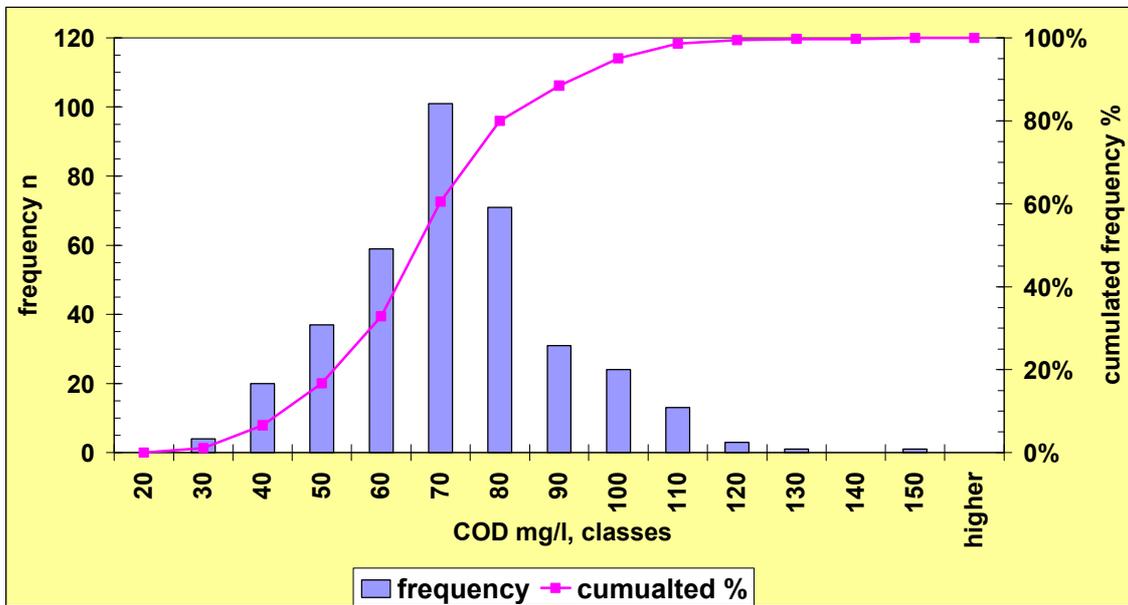


Figure 36: Histogram of COD concentrations in the effluent of a wwtp

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