Proposal of BAT candidates for prevention and reduction of emissions from hazardous chemicals

The EU funded INTERREG-project “Hazardous industrial chemicals in the IED BREFs (HAZBREF)” (2017–2020) has the objective to increase the knowledge of the industrial sources and measures to reduce the release of hazardous chemicals. The aim is to improve or complement the way these substances are addressed in IED BREFs by inter alia making better and more systematic use of data from various EU regulatory frameworks (namely REACH, Water Framework Directive). This will contribute to reducing the use of hazardous substances in industrial installations and diminish the emissions to the environment. (https://www.syke.fi/projects/hazbref)

To increase the knowledge on the management of hazardous chemicals in industries case studies were carried out in three different sectors, including the textile sector. The aim of the case studies was to analyse current best practices of environmental permitting and chemical management and to identify options for prevention and reduction of emissions. In the textile sector four case studies have been carried out in installations located in Germany, Poland and Sweden.

One output of the case studies are descriptions of potential BAT candidates described according to the 10-heading structure outlines in the BREF-Guidance (2012/119/EU). The purpose of this contribution is to feed into the ongoing TXT review process so that the proposed 5 techniques can be considered and assessed by TWG members and the EIPPCB. The following five proposed BAT candidates relate to both general chemical management (two descriptions) as well as in-process and end-of process treatment of chemical containing waste streams (three descriptions).These techniques are not yet listed in the TXT BREF. Several of these techniques have been identified from the four case study companies covered under the scope of HAZBREF project. With regard to one technique, the case study company which applies this technique did not consent being named as a reference company. The case studies revealed that participating companies apply various BATs already listed in the current TXT BREF (2003). Since these case studies represent only a small and not necessarily representative sampling of the sector as a whole, some additional techniques have been identified drawing from experiences with other companies outside the three case study countries. In that case, the company and country are specifically mentioned. While reference is being made in the TXT BREF to general management of chemicals, systematic approaches such as described in the corresponding BAT candidate descriptions are not yet specified in the TXT BREF 2003. However, analysis of the case companies and experience from interaction with textile companies in and outside Europe indicate that these are generally and increasingly demanded to enhance transparency about and control of chemicals. With regard to the emission factor as mentioned in the description of technique “Treatment of waste gas from stenters with special consideration of methanol”, the concept follows the prevention principle to only use products with a low emission potential. Thus, in many cases, waste gas treatment is not required as emission limit values are complied with. Against this background, the emission factor concept can be considered as a very cost-effective approach.

The following five BAT candidate descriptions are provided for the purpose of being considered by the TWG and the EIPPCB in the context of the ongoing TXT BREF review process.

Establishment and use of a central chemical database as fundament and tool for systematic chemicals management

Description:

Textile finishing industries use a considerable number of chemical products[1] (100 – 300) for the different finishing processes (pre-treatment, dyeing, printing and final finishing). The chemical products have to be selected not only with respect to their finishing effects (desired product qualities) but also regarding their environmental properties (e.g. acute/chronic human and aquatic toxicity, biodegradability/eliminability).

Technical description:

In order to ensure the availability and completeness of information necessary for a responsible chemical management, the relevant data for the chemical auxiliaries and process chemicals used are entered, collected and managed in one dedicated database by the respective installation. From the collected data a tailored compilation and assessment of information can be generated which can serve the specific information requirements of different organizational units within the installation. The main and commonly used sources of data used for the different chemical products are the material safety data sheets (MSDS)[2] and to some extent the Technical Instruction Sheets. In order to allow just-in-time evaluations it is further important to link this data base with a comprehensive modern production planning and control system.

The data base serves as the starting point for making compilations and conducting evaluations relevant for the different chemicals management needs such as:

- Compilation of all products in forms showing the information for the products grouped as follows (see example in Table 1), for example in form of a chemical inventory
- Identification of chemical products with acute aquatic toxicity
- Identification of chemical products which are readily, inherently or non-biodegradable in industrial wastewater treatment
- Identification of all combustible/flammable products and those which can decompose (thermally or by reaction with other chemicals)
- Compilation of relevant data required for planning and implementing adequate storage and handling
- Assessing compatibility of substances and preparing according storage layout plan
- Compilation of data relevant for communication, reporting and/or certification purposes such as for authorities or customers (e.g. Oekotex STeP[3], GOTS[4])
- Cross-referencing with manufacturing restricted and/or positive substances lists (e.g. ZDHC Manufacturer restricted substances list, bluesign® system substances list), specific customer restricted substances lists or other lists (e.g. ECHA-SVHC list)

Concerning emissions to air from stenters, special reference is made to the product-specific emissions factors for chemical products used for final finishing on these machines (also see Textile BREF, 2003)[5]. From the emission factors for the various products, the emission factors for applied recipes

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[1] Chemical products are those which are provided from chemical suppliers. These products are usually formulations containing different chemical substances. For textile finishing, according to specific recipes, different chemical products may be mixed prior to their application

[2] The short-comings of MSDS in terms of their comprehensiveness and quality of information need to be taken into account and may require further inquiries with the chemical supplier, particularly as far as the complete disclosure of chemical product compositions is concerned.

[3] Oekotex Sustainable Textile Production (STeP)

[4] Global Organic Textile Standard (GOTS)

[5] For every chemical product which is used to create a formulation (mixture of different chemical products) which is applied on a stenter, the emission factor is determined by means of a laboratory stenter. Then, the emission factor for the formulation is calculated by using the factors of the different components. This factor is compared with the emission limit. Every three years,

(formulation of different chemical products) can be calculated and compared to specific emission limit values.

Achieved environmental benefits:

The chemical inventory derived from the data base, combined with different filtering and evaluation options allows for a systematic identification of substances with undesirable environmental and toxicological (adverse) properties. This is turn facilitates the systematic planning and monitoring of an improvement in the selection of chemical products in terms of avoidance of hazardous substances. Among others, this also helps streamlining the coordination with chemical suppliers asking for products with improved environmental properties.

Environmental performance and operational data

The data from the 16 sections of the respective MSDS (as per European CLP/GHS) is systematically inserted into the data base, enabling different options of evaluation:

- Section 1: Identification of the substance/mixture and of the company/undertaking
- Section 2: Hazards identification
- Section 3: Composition/information on classified ingredients[6]
- Section 4: First aid measures
- Section 5: Firefighting measures
- Section 6: Accidental release measure
- Section 7: Handling and storage
- Section 8: Exposure controls/personal protection
- Section 9: Physical and chemical properties
- Section 10: Stability and reactivity
- Section 11: Toxicological information
- Section 12: Ecological information
- Section 13: Disposal considerations
- Section 14: Transport information
- Section 15: Regulatory information
- Section 16: Other information

With regard to environmental protection, information on chemical composition of the respective chemical products, information on handling and storage as well as the ecological information are most relevant in practice.

Annex 1 shows an exemplary outline of a chemical inventory containing all relevant environmental data of chemical products used for dyeing which can be used for compilation of information or evaluation against certain criteria.

Concerning emissions to air from final finishing processes on stenters, the required emission factors for the various products are not contained in the MSDS but have to be provided separately by the suppliers. Thus, updating information on emissions factors for the products concerned requires regular contact to chemical suppliers. To date, only one German company has established a laboratory stenter to determine the emission factors for the chemical products. However, any concerned company can also establish such a facility.

Cross-media effects:

No cross-media effects expected.

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the calculated emission factors of the formulations with the highest factors are verified by onsite measurements by a certified third party measurement firm.

[6] If possible, the complete composition of the product

Technical consideration relevant to applicability:

This measure is applicable to any textile finishing industry. It is then part of Good Housekeeping and responsible chemicals management. The necessary software application for the establishment and implementation of such a data base and respective evaluation tools can be either obtained by a range of providers available on the market (as part of an integrated business or stand-alone application) or developed in-house for smaller inventories.

Economics:

The investment and operating costs for a chemical data base depend on the level of sophistication intended. Preliminary estimates put the investment costs into the range of 20,000 to 50,000 €. Savings usually arise from streamlined stocks, improved management of surplus chemicals, simplification or automation of procedures/processes (e.g. by using chemical inventory software) as well as indirectly from reduced environmental management costs based of the gradual substitution of hazardous chemicals and emissions to the environment.

Driving force for implementation:

Substitution of hazardous substances

Availability and maintenance of chemicals management have become a common requirement in international supply chain management. Buyers` Code of Conducts commonly refer to the need of maintaining and using an up-to-date inventory of all substances used (see for example: Sustainable Apparel Coalition-Higgs FEM, Zero-Discharge of Hazardous Chemicals - ZDHC).

Companies may be required by law to maintain a chemical inventory (see for example German Hazardous Substances Ordinance (GefStoffV), section 3, para 6, point 12, revised 29th March 2017, see translation of relevant point in subnote[7])

A chemical product database allows continuous improvement in the selection of chemical products according to the environmental performance of their ingredients. It further helps to optimize production performance by improving and simplifying production planning and control systems (Performance data is included) and the operation of industrial wastewater treatment plants.

With respect to emission to air from stenters, a successful realization of a chemical database also allows the implementation of the emission factor concept (see section 4.3.2, Textile BREF, 2003). This in turn enables the calculation of emissions to air of different recipes, thus simplifying compliance with emission limit values and prescribed documentation duties.

Example plants:

Many textile industries in and outside Europe have established and use such a chemical as an integral part of their production planning and control system.

Reference literature:

- Chemical Management System Guidance Manual, Zero Discharge of Hazardous Chemicals (ZDHC), 2015, Section 2.1.4 Creating a Comprehensive Chemical List www.roadmaptozero.com/fileadmin/layout/media/downloads/en/CMS_EN.pdf
- GIZ Practical Chemical Management Toolkit, 2017
- German TRSG 400, section 5.8 Hazardous Substances Lists

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[7] www.baua.de/DE/Themen/Arbeitsgestaltung-im-Betrieb/Gefahrstoffe/Arbeiten-mit-Gefahrstoffen/pdf/Gefahrstoffverordnung-Aenderungen.pdf?__blob=publicationFile&v=2 – "…. the employer must keep a list of the hazardous substances used in the company in which reference is made to the corresponding safety data sheets. The list must contain at least the following information: 1. the name of the dangerous substance, 2. classification of the hazardous substance or information on its hazardous properties, 3. information on the tonnage ranges used in the establishment, 4. designation of the working areas in which employees are exposed to the hazardous substance…"

- Chemical Inventory Collection Template, Partnership for Sustainable Textiles, www.textilbuendnis.com/wp-content/uploads/2018/03/Partnership-for-sustainable-textiles-Chemical-Inventory-Collection-Template_bsv.xlsx
- Supplier Handbook Chemical Management – Section: Documentation (Inventory/SDS) www.tchibo.com/servlet/cb/1199382/data/-/TrainingshandbuchChemikalienmanagement.pdf

Annex 1 - Example for compilation of data extracted from a data base for compilations or evaluations

Form 3

List of used chemicals
sorted according to annual consumption quantities

Name of the textile finishing industry

Year:

3. Textile auxiliaries for dyeing and printing

3.1 Dyestuff solubilizing and hydrophobic agents
3.2 Dispersing agents and protective colloids
3.3 Dyeing wetting agents, deaeration agents
3.4 Levelling agents
3.5 Carriers
3.6 Crease-preventing agents
3.7 Dyestuff protecting agents, boildown protecting agents
3.8 Padding auxiliaries
3.9 Fixing accelerators for continuous dyeing and printing
3.10 Aftertreatment agents for fastness improvement
3.11 Bonding agents for pig
3.12 Printing thickeners
3.13 Emulsifiers for gasolin
3.14 Agents to remove prin
3.15 Printing and edge adhesives
3.16 Oxidizing agents
3.17 Reducing agents
3.18 Discharging agents and discharging assistants
3.19 Resist agents
3.20 Mordants
3.21 Brightening and stripping agents
3.22 Fibre-protective agents
3.23 pH-regulators, acid and alkali dispensers

No.	Commercial name	Producer	Chemical characterisation General and individual substances if available (see CAS no.)	Known CAS no.	Process, application	Annual consumption [kg/yr]	MSDS date	GHS Hazard	Cont. haz. substances according to SVHC, ZDHC, PBT and vPvB in [weight-%] for indiv. subst.	Ionogenic character	Biolog. degradation/elimination product and invidual substances in [%] and test duration [d] and testing method	spec. COD-value [mg O_2/g]	spec. BOD_5-value [mg O_2/g]	Heavy metal content [mg/g]	Org. halogen content [mg/g]	Total nitrogen [mg N/g]	Total phosphorus [mg P/g]	Classification wastewater relevance	Toxicity bacteria EC50 [mg/l]	Toxicity algae EC50 [mg/l]	Toxicity daphnia EC50 [mg/l]	Toxicity fish LC50 [mg/l]	Max. quantity stored [t]	Classification conc. storage
3.8.1	Ruco Print PMI	Rudolf GmbH	Polyacrylat	55965-84-9	Appretur		42971	H317	0,0025-<0,01 Mixture from 5-Chlor		< 30 [OECD 302B]	190	< 10					1			>1500			12
3.11	Peripret PW	Textilchemie Dr. Petry Gm	Polyacrylat Copolymere, wässrige Dispersion		Appretur		16.05.2017			weakly anionic	> 70 [OECD 302B]	365	5					1	> 1000			>100		12
3.2	Dekol SN New liq	Archroma Distribution and	Polycarboxylat, Copolymerisat, Natriumsalz, in water		Färberei		23.01.2015				> 70 [OECD 302B]							1	> 1000		>100	>100		-
3.8	Primasol NF liq	Archroma Distribution	Alkylphosphat, Ammoniumsalz, in water	298-07-7	Färberei		26.10.2016	H318	>= 5 - < 15 Bis(2-ethylhexyl)hydrogenphosphat		> 70 [OECD 302B][28]	995	90					2	> 1000			100-500		10
				4971-47-5					>= 20 - <= 30 ammonium bis(2-ethylhexyl) phosphate															
				78-42-2					>= 1 - < 3 Tris(2-ethylhexyl)phosphat															
3.2	Setamol Disperse WS	Archroma Distribution and	naphthalenesulfonic acid-formaldehyde-polycondensate as sodium salt		Färberei		20.08.2015				20 - 70 [OECD 303A]	1300						1	EC10: >1000mg/l			100 - 500		
3.17	Redulit EX	CHT	Reduktionsmittel	310-73-2	Färberei		27.11.2017	H302; H290; H314; H360; EHU014	>= 30 - < 50 Natriumhydroxid									2	750		25			6.1C
				16940-66-2					>= 10 - < 20 Natriumtetrahydroborat															
3.2	Meropan DPE	CHT	Kombination aus Polycarboxylaten und Phosphonaten		Färberei		06.02.2017				30 - 60 [OECD 302B][28]	210	< 5			0,230	1,550	2	> 1000		3350			12
3.3	Kollasol IND	CHT	Phosphorsäureester	68186-64-1	Färberei		05.12.2017	H315; H318	>= 10 - < 20 Phosphorsäure, 2-Ethylhexylester, Natrium-salz							0,740	2,400	2						
				73070-48-1					>= 10 - < 20 Phosphorsäure, 2-Ethylhexylester, Verbin-dung mit 2,2'-Iminobis[ethanol]															
				27458-92-0					>= 5 - < 10 Isotridecan-1-ol		leicht biol. Abbaubar [Literaturwert]										> 0,1 - 1	> 0,1 - 1		
				143-22-6					>= 3 - < 10 2-[2-(2-Butoxyethoxy)ethoxy]ethanol		92 [OECD 301E][21]										< 500	2400		
				68155-07-7					>= 5 - < 10 Amide, C8-18- und C18-ungesättigt, N,N-Bis(hydroxyethyl)-		92 [OECD 301B]										< 1 - 10	< 1 - 10		
				107-41-5					>= 5 - < 10 2-Methyl-2,4-pentandiol		> 70 [OECD301F][28]									> 429	> 5000			
				69011-36-5					>= 1 - < 3 Isotridecanolethoxylat		> 60 [OECD 301B][28]									> 1 - 10	> 1 - 10	> 1 - 10		
				1559-34-8					>= 1 - < 3 3,6,9,12-Tetraoxahexadecan-1-ol															
				104-76-7					>= 1 - < 3 2-Ethylhexan-1-ol		> 80 [OECD301C][14]									> 100	> 100	17.1		
				112-34-5					>= 1 - < 3 2-(2-Butoxyethoxy)ethanol		85 [OECD301C] [28]													
				34590-94-8					>= 1 - < 10 (2-Methoxymethylethoxy)propanol		73 [OECD301E][28]									> 969	> 100	> 10 000		
				Kollasol IND					Kollasol IND		> 70 [OECD 302B][28]	1777	343						> 1000		1 - 10	10-100		10

Note:

When entering relevant data on substances` biodegradability and bioeliminability respectively, it is important to always list this information together with the respective test applied. Furthermore, when using test results from OECD 302 B to assess the biodegradability of a product, it is important to also include the results from OECD 301 tests in order to create a better understanding of the results[8]*.*

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[8] If both the OECD 301 test and the OECD 302 B test are positive, it can be concluded that the chemical compounds concerned are biodegradable. If the result of the OECD 301 test is negative and the result of the OECD 302 B test positive, the chemical compounds concerned may be non-biodegradable but are adsorbed by the sludge in the OECD 302 B test. However, it could also be the case that the chemical compounds concerned require adaptation which may not be given in an OECD 301 test but which can develop in the OECD 302 B test.

Proper unloading, storage and handling of chemicals

Description

Textile finishing industries use various chemical products in significant quantities. Their labeling and handling according to their risk potential for water and solid contamination is a pre-requisite for preventive measures. In Germany, the Water Hazard Classification (WGK) scheme has been introduced more than 20 years ago and proven to be successful in grouping chemicals accordingly. In order to avoid hazards and accidents, including accidental release of chemicals into the environment threshold values have been developed which concern the quantities stored and specify respective protective measures to be taken[9]. Chemical products, exceeding these quantitative threshold values are required to be received and unloaded in secured areas, stored properly and handled safely as part of general good chemical management practices.

Technical description

In order to prevent any unintended release (accidental release) of chemicals certain precautionary measures are to be taken. Liquid-bulk chemicals require dedicated areas for their unloading and shall be stored in double-walled tanks with overfill protection and leakage detection. Intermediate bulk containers and drums are to be stored at collection points where the minimum volume of the catchment facility determines the volume of the largest container or drum. Examples for proper unloading, storage and handling of chemicals are provided under “Environmental performance and operational data”.

When storing chemicals it is of particular importance to check for their respective storage compatibilities as certain chemicals cannot be stored together. In order to identify potential storage incompatibilities of chemicals, chemical segregation charts are available. Examples for chemicals with special storage requirements are hydrogen peroxide which shall be stored separately in a dedicated catchment facility and sodium dithionite which shall be even stored in a separate dry room. Chemical segregation charts (see figure 1 for an example from the German Technical Rule for Hazardous Substances TRGS 510 (2013) in section “Environmental performance and operational data”) should be used together with information gathered from the corresponding Material Safety Data Sheets (MSDS).

In addition to the measures described above, the following general measures should also be implemented:

- Any production and storage facility should be tight, bearing, robust and thermally and chemically resistant
- Any leakage should be detectable fast and reliably
- Catchment facilities should not have a drain
- Storage facilities should be equipped with sufficient lighting and ventilation
- All chemical products should be labelled clearly and unambiguously
- The entire staff should regularly receive competent training
- Emergency exits and escape routes shall be provided

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[9] For hazardous substances, dedicated storage is required for highly toxic substances (H Statements 300, 301, 310, 311, 330, 331, 370, 371) at quantities of more than 50 kg, for CMR substances (H Statements 340, 350) at quantities of more than 50 kg, for easily or highly inflammable substances (H Statements 224, 225, 226) at quantities of more than 20 – 100 kg, for substances which decompose at contact with water (H Statements 260, 261) at quantities of more than 200 kg, oxidizing substances (H Statements 271, 271) at quantities higher than 50 kg (Technical Rules for Hazardous Substances TRGS 510).
Concerning water hazard classification (German Regulation concerning installations handling substances hazardous to water - AwSV), the different categories for volumes stored are 0.22 – 1, 1 – 10, 10 – 100, 100 – 1000, and > 1000 m^3 or t m^3 or t, and the measures to be taken also depend on the category; there are three categories: 0, 1, 2, and 3. The higher the figure the more hazardous is the substance or chemical product.

Achieved environmental benefits

Proper unloading, storage and handling of chemicals, combined with a general staff awareness of hazards and a high level of precaution, can significantly reduce the likelihood of accidental release of chemical products used for textile finishing.

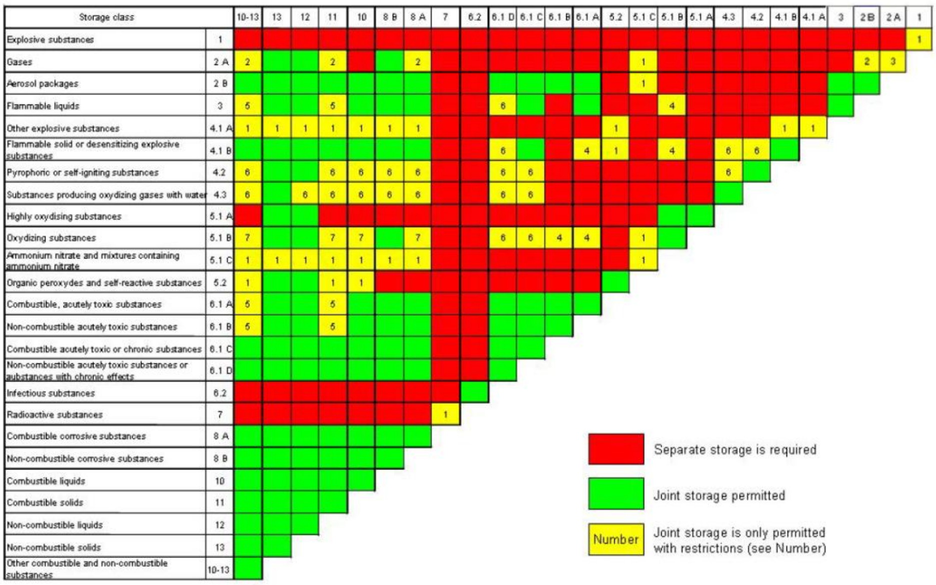
Environmental performance and operational data

The following table outlines exemplary measures (common good chemicals management practices) for the proper discharge, storage and handling of chemical products:

Dedicated unloading area with precautionary measures in case of spillages for liquid bulk chemicals; typically acetic acid, NaOH, KOH, H_2O_2, urea, main surfactants; stormwater drain needs to be connected to the treatment plant (Photo: Dr. Harald Schönberger)	 Locked door for fixing the flexible pipe for unloading liquid bulk chemicals Stormwater drain: Underground, there is a valve and tank to catch accidential relases of chemicals during unloading (during unloading, the valve is switchend to the catchment tank)
Double-walled tanks with overfilling prevention and leakage detection for bulk chemicals (NaOH, KOH, H_2O_2, detergents, urea); for H_2O_2, explosion prevention is required (also a safety relief valve and an over-roof pipe) (Photo: Dr. Harald Schönberger)	
Single-walled tank are placed in a catchment facility where its volume shall be determined by the volume of the tank, or, where several tanks are placed in one catchment facility, the volume of the largest tank (Photo: Dr. Harald Schönberger)	

All IBCs, small tanks and drums are placed on catchment facilities (secondary containments) (secondary containment units should be able contain 10% of the total volume of all containers or 100% of the largest container; holding capacity ideally 110% of the maximum capacity of the largest tank or drum) (Photo: Dr. Harald Schönberger)	

Figure 1: Storage class compatibility check used in Germany (source: Technical Rules for Hazardous Substances TRGS 510)



Storage class		10-13	13	12	11	10	8 B	8 A	7	6.2	6.1 D	6.1 C	6.1 B	6.1 A	5.2	5.1 C	5.1 B	5.1 A	4.3	4.2	4.1 B	4.1 A	3	2B	2A	1
Explosive substances	1	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	1
Gases	2 A	2	🟩	🟩	2	🟥	🟩	2	🟥	🟥	🟥	🟥	🟥	🟥	🟥	1	🟥	🟥	🟥	🟥	🟥	🟥	🟥	2	3	
Aerosol packages	2 B	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟥	🟥	🟩	🟩	🟩	🟩	🟥	1	🟥	🟥	🟥	🟥	🟥	🟥	🟩	🟩		
Flammable liquids	3	5	🟩	🟩	5	🟩	🟩	🟩	🟥	🟥	6	🟩	🟥	🟩	🟥	🟥	4	🟥	🟥	🟥	🟥	🟥	🟩			
Other explosive substances	4.1 A	1	1	1	1	1	1	1	🟥	🟥	🟥	🟥	🟥	🟥	1	🟥	🟥	🟥	🟥	🟥	1	1				
Flammable solid or desensitizing explosive substances	4.1 B	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟥	🟥	6	🟩	🟥	4	1	🟥	4	🟥	6	6	🟩					
Pyrophoric or self-igniting substances	4.2	6	🟩	🟩	6	6	6	6	🟥	🟥	6	6	🟥	🟥	🟥	🟥	🟥	🟥	6	🟩						
Substances producing oxydizing gases with water	4.3	6	🟩	6	6	6	6	6	🟥	🟥	6	6	🟥	🟥	🟥	🟥	🟥	🟥	🟩							
Highly oxydising substances	5.1 A	🟥	🟩	🟩	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟩	🟩								
Oxydizing substances	5.1 B	7	🟩	🟩	7	7	🟩	7	🟥	🟥	6	6	4	4	🟥	1	🟩									
Ammonium nitrate and mixtures containing ammonium nitrate	5.1 C	1	1	1	1	1	1	1	🟥	🟥	🟥	🟥	🟥	🟥	🟥	1										
Organic peroxydes and self-reactive substances	5.2	1	🟩	🟩	1	1	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟩											
Combustible, acutely toxic substances	6.1 A	5	🟩	🟩	5	🟩	🟩	🟩	🟥	🟥	🟩	🟩	🟩	🟩												
Non-combustible acutely toxic substances	6.1 B	5	🟩	🟩	5	🟩	🟩	🟩	🟥	🟥	🟩	🟩	🟩													
Combustible acutely toxic or chronic substances	6.1 C	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟥	🟥	🟩	🟩														
Non-combustible acutely toxic substances or substances with chronic effects	6.1 D	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟥	🟥	🟩															
Infectious substances	6.2	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟥	🟩																
Radioactive substances	7	🟥	🟥	🟥	🟥	🟥	🟥	🟥	1																	
Combustible corrosive substances	8 A	🟩	🟩	🟩	🟩	🟩	🟩	🟩																		
Non-combustible corrosive substances	8 B	🟩	🟩	🟩	🟩	🟩	🟩																			
Combustible liquids	10	🟩	🟩	🟩	🟩	🟩																				
Combustible solids	11	🟩	🟩	🟩	🟩																					
Non-combustible liquids	12	🟩	🟩	🟩																						
Non-combustible solids	13	🟩	🟩																							
Other combustible and non-combustible substances	10-13	🟩																								

🟥 Separate storage is required
🟩 Joint storage permitted
Number Joint storage is only permitted with restrictions (see Number)

Note: The figures in the first row as well as in the second column correspond to the designated “storage groups/classes” which may be given for the chemical product in the MSDS (ref. section 7). Alternatively, storage classes can be assigned using the procedure as outlined in annex 4, of BG RCI Code of practice M 062e, Hazardous Substances - Storage of Hazardous Substances, BG RCI (November 2013). This not only forms the basis for the development of a chemical storage (layout) plan but also serves as an instrument for reducing the risk of adverse effects emanating from accidental mixing of incompatible chemicals during further handling and disposal.

Technical consideration relevant to applicability

There are no technical restrictions known for the applicability of the measures described.

Economics

There are no precise figures available yet for the different measures described. Potential savings arise from reduced risks of uncontrolled reactions and connected costs (losses, damages, insurance costs).

Driving force for implementation

Proper unloading, storage and handling of chemicals is a common compliance requirement for many companies adhering to environmental management systems. In addition, the measures described above facilitate the receipt of insurance benefits and help to meet the necessary requirements of the competent authorities.

Example plants

Many textile finishing industries in Europe apply measures described above, at least part of them.

Reference literature

- TRGS 510: Storage of hazardous substances in non-stationary containers, Technical Rule for Hazardous Substances, Version: January 2013, GMBl 2013 p. 446–475 of 15 May 2013 [No. 22], amended and supplemented: GMBl 2014 p. 1346 of 19.11.2014 [No. 66-67]
- Chemical warehousing - The storage of packaged dangerous substances, HSG71, HSE, UK, www.hse.gov.uk/pubns/priced/hsg71.pdf
- Hazardous Substances - Storage of Hazardous Substances, Code of practice M 062e, BG RCI, November 2013
- Guidance on the compilation of safety data sheets, ECHA, Version 3.1, November 2015

HAZBREF
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Separation and specific disposal of concentrates containing recalcitrant chemicals

Description

In wet textile processing various highly concentrated liquors or pastes are used. The required quantity of these residual padding liquors and printing pastes can be minimized by separating residues and disposing of concentrate in a targeted manner.

Technical Description

During textile wet processing, the following highly concentrated liquors or pastes are applied:

- Padding dyeing liquors for semi-continuous (cold pad batch) and continuous dyeing which may contain direct, reactive, vat, sulphur or disperse dyestuffs
- Printing pastes which may contain organic pigments, reactive, vat or disperse dyestuffs
- Padding liquors for final finishing; the chemicals used are very divers and depend on the targeted effect. They include amongst others softeners, optical brighteners, ethylene urea derivatives, flame retardants, oil and water repellents (organofluorine compounds are used), biocides (e.g. cypermethrine, zinc pyrithione etc.).

The required amount of residual padding liquors and printing pastes can be minimized by a number of techniques such as:

- Minimization of excess liquor/paste by automated liquor and printing paste preparation systems
- Minimization of the system volume for the application of the aforementioned concentrates (small-volume pipes, squeegees, screens and pumps in case of rotary printing)
- Minimized padder volume in case of semi-continuous and continuous dyeing and final finishing
- Just-in-time preparation of liquors

All of the above techniques are comprehensively described in the Best Available Techniques Reference Document for the Textiles Industry from 2003 [Textile BREF, 2003].

The three aforementioned residues have to be separated. While in the case of residual printing pastes this is easy to achieve, separating residual padding liquors from dyeing and final finishing requires additional efforts as the residual padding liquor has to be pumped from the padder to an intermediate bulk container (IBC) or another type of appropriate container. This can either be done automatically by adequate programming and the installation of valves or by using a manually operated pump to empty the padder and the residue in the padder liquor preparation tank.

Once separated the waste concentrates require further treatment. The various treatment options are indicated in Table 1.

Table 1: Technical options to treat/dispose residual padding liquors and printing pastes

Type of residue	Treatment option
Residual dyeing padding liquor	
Option 1	The residual dyeing padding liquor is oxidized (at least to fragments which arte biodegradable) by means of a wet oxidation process as described in the [Textile BREF, 2003]. This is possible for all relevant groups of dyestuffs such as reactive, direct, vat, sulphur and disperse dyestuffs
Option 2	In case of reactive dyestuffs, the dyestuffs can be precipitated/flocculated by means of an organic cationic flocculant. The sludge formed is separated by dewatering (e.g. in a chamber filter press) and disposed of in a BAT incineration plant.
Option 3	In case of vat and sulphur dyestuffs in their oxidized form as well as in case of vat dyestuffs, the dyestuffs can be separated by precipitation/flocculation by means of a combination of inorganic precipitating agents (iron or aluminum salts) and a polyelectrolyte. The sludge is separated by dewatering (e.g. in a chamber filter press) and disposed of in a BAT incineration plant.
Residual printing paste	
Option 1	In case of pigment printing paste, inorganic precipitating agents can be used. The sludge formed is separated by dewatering (e.g. in a chamber filter press) and disposed of in an incineration plant. It is also appropriate to directly incinerate the residual pigment printing paste.
Option 2	Residual paste containing reactive dyestuffs can be fed to an anaerobic digester as most (not all) reactive dyestuffs are azo dyestuffs and under anaerobic conditions, the azo groups are cleaved. However, the resulting aromatic amines are non-biodegradable and reach the aerobic part of a treatment plant with the digester´s overflow and the filtrate and can thus reach the natural water.
Residual final finishing padding liquor	
	There are many different chemical compounds used and each has its individual chemical properties. In general, it is best to directly incinerate the residual final finishing padding liquors unless the compounds exclusively consist of readily biodegradable compounds such as fatty acids esters applied as softeners.

Achieved environmental benefits

The segregation and specific disposal of the aforementioned concentrates can considerably reduce the load of non-biodegradable compounds and thus water pollution.

Environmental performance and operational data

Possibilities to segregate the residual padding liquors are shown in Figures 1 – 3.

Figure 1: On the left, the photo shows the padder of a stenter and on the right an intermediate bulk container (IBC) equipped with a pump and pipes to manually empty the padder (Photos: Dr. Harald Schönberger)

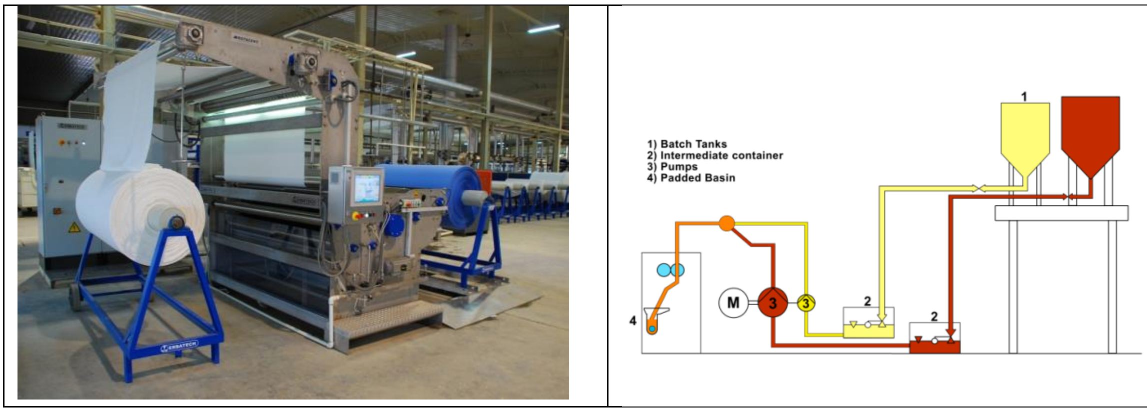

Figure 2: On the left, there is a cold pad batch dyeing facility with the padder and on the right a scheme showing the preparation and application of the dyeing padder liquor (preparation tank and padder) (Photo: Dr. Harald Schönberger)

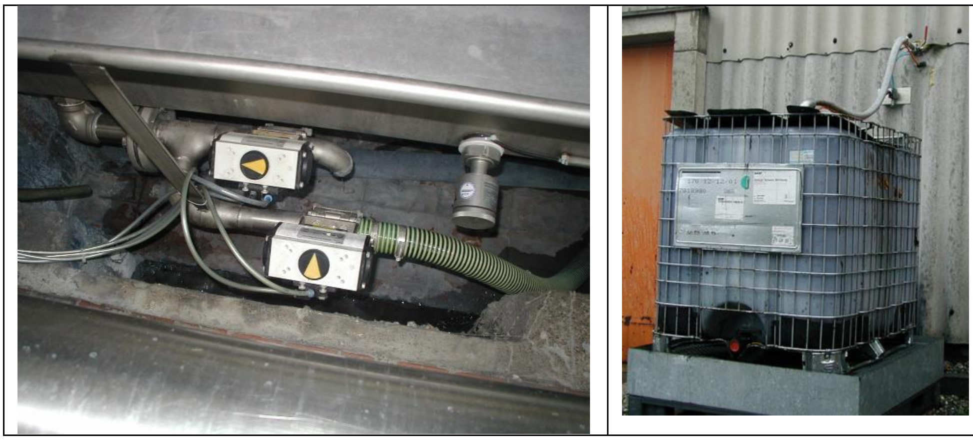

Figure 3: On the left, there is an automated system to segregate the residual dyeing padding liquor and on the right the IBC to collect it (Photos: Dr. Harald Schönberger)

Cross-media effects

As the residual padding liquors and printing pastes are incinerated (possible subsequent to precipitation/flocculation), additional emissions to air have to be considered. However, in waste incineration plants which apply best available techniques, emission to air usually are very low so that the additional emission load caused by the incineration of concentrates is insignificant. In general the benefits of proper incineration easily outweigh the relatively low cross-media effects.

It is nevertheless important that the quantity of residues is minimized prior to disposal.

Technical consideration relevant to applicability

The technique is applicable for both existing and new installations. There are no technical restrictions with respect to the application of the technique.

Economics

For a padder, the investment costs for an automated system for the segregation of residual padding liquors (valves, tank below the padder from where the residual padding liquor is pumped to an IBC) are in the range of 20,000 – 30,000 €. Investment costs for the manually operated separation system (flexible pipes and a flexible pump) are around 5,000 €. Operating costs are negligible. The costs for the treatment of residual printing pastes and residual padding liquors depend on the techniques applied and may be in the range of a few €/t (in case of anaerobic treatment) to 300 – 500 €/t in case of direct incineration.

Driving force for implementation

The reduction of COD and colour load discharged as well as compliance with existing regulations are the main driving forces.

Example plants

AG Cilander AG, CH-Herisau (direct incineration of residual padding liquors), Textilveredlung an der Wiese and Lauffenmühle, both located in Loerrach/Germany (anaerobic co-fermentation of residual dyeing padding liquors in the municipal anaerobic digester).

Reference literature

Not available

Treatment of waste gas from stenters with special consideration of methanol

Description

In textile finishing, emissions of organic chemicals to air usually emanate from stenters and continuous dyeing of polyester. The release of methanol poses a particular problem which has to be addressed by adequate abatement measures such as the combination of various end-of-pipe techniques.

Technical description

Possible sources for emissions of organic compounds to air from stenters may include:

- Organic compounds present in the textile substrate from up-stream processes (fibre production, spinning, knitting) such as primary and secondary preparations, spinning and knitting oils,
- Organic compounds from dyeing, printing or coating which then can be volatilized during stenter operation, such as carriers, levelling agents, after-treatment agents, wetting agents, hydrocarbons from printing pastes, acetic acid, tetrachloro ethene (if dry-cleaning is carried out) (Textile BREF, 2003).
- Organic compounds which are applied on the stenter and which may enter waste gas during thermal treatment in the stenter such as finishing agents (stiffening cross-linking agents), de-aeration agents, antistatic agents, softeners, optical brighteners, flame retardants, coating agents (e.g. polyvinyl acetate or polyurethane), easy-care finishing, finishing with oil or water repellents etc. (Textile BREF, 2003).
- The release of methanol poses a particular problem. For certain products, especially for men's shirts, moist cross-linking agents are applied at low pH value. Formerly, this process was connected to the release of significant amounts of formaldehyde. Today, however, chemical products are used that release methanol instead. In Germany, the emission limit value of methanol is 20 mg/Nm^3 which corresponds with an emission factor of 0.4 g methanol/kg textile processed. There are, however, cases where the untreated waste gas contains about 15 times higher concentrations and emission factors respectively.
- Other possible sources, which will not be covered in the following, include emissions from coating facilities

Measures to prevent the emission of organic compounds at the source have top priority. They include among other things the application of thermos-stable or more thermos-stable (compared to conventional products) preparations, the substitution of mineral oil in spinning or knitting oils and the use of easy-care finishing products which release no or very low quantities of formaldehyde or methanol. However, in many cases, the residual contamination is still high, making additional end-of-pipe techniques necessary. Here, a number of techniques, often combined with each other, are applied (e.g. scrubbers after heat exchanger followed by an electrostatic precipitator).

Achieved environmental benefits

The emission minimisation of organic compounds - determined in the form of the sum parameter volatile organic carbon (VOC), or detected as individual substances, such as formaldehyde or methanol (two compounds which are considered to be toxic) - as well as particulates and compounds causing odour nuisances is achieved.

Environmental performance and operational data

The design of an end-of-pipe treatment system depends on the type and concentration of pollutants. In the case of oily compounds and particles as well as some easily water-soluble compounds, a combination of a two stage heat exchanger, followed by a fine-mist scrubber and an electrostatic precipitator could for instance reduce the aforementioned components by 90 %. The scrubber can often further reduce the waste gas temperature which also improves the efficiency of the electrostatic precipitator. The combination of techniques described above is shown in Figure 1.

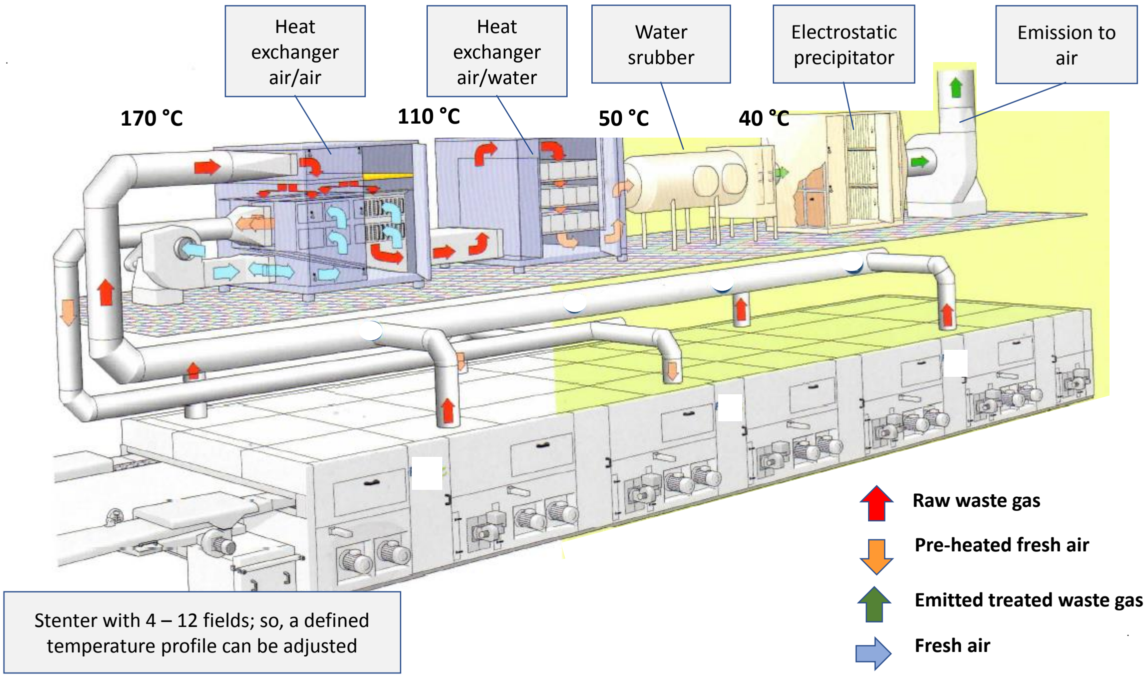

Figure 1: Combination of heat exchanger, fine-mist scrubber and electrostatic precipitator for the removal of oily and water-soluble waste gas components (Figure based on Brückner leaflet "ECO TECHNOLOGIES", 2019)

In case of formaldehyde, the scrubber can be operated with addition of hydrogen peroxide at alkaline pH value. The scrubbing liquor is usually circulated and thus warms up quickly.

In case of methanol, the removal efficiency depends on the concentration in the untreated waste gas, the quantity of water used for scrubbing and the temperature of the circulating scrubber liquor. A possible scrubber setup is shown in Figure 2.

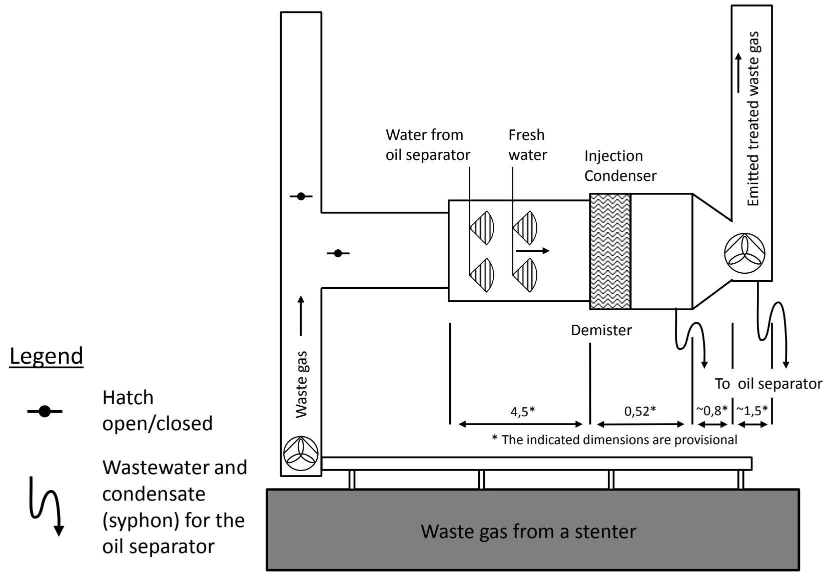

Figure 2: Scheme of a scrubber for the removal of water-soluble, partly also of water-insoluble, components; the scrubber water is sprayed as fine mist into the waste gas

Provided that the waste gas temperature is not higher than 50 °C after heat exchange, the specific water consumption is in the order of 0.2 – 0.4 l/Nm^3 for a methanol removal efficiency of 50 – 60 % and can be as high as 2 l/Nm^3 for a removal efficiency of about 90 %. However, by cooling the circulating scrubbing liquor, the specific water consumption for high removal efficiencies can be significantly reduced.

It is important to regularly clean the heat exchanger and the electrostatic precipitator. The required frequency depends on the type of compounds and their concentration in the untreated waste gas. For example, in case of raw fixation of synthetic knitwear, heat exchangers and electrostatic precipitators have to be cleaned very often, i.e. weekly.

Usually, a thermal treatment of waste gas from stenters (as coating is not covered here) is not considered as proportionate due to the low VOC content of the untreated waste gas (less than 500 mg/Nm^3) and the high energy consumption required for thermal oxidation.

Cross-media effects

In wet scrubbers, the pollutants are shifted from waste gas to waste water. However, they can easily be removed and broken down respectively by conventional wastewater treatment, such as separation of oily components in oil/water separators and biological treatment of biodegradable compounds, such as formaldehyde (the concentrations are low and thus it does not have an inhibiting effect) or methanol. The treatment can also be carried out in municipal or industrial wastewater treatment plants.

Technical consideration relevant to applicability

The technique can be applied both for existing and new installations. The combination of different components depends on the composition of organic compounds and has to be adapted accordingly.

Economics

The investment costs for heat exchange, fine mist scrubber and electrostatic precipitator for a stenter (based on a waste gas flow in the range of 7,000 – 10,000 Nm^3/h) is in the order of 200,000 €.

The operating costs relate to electricity and water consumption, costs for staff to carry out cleaning and other maintenance operations and the disposal of separated oil from the electrostatic precipitator. Further costs can arise for chemicals dosed into the scrubber liquor. Exact cost calculations are not yet available.

Driving force for implementation

Regulatory requirements by competent authorities, requirements posed by customers and neighbourhood conflicts as well as the operator’s intrinsic motivation to minimise emission to air are the main driving forces.

Example plants

A number of textile finishing industries in Europe apply techniques as described above.

Reference literature

Not available yet

Biological pre-treatment of PVA-containing segregated streams

Description

Polyvinyl alcohol (PVA) is the most important synthetic sizing agent in the textile sector and is increasingly used for high-speed weaving looms. During desizing (part of textile pre-treatment), PVA is virtually removed from the fabric. In principle, PVA is biodegradable, but only under certain conditions that must be adjusted and maintained in order to achieve high removal efficiencies.

Technical description

PVA is only biodegradable when certain system conditions are met. These include a wastewater temperature of more than 15 °C, a food-to-microorganism ratio of less than 0.15 kg BOD_5/kg MLSS x d and adaptation of the biomass (Schönberger et al. 1997). If in an industrial or municipal biological wastewater treatment plant these conditions cannot be maintained over the entire year (e.g. due to very low wastewater temperature in winter), additional biological pre-treatment is required. Possible measures include

- the precipitation with boron salts (not preferable as a sludge is generated very difficult to dispose of)
- the wet oxidation of the desizing liquor, preferably by a continuous Fenton's oxidation process (Textile BREF, 2003)
- biological pretreatment in a membrane biological reactor (MBR)

It is recommended to use a MBR which is equipped with an ultrafiltration membrane, preventing residual PVA from leaving the reactor (as the size of this polymer is too large to pass the membrane). As a result the PVA is retained in the activated sludge system. The membrane can either be separately installed or directly submerged in the activated sludge tank.

Achieved environmental benefits

The emission of PVA to water bodies is drastically minimized over the entire year, including winter time with low wastewater temperature.

Environmental performance and operational data

Figure 1 shows an exemplary waste water treatment plant with PVA containing streams originating from two machines where desizing is carried out. The wastewater streams are then segregated by automated valves and directed to an equalization tank from where the streams are fed to the tube flocculator and subsequently to the membrane bio reactor (MBR). The food-to-microorganism ratio is about 0.2 kg BOD_5/kg MLSS x d. PVA is degraded between 95% and 98%, even at temperatures of 40 °C when it is usually not biodegradable anymore (Sträßner, 1994; Chamoun, 2018). To still enable biodegradation the PVA-degrading microorganisms have been adapted to elevated temperature levels.

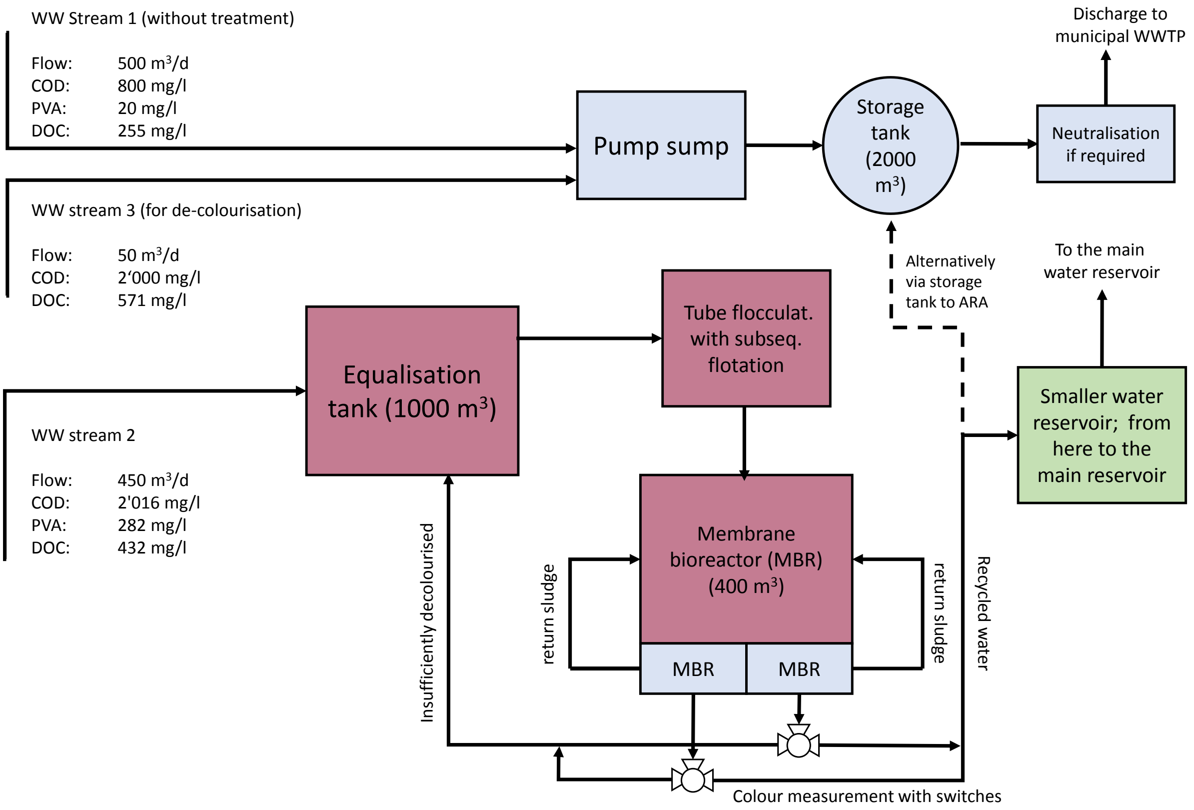

Figure 1 - Scheme of the wastewater pre-treatment plant with a membrane bioreactor (MBR) for the biological PVA degradation (based on: Wastewater disposal scheme of Cilander AG in CH-Herisau)

Cross-media effects

Compared to the treatment in a conventional activated sludge system or in a municipal wastewater treatment plant, biological treatment in a MBR requires additional energy as the energy consumption of a MBR plant is higher than that of conventional activated sludge systems.

Technical consideration relevant to applicability

The technique is applicable to both new and existing plants. However, in existing plants, sufficient space for equalization tanks and the MBR plant is a pre-requisite. Furthermore, in existing plants additional wastewater pipes have to be retrofitted to enable proper segregation of the different wastewater streams. It can be expected that low wastewater temperatures (where PVA degradation is low) usually only occur in municipal wastewater treatment plants in colder parts of Europe (e.g. Central and Northern Europe).

Economics

The investment costs for the plant shown in Figure 1 are about 1.5 million €. The treatment costs are about 1 – 1.5 €/m^3.

Driving force for implementation

Strict requirements, emission limit values and the reduction of wastewater fees (in case of indirect discharge) are the most important driving forces for this technique.

Example plants

Cilander AG, Herisau/Switzerland

Reference literature

Chamoun, C.C. (2018), Study of the biodegradation of polyvinyl alcohol as a function of temperature, Master thesis at the Institut für Siedlungswasserbau, Wassergüte- und Abfallwirtschaft (ISWA) at the University of Stuttgart

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