International workshop about textile waste

Site visit in the framework of the ENTeR project

Cooperation on innovation to make CENTRAL EUROPE more competitive

12th – 13th June, 2018

Óbuda University

Waste reduction in finishing

„What is waste for one, is of value to the other.
A wide range of materials can be recycled and reused”

Dr. András Víg

Budapest University of Technology and Economics
Department of Organic Chemistry and Technology


Hungary


POLAND
Prague
Vienna
Budapest
HUNGARY
Szeged
ROMANIA
Timisoara
Brasov
Bucharest
Zagreb
Belgrade
Craiova

Budapest University of Technology and Economics

Budapest University of Technology and Economics

January 1, 2000: the change in the faculty structure was also reflected in the new name of our University:

Budapest University of Technology and Economics

F building

K building

Introduction

Elements of the environment to be protected

- Air
- Water
- Soil
- Noise
- Landscape
- Waste treatment

Water protection

Green chemistry
Best Available Technology BAT
Industrial wastewater treatment
Municipal wastewater treatment

Air protection

Reduce the amount of Pollutants (SO_2, NO_2, NO_3, CO, O_3, sediment dust
Industry power plant, waste incineration
Transport
Biomass, biogas
Renewable energy water, wind, sun, geothermal

Waste management

Prevention of waste generation

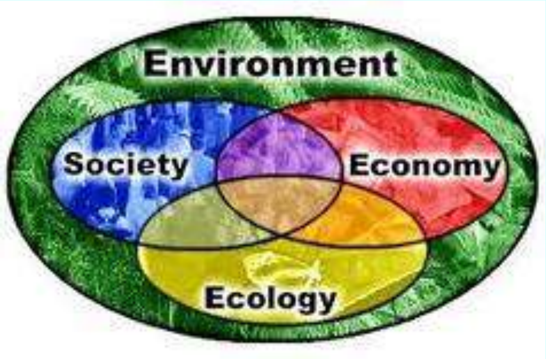
To reduce the risk of waste

Reuse, Recovery

Safe disposal

The 4 E chemistry

- **Intelligent and sustainable processes,**
- **Environment, Ecology, Efficiency, Economy,**
- **Result: sustainability of products and processes.**



Textile ecology

Enforcing a lifecycle approach

Sustainable textile production
Optimalization of technologies and working conditions

STeP → Sustainable Textile Production

Development of Oeko-Tex Standard 1000 From June 2013.

Change of logos STeP® and OEKO-TEX®

old

SUSTAINABLE TEXTILE PRODUCTION
STeP
12345678
CERTIFIED BY OEKO-TEX®

CONFIDENCE IN TEXTILES
Tested for harmful substances
according to Oeko-Tex® Standard 100
00000000 Institute

new

OEKO-TEX®
CONFIDENCE IN TEXTILES
STeP
00000000 TESTEX
Sustainable Textile Production.
www.oeko-tex.com/step

OEKO-TEX®
CONFIDENCE IN TEXTILES
ECO PASSPORT
000000000 HOHENSTEIN HTTI
Textile chemicals. Tested and verified.
www.oeko-tex.com/ecopassport

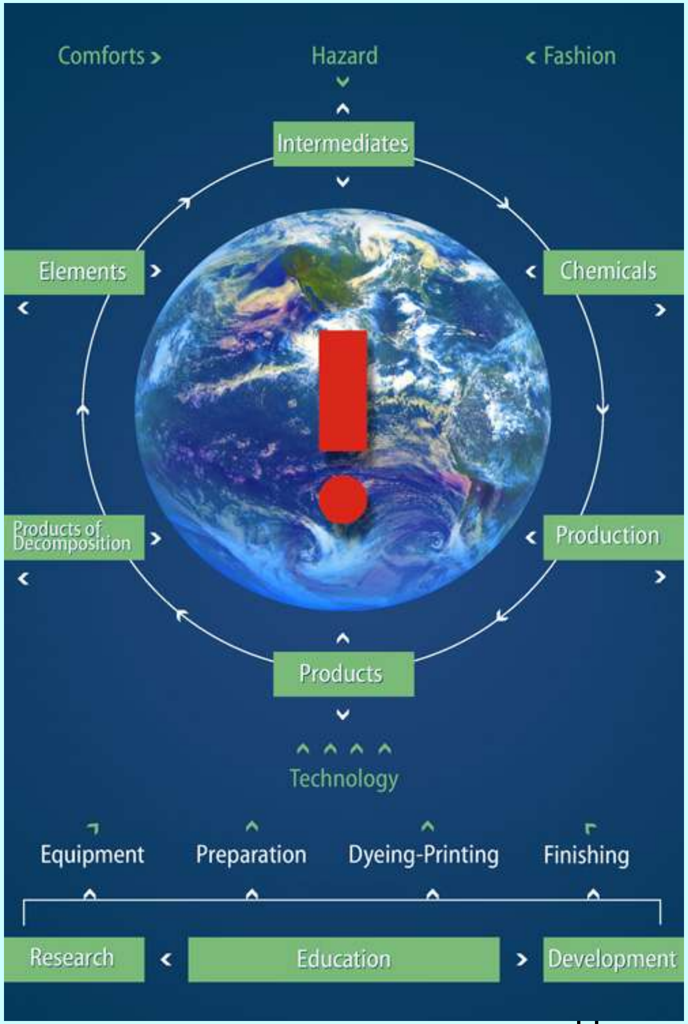
To elaborate Environmentally Friendly Cycles has been the Goal!

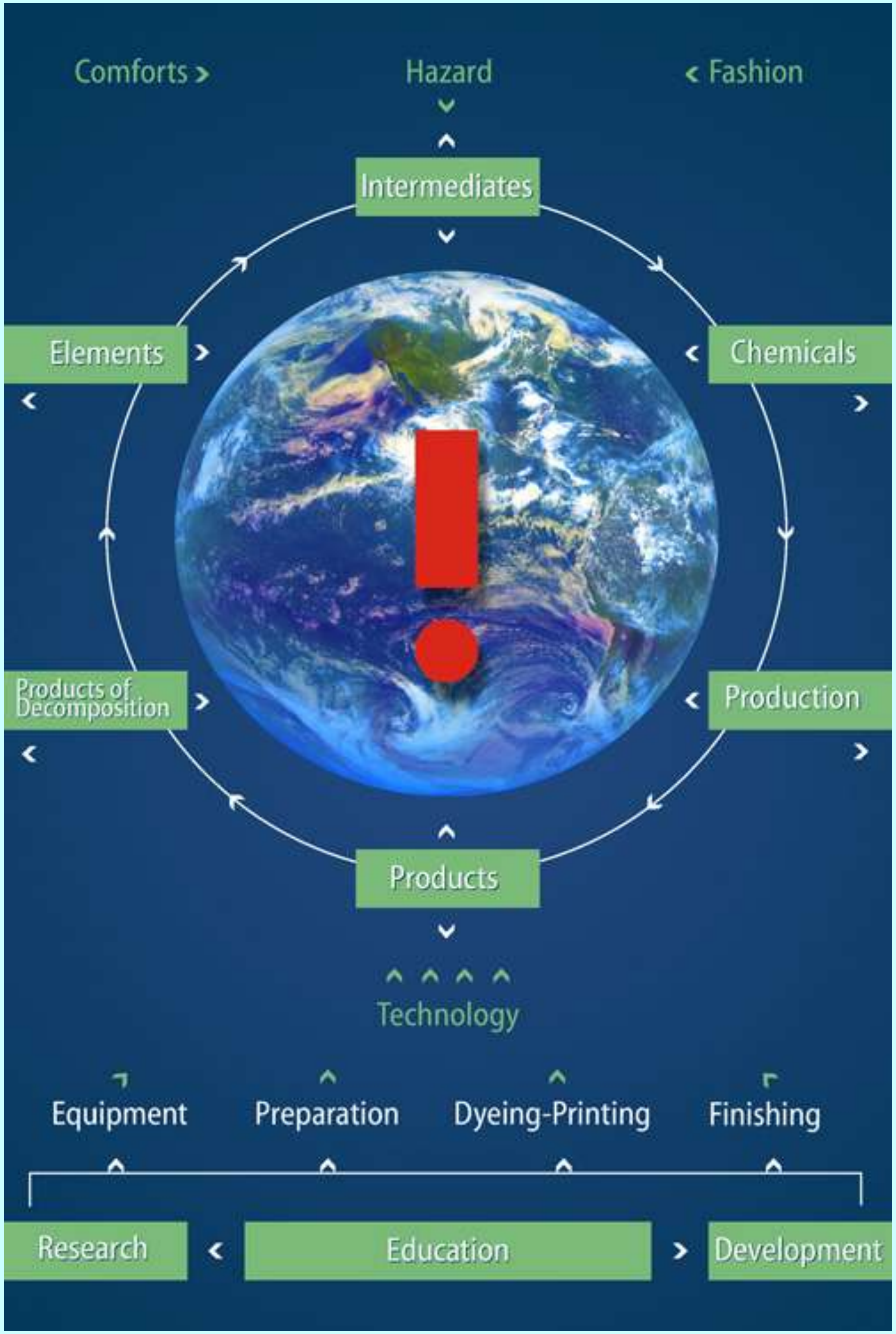
Invitation
to the 23rd IFATCC Congress
Budapest, 8 - 10 May 2013

We hope you will visit us; we are looking forward to your attendance, active participation and contributions

Ágota Orbán
Secretary

András Víg
Chairman





”We had the pleasure to greet altogether more than 200 attendants during the Congress representing 25 Countries from 5 Continents except Antarctic. The foreseen 57 oral and 63 poster presentation have been performed.

The central topic that is the main goal of the 23rd IFATCC Congress was the development of the textile chemical processes and operations in the direction of environmentally and consumer friendly so called Green technology.”

Eco-friendly Research for the Light Industry at the Department of Organic Chemistry and Technology

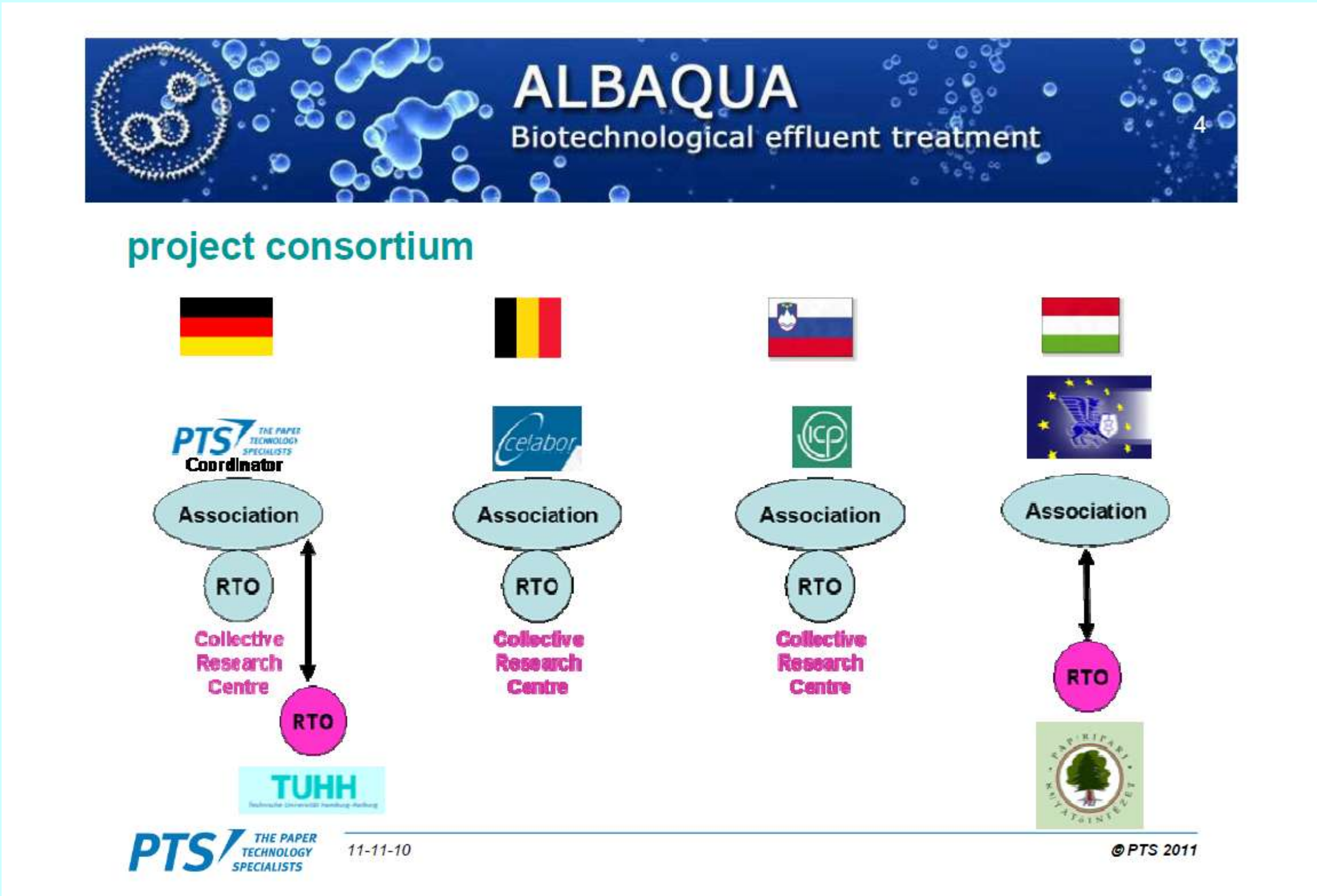
Paper Industry

1. **Waste water treatment in pulp and paper industry with algae (ALBAQUA)**
2. **Paper production from industrial grass, i.e. from an annually renewable source of cellulose**
3. **”Ecopaperloop” recycling of paper waste logistics and paper manufacturing technology**

Textile Industry

1. **Optimization of reactive dyeing technology**
2. **Lightfastness Improvement of reactive dyed cotton fabrics**
3. **Synthesis of inclusion complex-forming compounds for dyes recovery from used dye bath.**

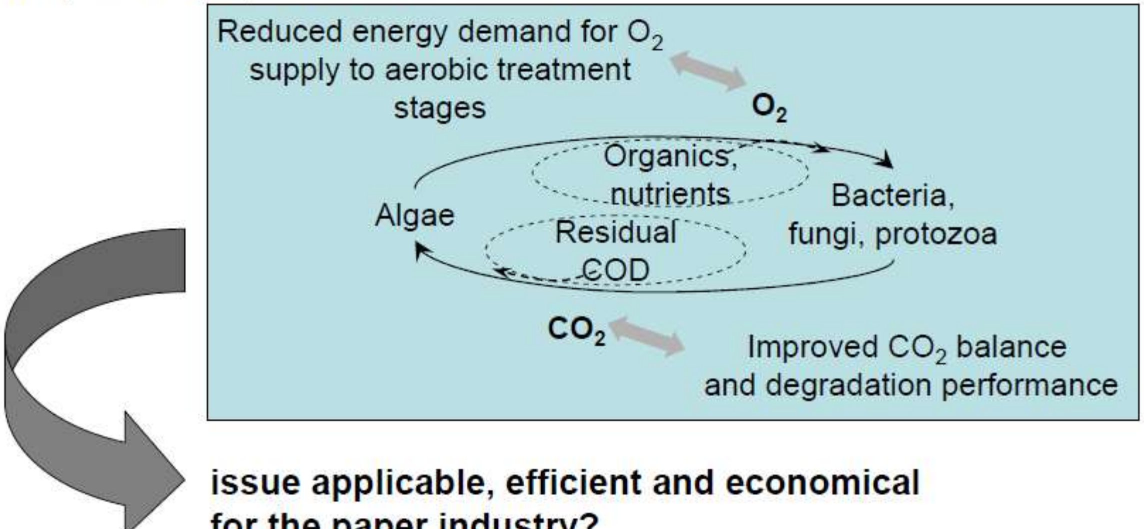
Paper Industry **ALBAQUA**



Paper Industry ALBAQUA

project basics and aim

Title: Combined **al**gal and **ba**cterial waste water treatment for high environmental **qua**lity effluents (ALBAQUA)



issue applicable, efficient and economical for the paper industry?

Background / Problem statement

The conventional way for treating effluents of the paper industry has been a selected biological purification.

Release of CO_2 into the environment has been disadvantage of this process.

Combining the generally used process with algae (which is consuming CO_2 in the course of photosynthesis) might improve the process by decreasing the amount of released CO_2.

This result has been reached with the realization of symbiosis of algae and the bacterial sludge.

Waste water cleaning with three different algae

Chlorella Vulgaris Hamburgenesis	Chlorella Vulgaris Tihanyi	Cyanobacteria Oscillotoria
		

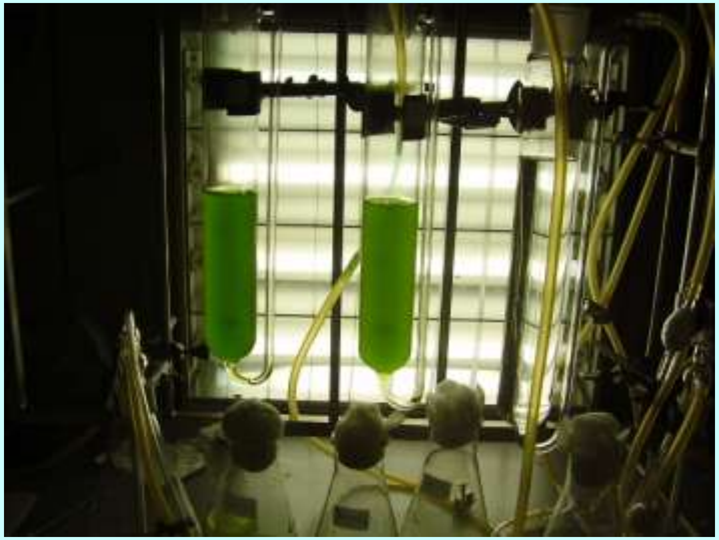
Paper Industry ALBAQUA

Single algae bioreactors of two types has been evaluated namely the perfusion airlifting bioreactor and the tubular recycle photo-bioreactor.

Reactors:

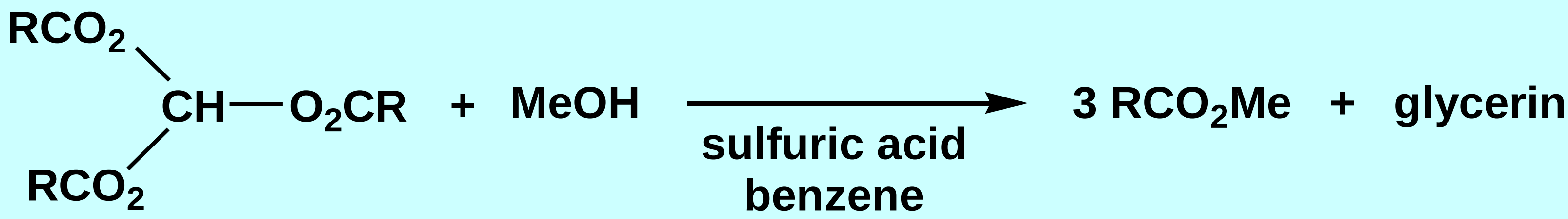
Perfusion airlift photo-bioreactor: airlift operation uniformly suspends microplantlets and improves exposure to light.

Tubular recycle photo-bioreactor (CO_2 mass transfer occurs only in aeration tank), tube diameter has short light path to reduce light attenuation through culture suspension.



Determination of the ratio of Algae suitable for production of biodisel with gas chromatography after methanolysis.

(Data from diploma work of Péter PERJÉS)



Fatty acid	Mass [mg]
C-14 acids	13.4
C-16 acids	22.1
C-18 acids	3.6
Oleic acid	0.04
Arachidin acid	2.5
Arachidon acid	2.2
Tricosan acid	2.5

Lipid content of Algae: 22%

Paper Industry ALBAQUA

The ALBA-floc process proofed applicable for purification of paper mill effluents in the range up to COD = 800 mg/l (1000mg/l) and can be operated stable. Aeration is not necessary, circulation/mixing of the system is required. In total a reduced energy input leading to lower operational costs can be found for the ALBA-floc process compared with the conventional activated sludge process.

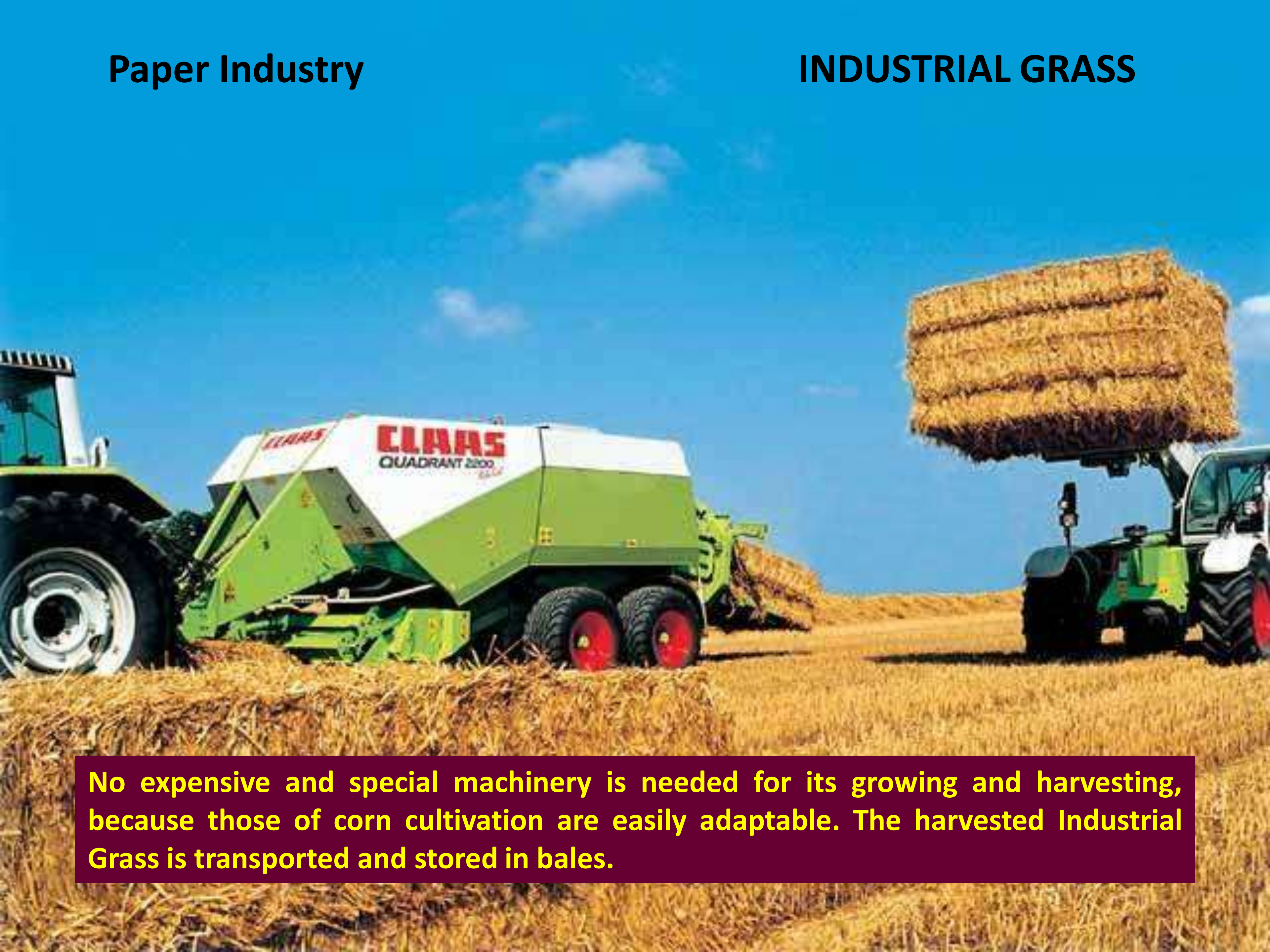
NEW ANNUAL PLANT (INDUSTRIAL GRASS) AS RAW MATERIAL FOR PULP AND PAPER INDUSTRY 2; PHYSICAL-MECHANICAL CHARACTERISTICS OF PULPS MADE AT LABORATORY-, PILOT PLANT- AND INDUSTRIAL LEVEL OF PRODUCTION

András Víg[1], Mariann Lele[2], István Lele[2], Zsolt Janowszky[3] and János Janowszky[3]

[1]Budapest University of Technology and Economics, Department of Organic Chemistry and Technology, 1521 Budapest, Hungary
[2]University of West Hungary, Faculty of Wood Sciences, Paper Research Institute, 9400 Sopron, Bajcsy-Zs. u. 4, Hungary
[3]Greenline Hungary Ltd., 5540 Szarvas, Hungary

Paper Industry

INDUSTRIAL GRASS



No expensive and special machinery is needed for its growing and harvesting, because those of corn cultivation are easily adaptable. The harvested Industrial Grass is transported and stored in bales.

Produced biomass by one hectare

Raw material	Biomass suitable for industrial utilisation, t/year/hectare
Coniferous	1.5 – 2.0
Broad-leaved trees	2.5 – 3.0
Grain straw	3.5 – 4.0
Flax	2.5 – 3.0
Hemp	6.0 – 8.0
Industrial grass	**10.0 – 15.0**

The yearly production of biomass/hectare of industrial grass compared with that of different plants are shown in the table. The relative yearly production of biomass by industrial grass is twice up to ten times of that by other plants.

Unbleached and bleached sheets

Sheets (80 and 110 g/m^2) have been produced by Rapid–Köthen device.

Conclusion

Environmentally friendly cooking and bleaching technology could be elaborated for industrial grasses.
The industrial grass cellulose proved to be in many cases more suitable for paper making than that of the straw one.
The unbleached industrial grass cellulose could be used only for wrap paper production while the bleached one by itself or in mixture with other bleached celluloses could be applied also in writing and printing paper making.

ECOPAPERLOOP   Project Partners

Innovhub-Stazioni Sperimentali per l'Industria (Innovhub-SSI)
Graziano Elegir, Project Coordinator

erma concepts (Paper Technology Consulting GmbH)
Andreas Faul

Technical University of Darmstadt (PMV)
Hans Putz

Technical University of Dresden (TUD)
Harald Grossmann

Polish Packaging Research and Development Centre (COBRO)
Greg Ganczewski

Pulp and Paper Institute Ljubljana (ICP)
Jania Zule

University of Ljubljana (UL)
Diana Gregor-Svetec

University of West Hungary, Faculty of Wood Sciences, Paper Research Institute (UWH/FWS/PRI)
Istvan Lele

National Consortium for the Recovery and Recycling of Cellulose-based Packaging (COMIECO)
Eliana Farotto

Lombardy region (Regione Lombardia, Italy)
Anna Cozzi

Supporting Organisations

WP5 - Eco-design for recycling

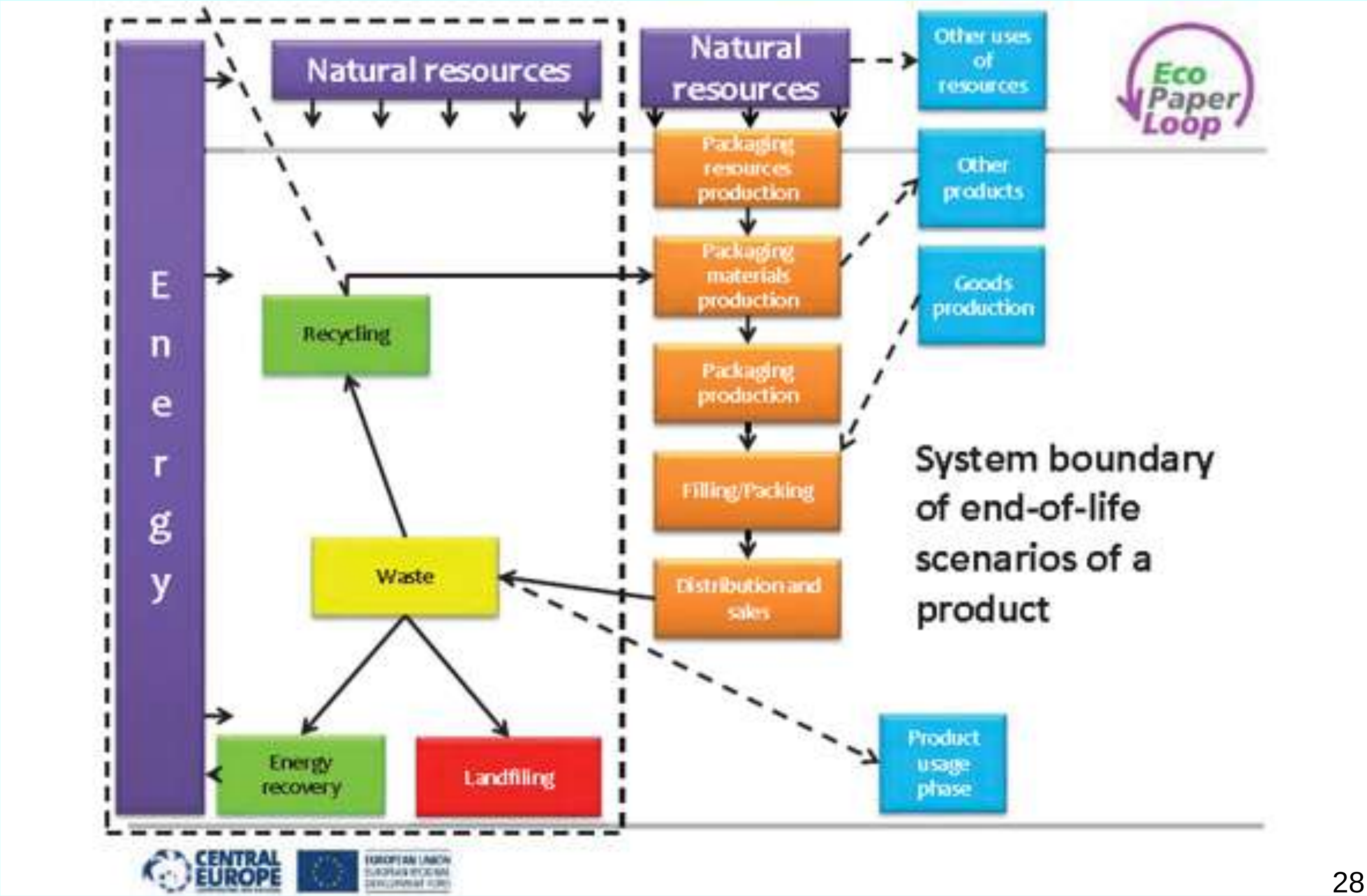
In ECOPAPERLOOP we look at the end of life of paper products – especially the step of recycling.

LCA will allow us to compare eco-design environmental impacts in recycling.

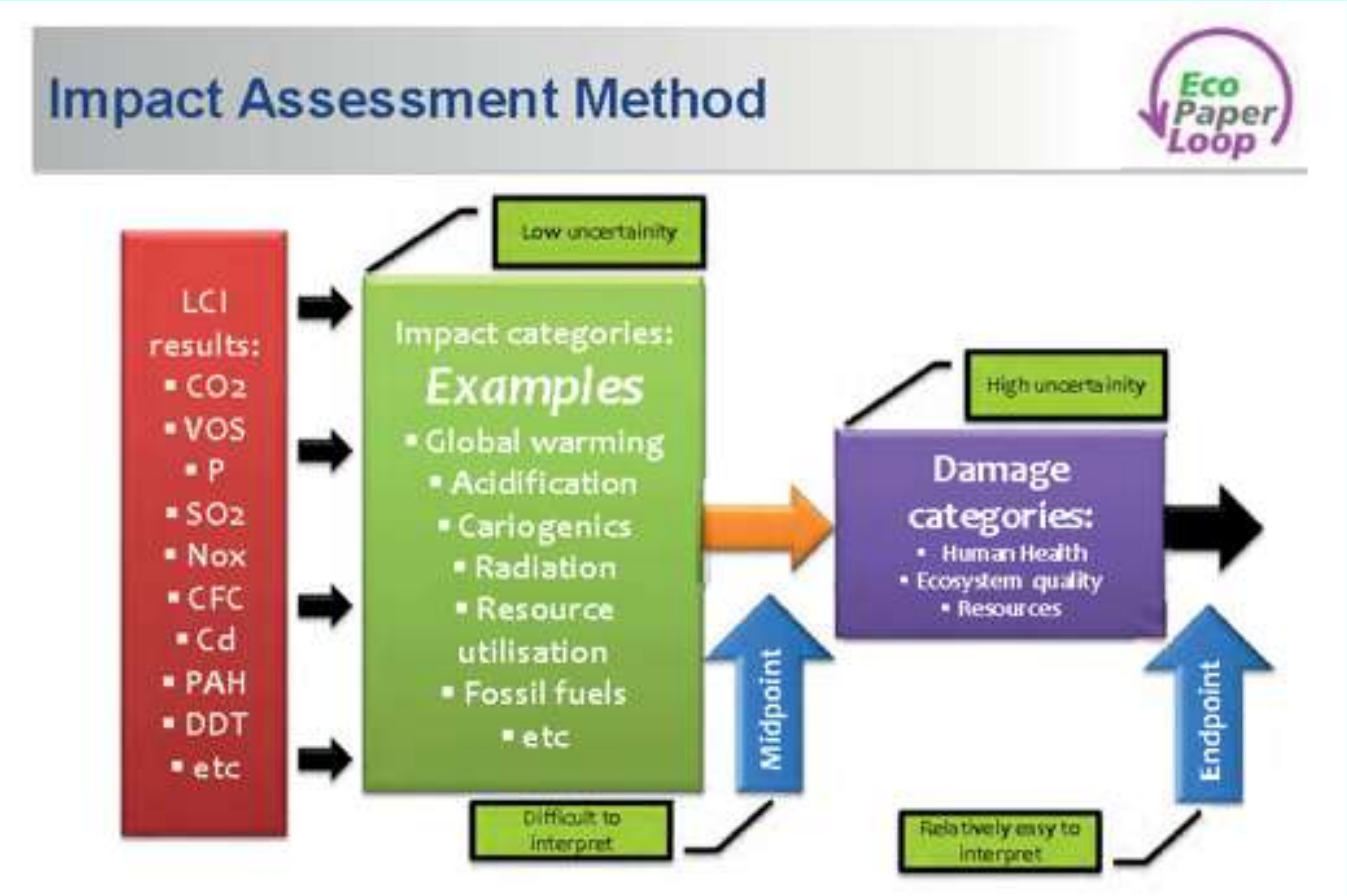
Assumptions:

- For better clarification and comparison potential LCA results will be shown in 2 modes:
  - Full life cycle of the product
  - Focus on the end-of-life processes – showing only emissions in end-of-life scenarios

Paper Industry **PAPER RECYCLING**



Paper Industry PAPER RECYCLING



Eco-friendly Research for the Light Industry at the Department of Organic Chemistry and Technology

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Textile Industry

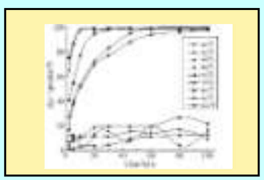
1. Optimization of reactive dyeing technology
2. Lightfastness Improvement of reactive dyed cotton fabrics
3. Synthesis of inclusion complex-forming compounds for dyes recovery from used dye bath.

Textile Industry

Environmentally-friendly dyeing, dye selection criteria

Dyeing properties

- solubility
- rate of dyeing
- levelling ability
- electrolyte sensitivity
- thermo sensitivity
- combinability



Colour fastness

- colour fastness in dye house
- colour fastness in use

Health and environment protection

Dyeing equipment accommodation

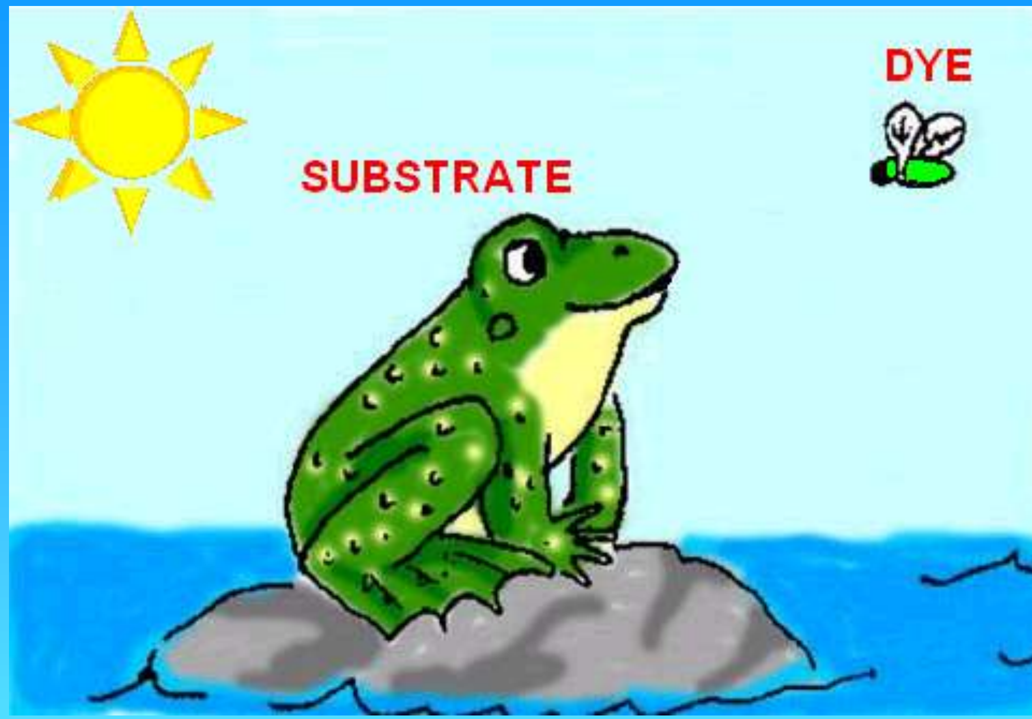
Reproducibility

Basic questions of the dyers:
How to achieve?

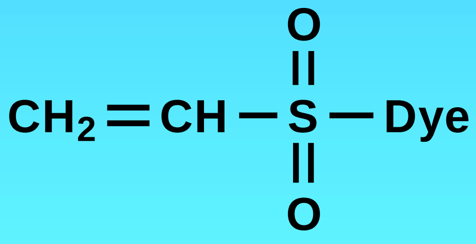
Complete **solubility** of the dye **in dyehouse**	→←	Complete **insolubility** of the dye **on the fabric**

Basic questions of the dyers:
How to achieve?

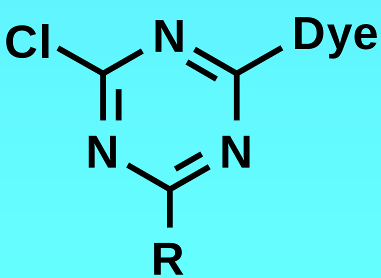
Complete solubility of the dye in dyehouse	→←	Complete insolubility of the dye on the fabric

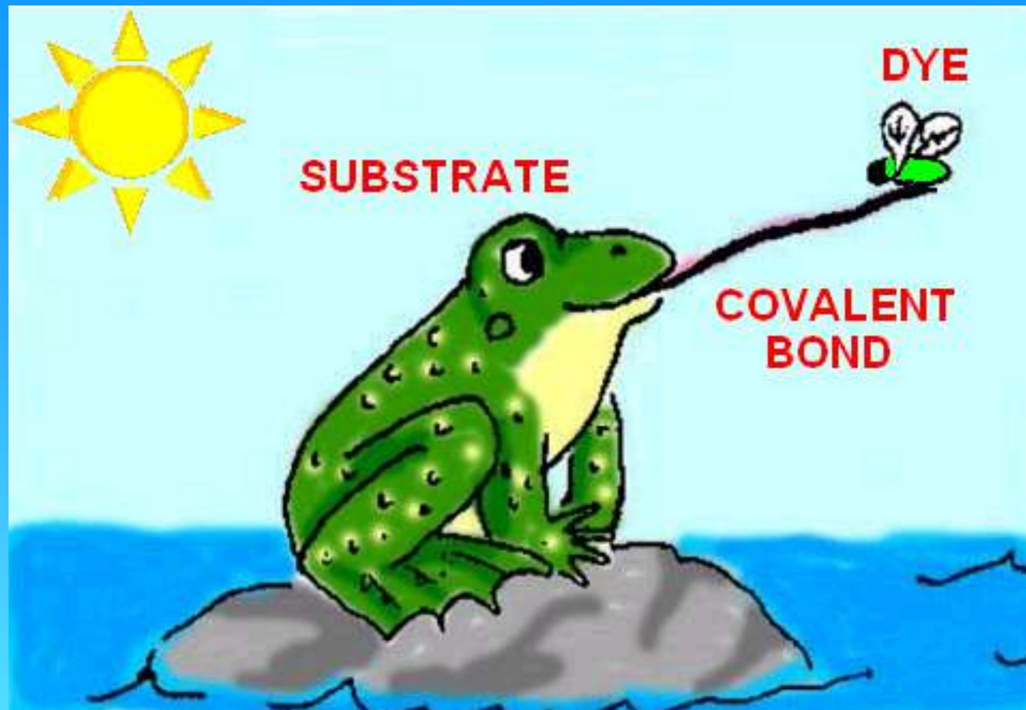


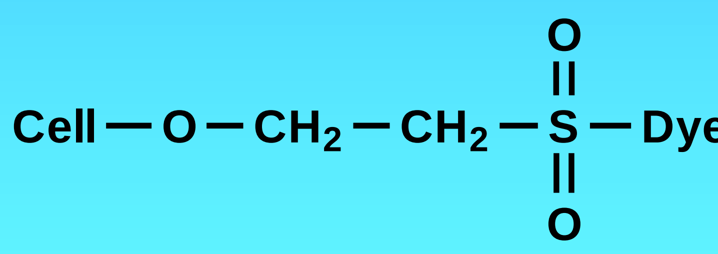
Cell — OH

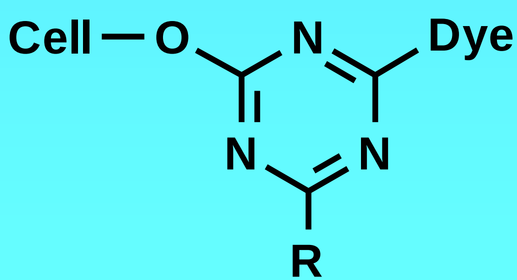


Cell — OH




DYE
SUBSTRATE
COVALENT
BOND


O
Cell — O — CH2 — CH2 — S — Dye
O


Cell — O
N
Dye
N
N
R

Environmentally friendly reactive dye

- advanced reactive dyes: eg. heterobifunctional dyes (such as triazine and vinyl sulfone reactive groups combined)→ more reactive groups, higher dye exhausting, increased fixation
- they are generally small molecules, well soluble in water and have low affinity so the electrolyte (salt) addition should be increased (Moderne LS=low salt, reactive dyes use1/3 amount of elektrolyte
- reactive dyes react with water (20-50% can therefore be lost), therefore (HF=high fixation) varieties have been developed; 90% of fixation is also available, few colorants go into the sewage,
- the modern reactive dyes are free of AOX (adsorbable organic halides)-

Textile Industry

1. Optimization of reactive dyeing technology

SUSTAINABLE DEVELOPMENTS OF THE CHEMICAL WASTEWATER TREATMENT IN TEXTILE DYEING

H. J. Nagy, K. Őrsi, M. L. Varga, Á. Orbán, Á. Tóth, I. Rusznák, P. Sallay, A. Víg

24th IFATCC INTERNATIONAL CONGRESS
Pardubice, June 2016.

Budapest University of Technology and Economics
Department of Organic Chemistry and Technology

1. COMPUTER AIDED SIMULATION OF TREATMENT OF DISSOLVED REACTIVE DYE-CONTAINING WASTEWATER

DYES

- The **DRIMAREN "K"** and **"HF-CL"** reactive dyes of **CLARIANT** (ARCHROMA) have been selected for our simulated studies. The "K" - series are mono-functional (Table 1) whereas the "HF-CL" - series are bi-functional (Table 2) reactive dyes.

Table 1: **DRIMAREN „K" - series**

	Shade	*Trichromatic basic dye*
DRIMAREN "K" -series	Light and mid-tone	Drimaren Yellow K-2R
		Drimaren Red K-4BL
		Drimaren Blue K-2RL
	Dark	Drimaren Yellow K-2R
		Drimaren Red K-8B
		Drimaren Navy K-BNN

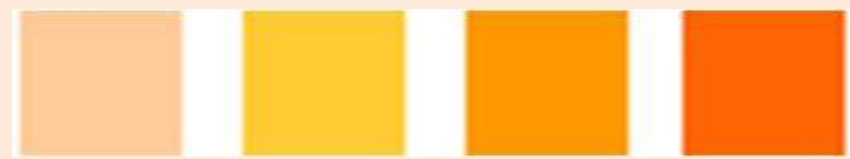
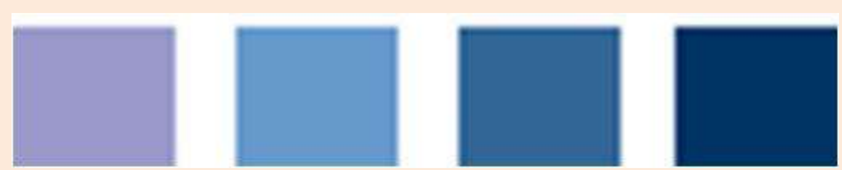


Table 2: **DRIMAREN „HF-CL" - series**

	Shade	*Trichromatic basic dye*
DRIMAREN "HF-CL" - series	Light and mid-tone	Drimaren Yellow CL-2R
		Drimaren Red CL-5B
		Drimaren Blue HF-RL
	Dark	Drimaren Yellow CL-2R
		Drimaren Red HF-3B, Drimaren Red CL-5B
		Drimaren Navy HF-GN, Drimaren Navy HF-B



a) CLARIANT Programme for optimising the reactive dyeing process

- The dyeing experiments have been **simulated** by using the software of **CLARIANT.** The mentioned program, establish correlations among the dyeing parameters and e.g. the fixed dye content of the fabric.
- *Exhaustive* (Fig. 1.) and cold *pad-batch* (Fig. 2.) procedures have been selected for establishing the applicability of the studied dyes. As well the dyeing parameters as the quantitative dye fixation have been optimised for different initial dye concentrations.

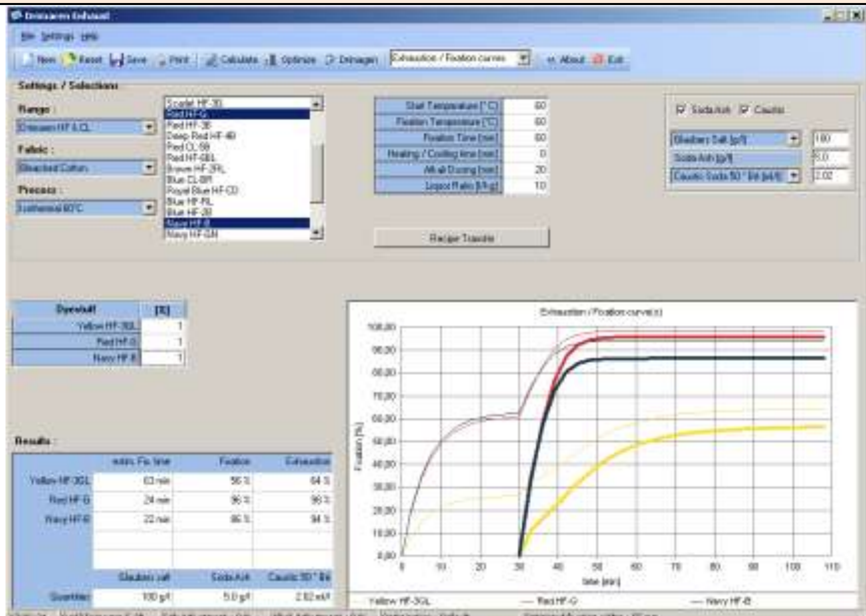


Figure 1.: CLARIANT DRIMAREN *Exhaust software*

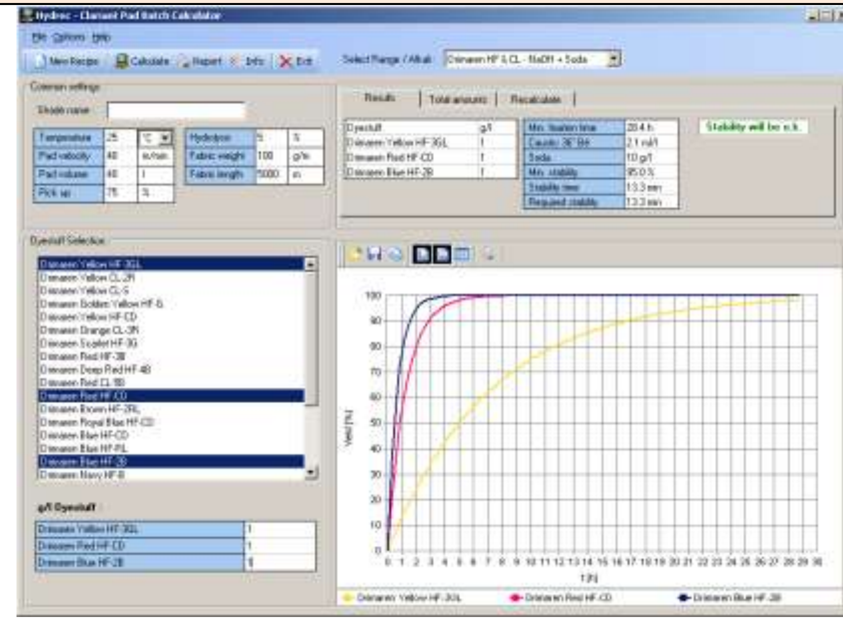
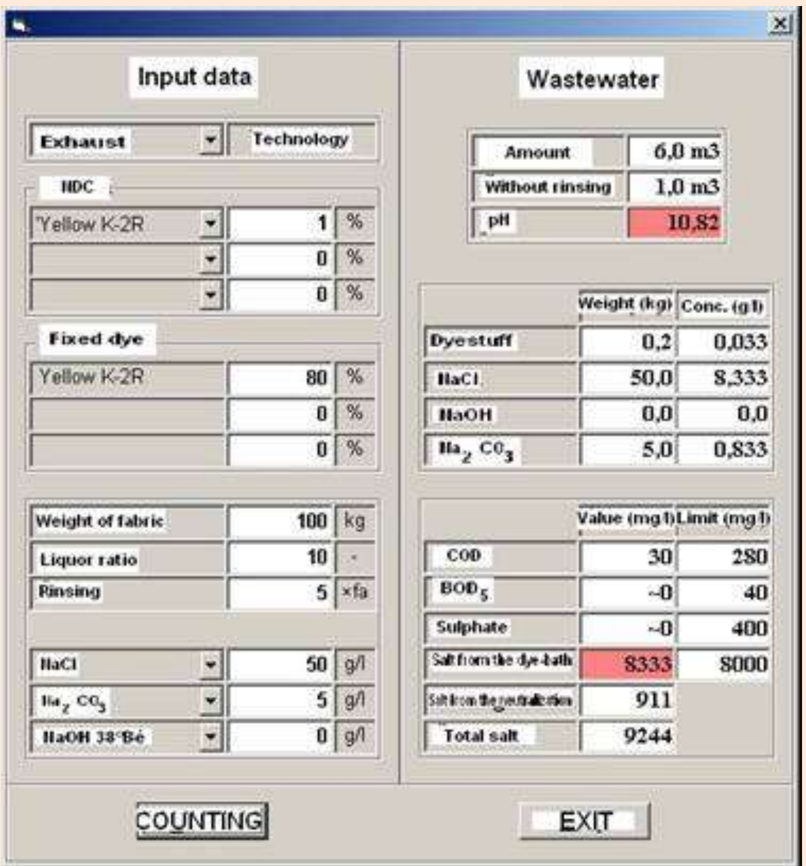


Figure 2.: CLARIANT DRIMAREN *Pad-Bach Calculator software*

b) Computer program for calculation of selected analytical data of wastewater subsequent to dyeings

- Computer program (Fig. 3.) for description of wastewater characteristics subsequent to dyeings discussed so far for supplementing of Exhaust and Pad Batch program of **CLARIANT** has been elaborated by Kálmán Örsi B.Sc. student. The computer program has been produced at *Delphi* programming language.



Our new computer program enabled calculation the following characteristics of the produced wastewater:

- volume (with and without rinsing water) [m^3],
- pH,
- following concentrations: dye, salts, NaOH and/or Na_2CO_3) [g/l],
- chemical oxygen demand (COD) [mg/l],
- biochemical oxygen demand (BOD) [mg/l],
- sulphate-content [mg/l]
- total salt-content [mg/l].

Figure 3.: Program for calculation of the wastewater characteristics

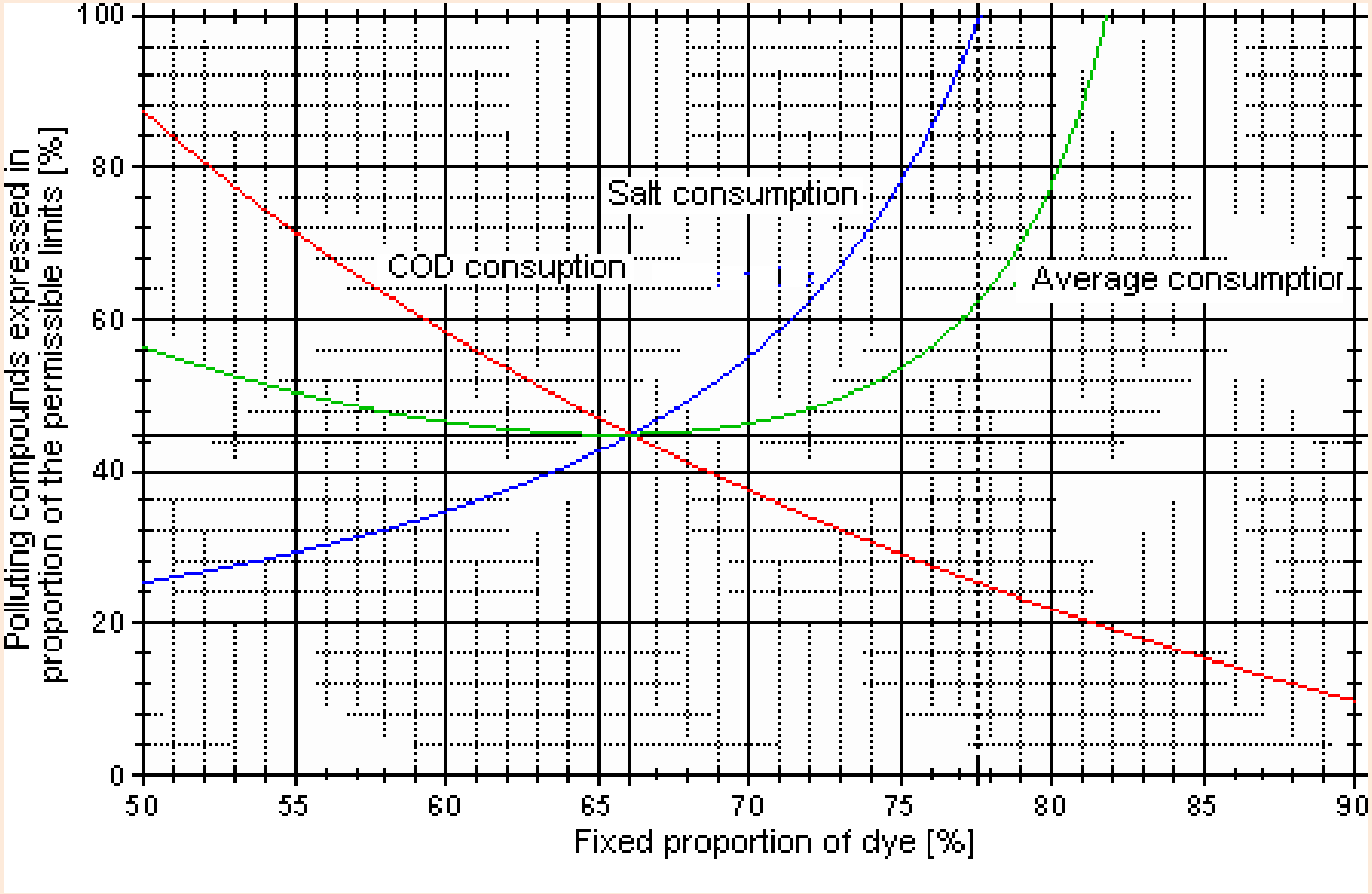
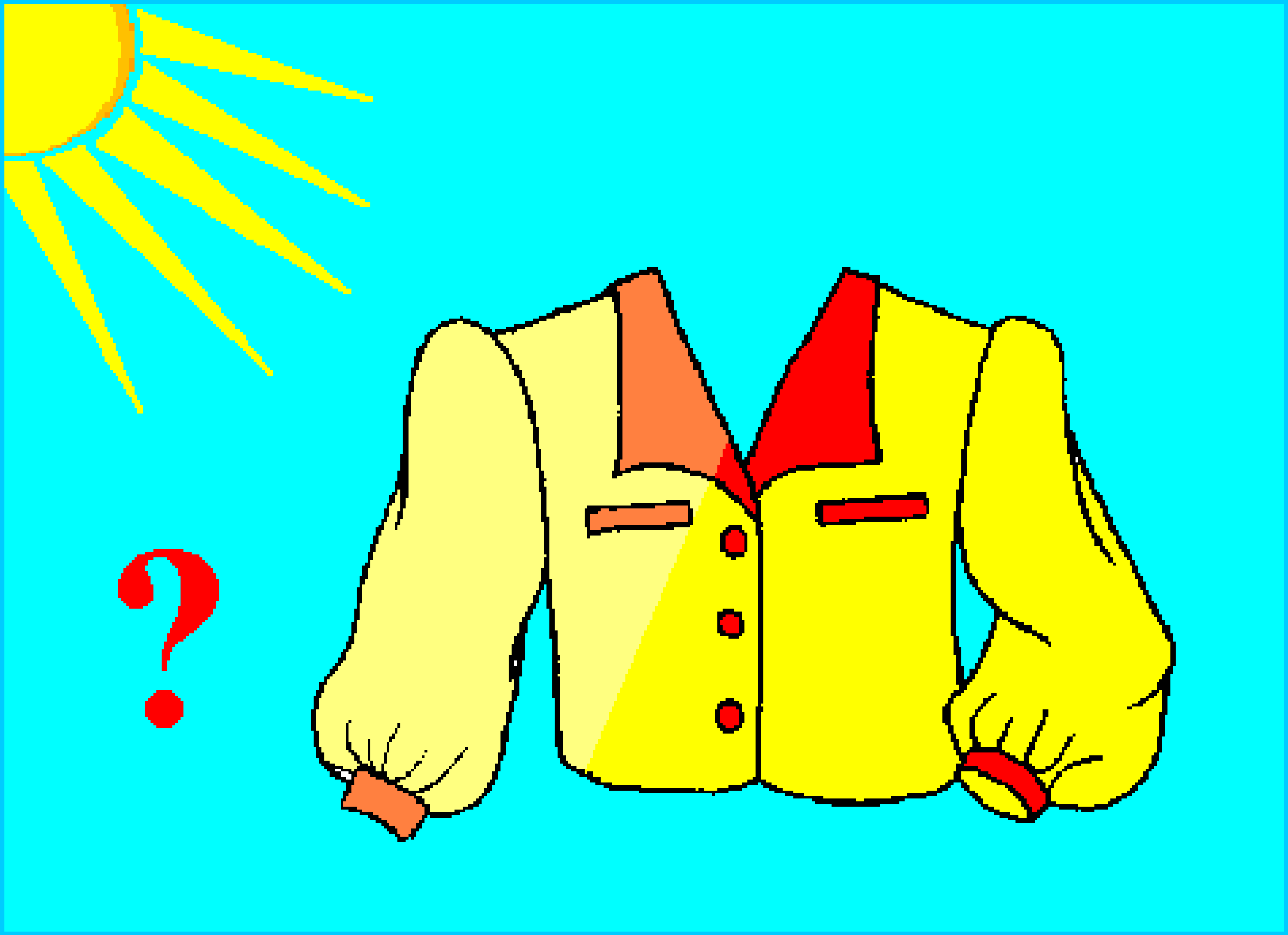


Figure 4. : The changes of the polluting compounds expressed in proportion of the permissible limits % in the function of fixed amount of dye (DRIMAREN Yellow K-2R dye (Standard Depth = SD: 1/1))

American and European consumer associations criticised the fading caused by light-related effects of garments, even when dyed with reactive dyes.

KNOW HOW? ← KNOW WHY?

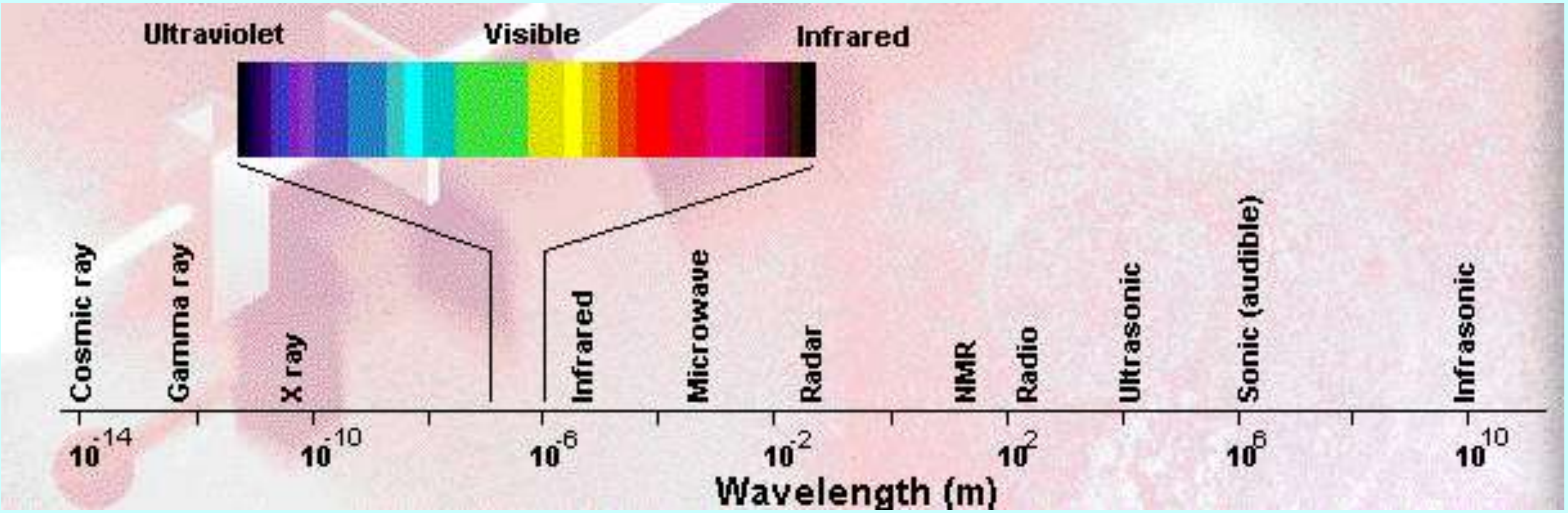


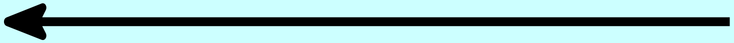
”KNOW WHY”

Photochemical background of the observed fading phenomena

Spectral characteristics of incident light

UV region has a particular influence on photo-degradation process





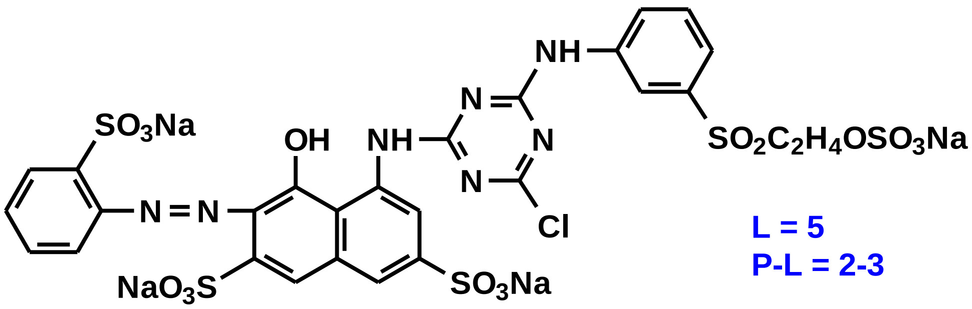
Increasing photofading

1. The impact of dye characteristics (chromophore, structure, concentration, mixture)

Studied dyes:

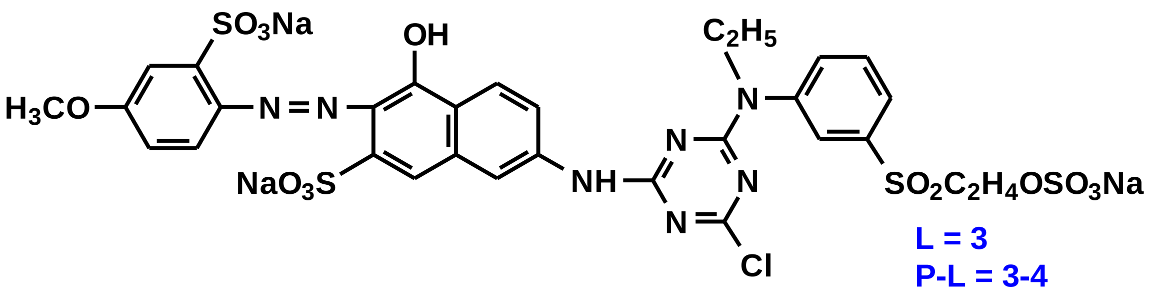
Heterobifunctional monoazo

A



L = 5
P-L = 2-3

B



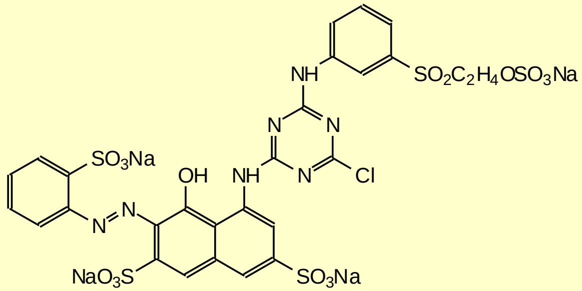
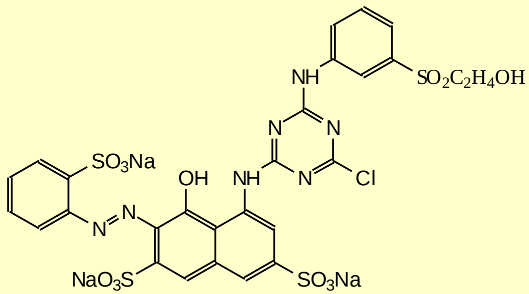
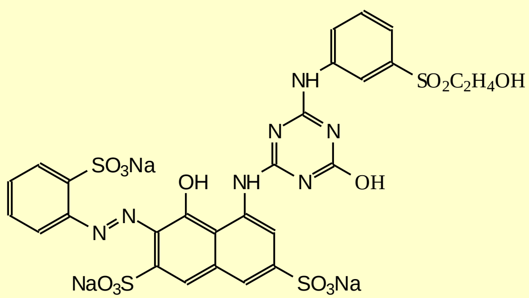
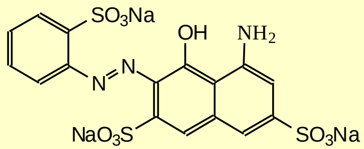
L = 3
P-L = 3-4

Results:

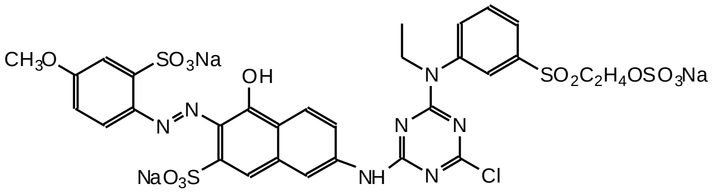
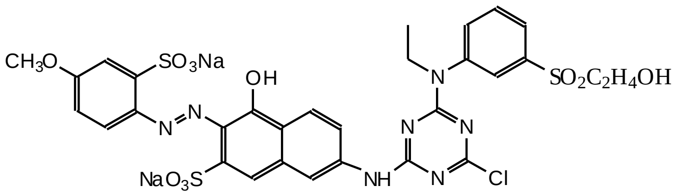
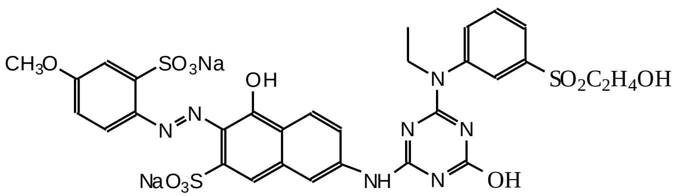
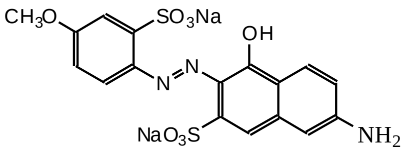
Significant different in light as well as in perspiration–lightfastness could be detected.

Víg et al. ***Dyes and Pigments*, 1994; *Dyes and Pigments*, 1998.**

Set of dyes

	Formula	Abbreviation	Explanation
A dyes		A(MCT-VS)	Heterobifunctional reactive azo dye
		A(MCT-VH)	(AMCT-VS) with hydrolysed VS group
		A(MH-VH)	A(MCT-VS) with hydrolysed MCT and VS groups
		A(Chr)	A chromophore (A(MCT-VS) without MCT and VS groups

Set of dyes

	Formula	Abbreviation	Explanation
B dyes		**B(MCT-VS)**	**Heterobifunctional reactive azo dye**
		**B(MCT-VH)**	**(BMCT-VS) with hydrolysed VS group**
		**B(MH-VH)**	**B(MCT-VS) with hydrolysed MCT and VS groups**
		**B(Chr)**	**A chromophore (B(MCT-VS) without MCT and VS groups**

Photochemical background
„**KNOW WHY**”
of the observed fading phenomena

The role of dye – fibre covalent bond

Excitation energy

Transferred → **Improved lightfastness**

Not transferred → **Unchanged lightfastness**

Krichewsky, *Photochemistry and photostabilisation of dyeings,* 1986;
Oakes, *Rev. Prog. Color*, 2001.

Breaking of the dye – fibre covalent bond

No change (without perspiration)

Marked deterioration of lightfastness (in the presence of perspiration)

Vig et al. *Dyes and Pigments, I, II*, 1998.

Photochemical background
„KNOW WHY”
of the observed fading phenomena

Role of Electrone

Donating and Withdrawing

Substituents

Oxidative photofading
(in the presence of water always oxidative)

Reductive photofading
(in the presence of alkaline perspiration (histidine) reductive)

Bredereck et al. *Dyes and Pigments*, 1993.

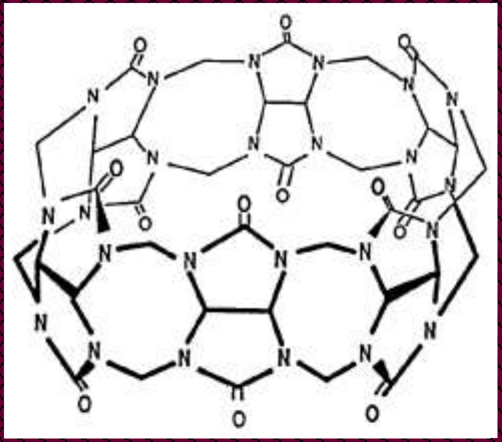
CONCLUSIONS

Photo-stabilizing effect could be demonstrated in case of adding the named additives dissolved in organic solvent.

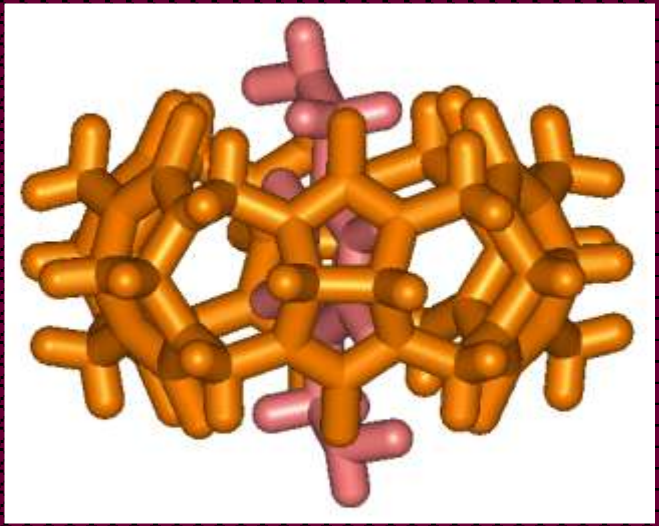
The effect of the additive is decreasing the luminescence of the dye.

1.0 – 1.5 increase in degree of lightfastness could be achieved.

The model of Cucurbit[6]uril (CU[6])

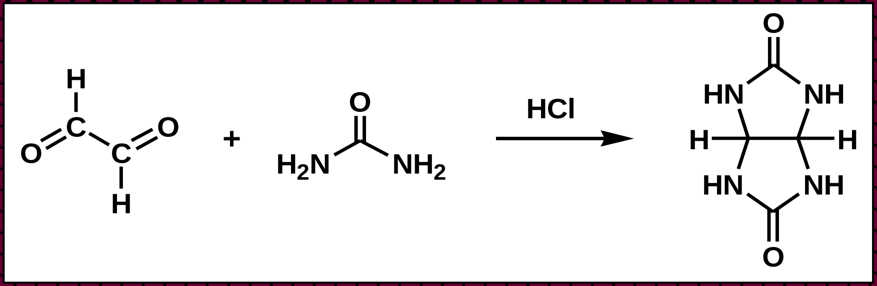


Cucurbita maxima

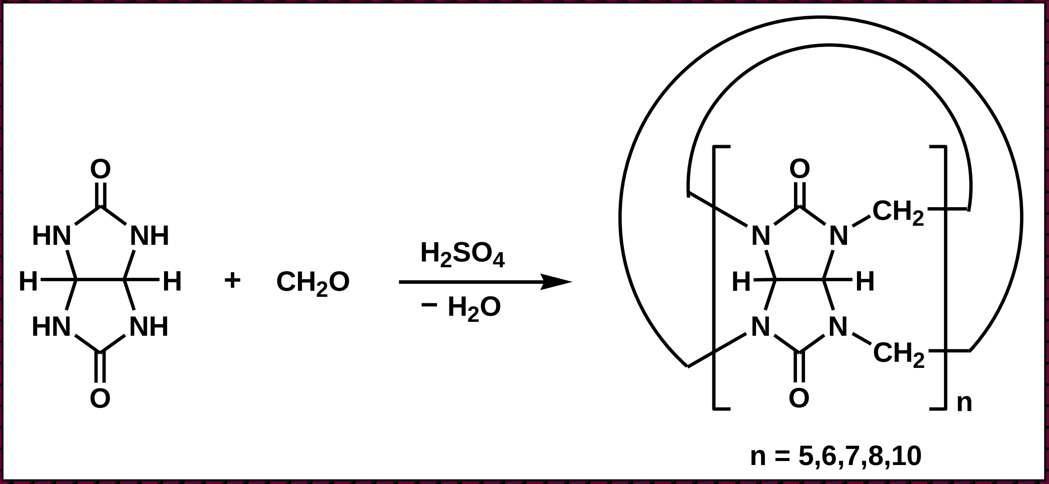


Preparation of Cucurbiturils

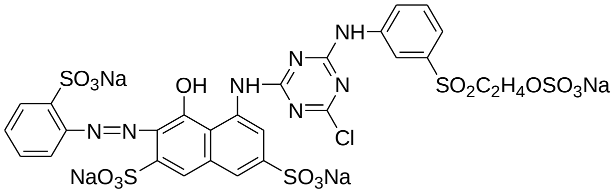
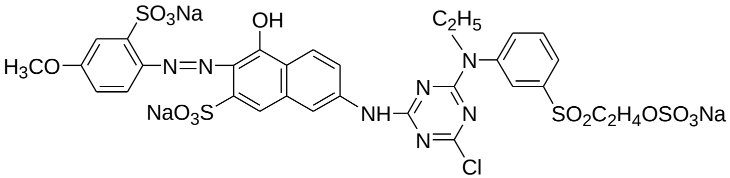
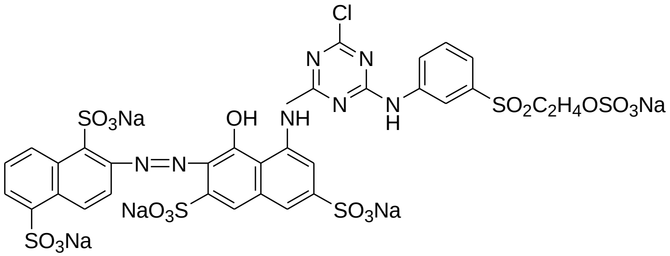
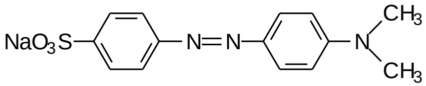
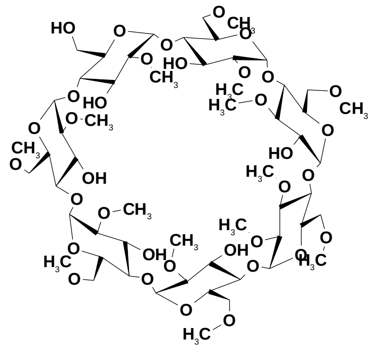
The production of glycoluril from glyoxal and urea is the first step of the synthesis of cucurbituril



Cucurbituril is the product of the reaction between glycoluril and formaldehyde in the presence of a mineral acid



Dyes and auxiliary (cont.)

Typ	Code	C.I. Generic Name	Structure
Reactive Dyes	**Sumitomo A**		
	Sumitomo B		
	Sumitomo C		
Acid Dye	**Methyl Orange**	**Acid Orange 56**	
–	**RAMEB**	**–**	

Efficiency of a reactive dye complexation by CU[8] has been studied in the presence of Na^{+}, K^{+}, Mg^{2+} and Ca^{2+} cations, respectively

Impact of selected cations on reactive B dye complexation by CU[8]

Cation	Removed dye [%]
Na^{+}	66.2
Mg^{2+}	74.0
K^{+}	73.0
Ca^{2+}	85.9

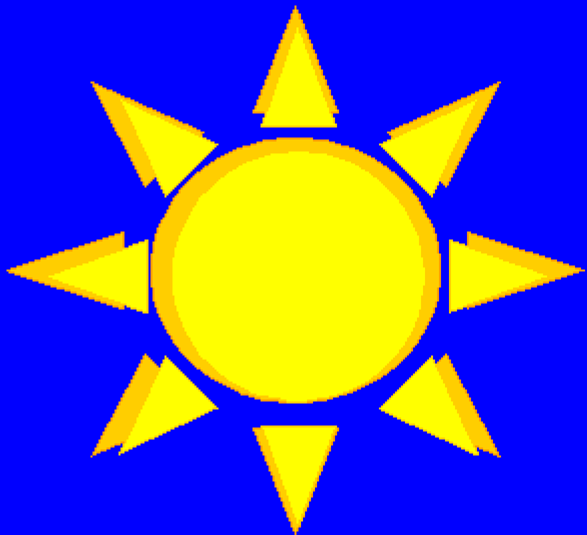
The impact of Na^{+} has been just detectible, that of K^{+}, Mg^{2+} ions was definite one and that by Ca^{2+} ion was the highest. Possible explanation: the compression of the diffuse electric double layer by the studied cations. This phenomenon enables the easier approach of CU by the dye anions.

Summary

Homologue mixture of basic molecules of cucurbiturils has been synthetised and cucurbituril[6] (CU[6] and cucurbituril[8] (CU[8]) have been isolated by means of solvent-extraction. Complex derivatives of different acid, reactive and disperse dyes have been produced by them. CU8] has been definitely more efficient in complex formation with all the studied dyes than CU[6].

Competitivity in complex formation between randomly methylated ß-cyclodextrin (RAMEB) and the respective cucurbiturils with disperse dyes has been studied and superiority of CU8] could be demonstrated.

If in water salts of Ca, Mg, K and Na respectively have been dissolved the complex forming efficiency of the cucurbiturils with acid and reactive dyes have markedly been increased.



Thank you for your kind attention

Az enzimes eljárások összefoglalása

pamut

előkészítés, lefőzés

fehérítés után peroxid-ölés

maghéj eltávolítás

göb-, pihe-mentesítés

selyem

hámtalanítás

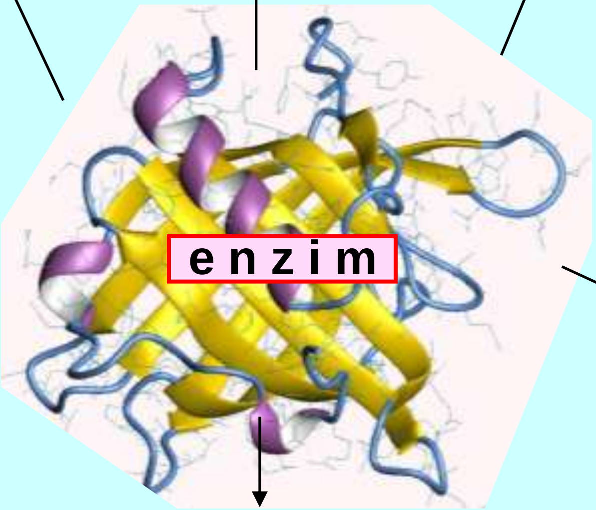
matt szálfelület elérése

gyapjú

zsírosgyapjú mosása

karbonizálás

nemezelődés-mentesítés



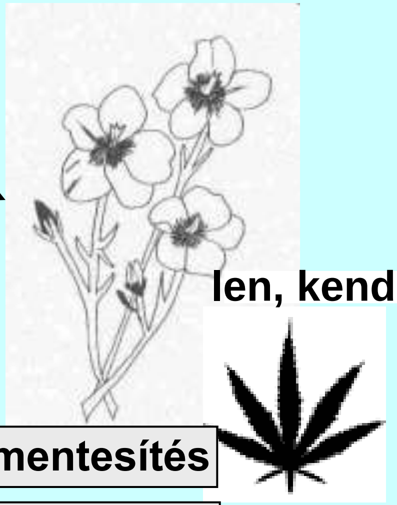
Denim cikkek

koptatás

szösz-mentesítés

LYOCELL BY LENZING

rostosító hatás

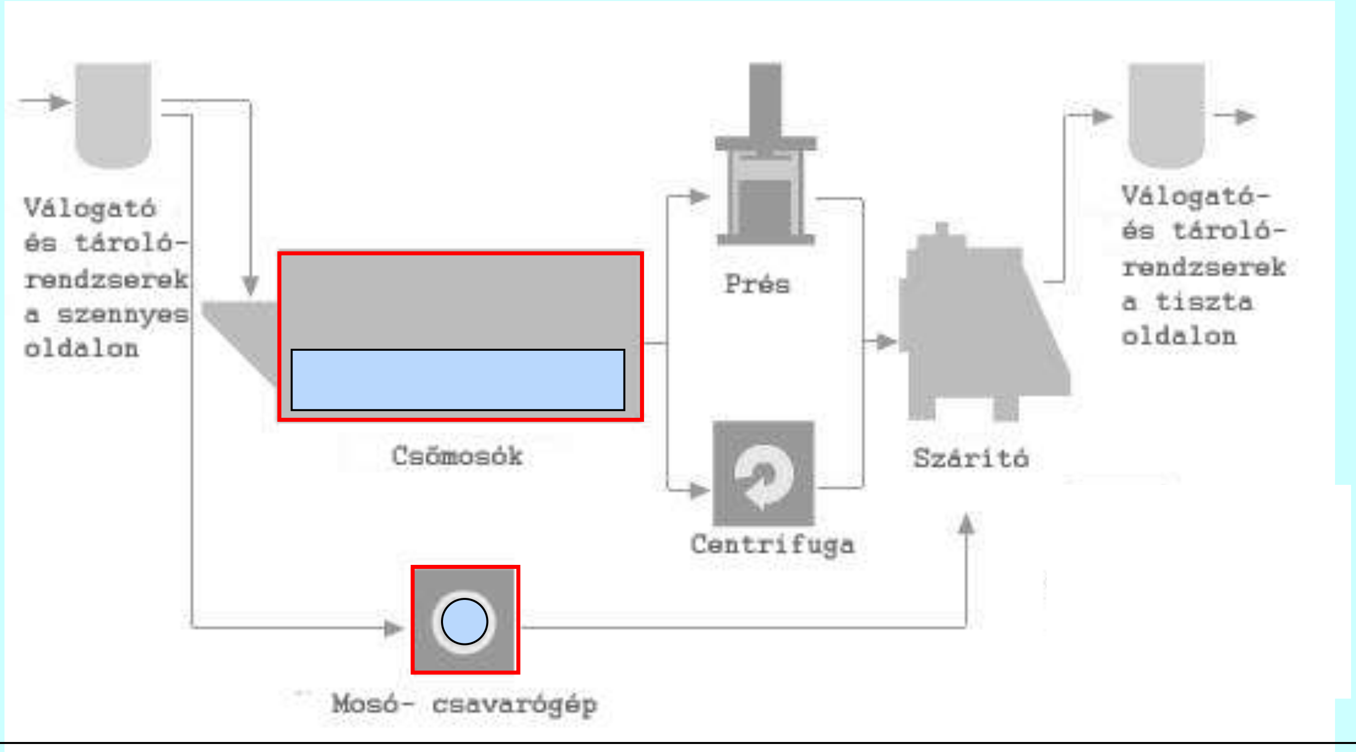


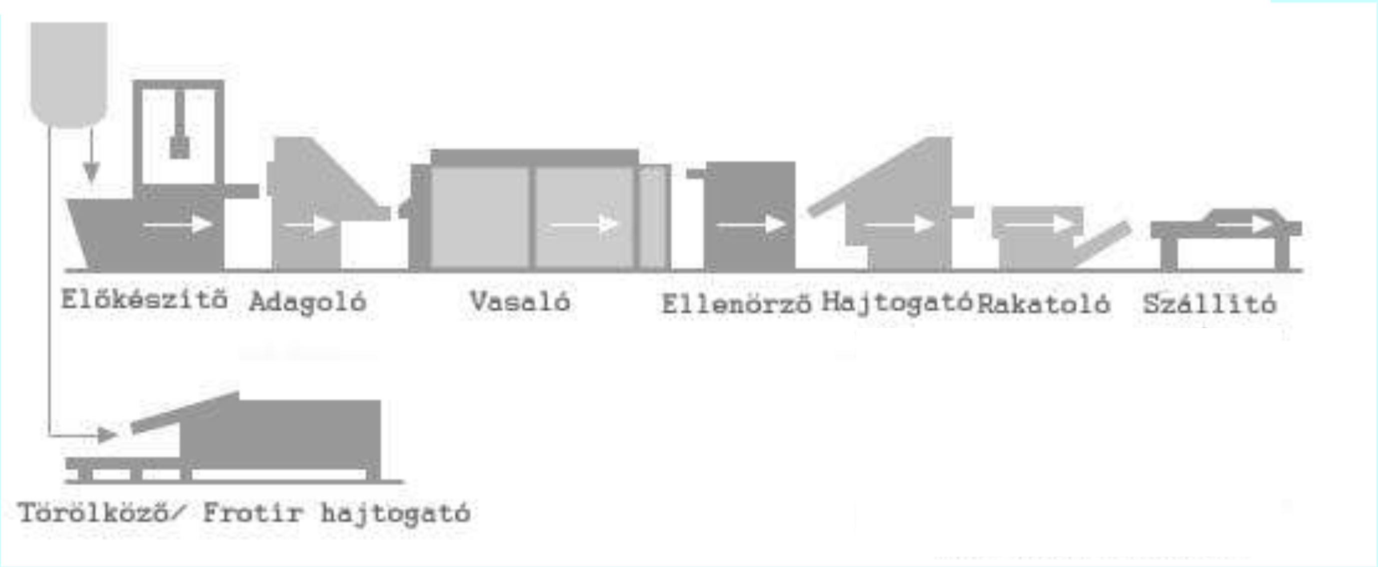
len, kender

göb-, pihe-mentesítés

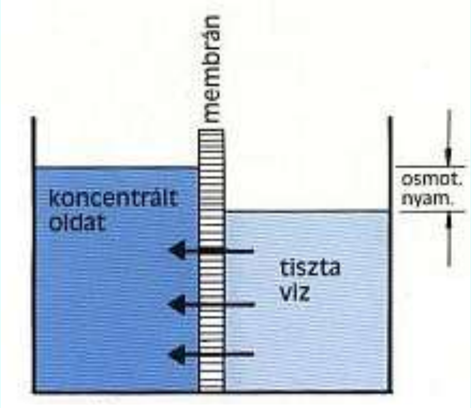
fogás javítás

A textiltisztítási eljárások összefoglalása – nagyüzemi mosás

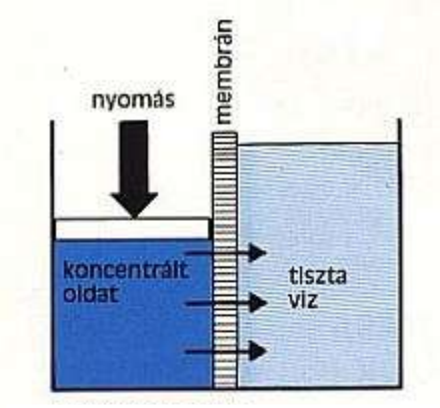




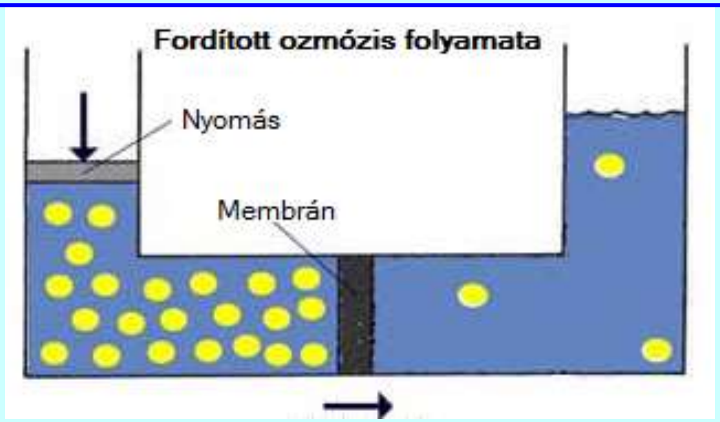
Vízlágyítás, -tisztítás fordított ozmózisnyomással



ozmózis jelensége



fordított ozmózis



a membrántechnológia kihasználja a féligáteresztõ membránoknak azt a tulajdonságát, hogy a vízmolekulákat áteresztik, de a vízben oldott sókat, ionokat, egyéb szennyeződéseket visszatartják

A textilkikészítő-ipari szennyvizek terhelő tényezői

- pH (pl. pamutipari üzemeknél lúgos, gyapjúiparban savas) → semlegesítés
- magas sótartalom → elkerülés
- magas foszfáttartalom → elkerülés
- színes jelleg → oxidáció, lebontás
- magas hőmérséklet → hőcserélővel hasznosítás
- esetleg nehézfém tartalom, szerves klórvegyület előfordulása → elkerülés
- szerves szennyeződések miatti magas kémiai (KOI)- ill. biológiai oxigénigény (BOI) → biológiai kezelés, levegőztetés