Scale up of biosorption process for the textile wastewaters treatment using a selected fungal biomass

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The main problems of textile and tannery industries

CONSUME OF WATER

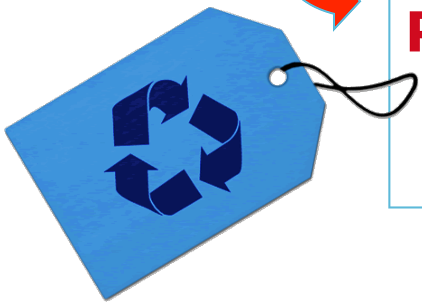
150-200 liters for 1 kg textile fabric (dyeing, washing, finishing, etc.)

GENERATION OF WASTEWATERS

High concentration and variety of pollutants:

colour, COD, salts, tensioactives
(up to 80% of dyes and 90% of salts remain in exaust dyebaths).

toxicity (**mandatory test!**)



They need to be PROPERLY TREATED and water should be REUSED!

Many countries issued restrictive regulation (2002/61/CE)

Italian legal threshold values for industrial wastewaters discharged in surface waters (DM 152/06):

- **colour**: not visible at 1:20 dilution;
- **COD**: ≤ 160 mg l^{-1};
- **salts**: SO_4^{2-}≤1000 mg l^{-1},Cl^-≤1200 mg l^{-1};
- **tensioactives**: ≤2 mg l^{-1};
- **toxicity** (**mandatory test!**): <EC 50.

Textile and tannery wastewaters are not properly treated in conventional WWTPs, because of their toxicity and recalcitrance.

Environment problems (aesthetic pollution, eutrophication, perturbations in aquatic life)

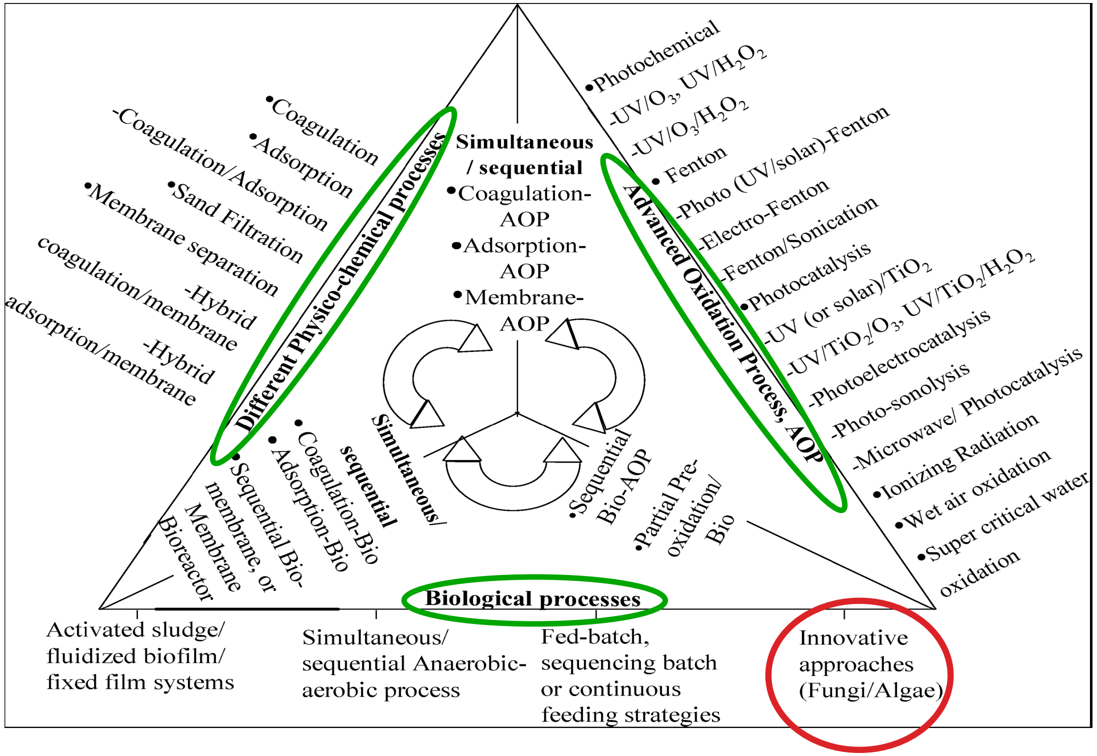
Health problems: (dye, their degradation products, salts and heavy metals have **toxic**, **carcinogenic**, **mutagenic** effects)

Ethical / social problems: (high costs, activated sludge in agriculture, polluted water for irrigation)

Toxic substances contained in coloured wastewaters should therefore be completely removed before being released into the environment.

Virtually all known physicochemical and biological techniques have been explored for treatment of these wastewaters; none, however, has emerged as a panacea.

Not always applicable and/or effective; high costs; use is restricted in scale of operation and pollution profile of the effluent



Cost competitive; rather ineffective; long time required; strictly controlled environments

A single universally applicable end-of-pipe solution appears to be unrealistic, and **combination of appropriate techniques** is deemed imperative to devise technically and economically feasible options

Biosorption can be regarded as a valid tool.

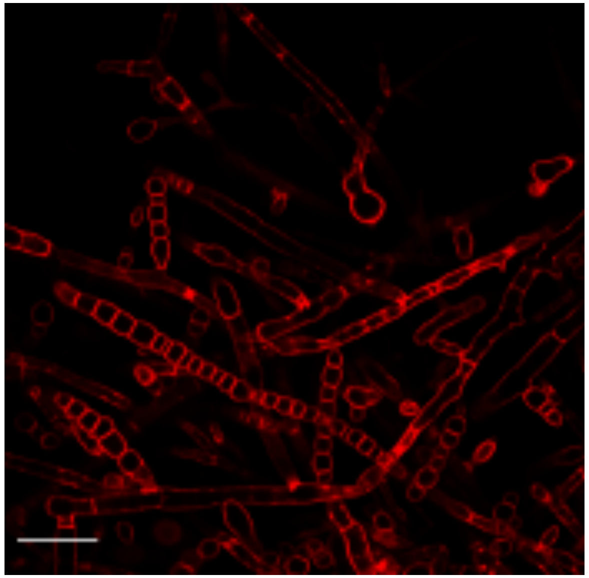
BIOSORPTION = the removal of pollutants from solutions using sorbents of biological origin.

Individual cells or cell components bind or take up pollutants by:

• adsorption onto a surface including ion exchange and complexing with ligands;

• uptake into the cell and sequestration by cytoplasmic components.

Dyes are mainly localized at the cell wall level.
metabolism-independent mechanisms involved in dye biosorption on fungal biomasses.

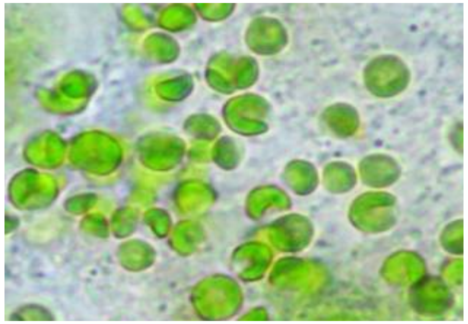


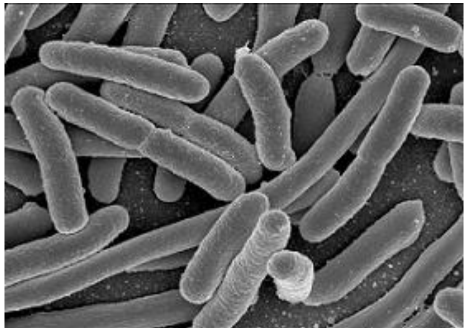
Main advantages of biosorption are:

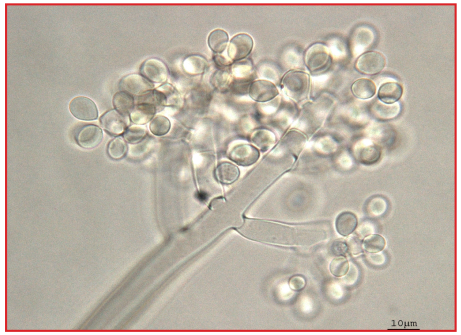
- high efficiency;
- cost effectiveness;
- good removal performance from large volumes of effluents;
- possible recovery of water and salts;
- possible use of inactivated biomasses.

- **Dead organisms** are not affected by waste toxicity;
- they do not pollute the environment realeasing toxins and/or propagules;
- they do not require a continuous supply of nutrients;
- they can be regenerated and reuse for many cycles.

Different kinds of organisms (algae, bacteria, yeasts, filamentous fungi…) have been tested for biosorption.







Among all these organisms fungi are the most promising ones.

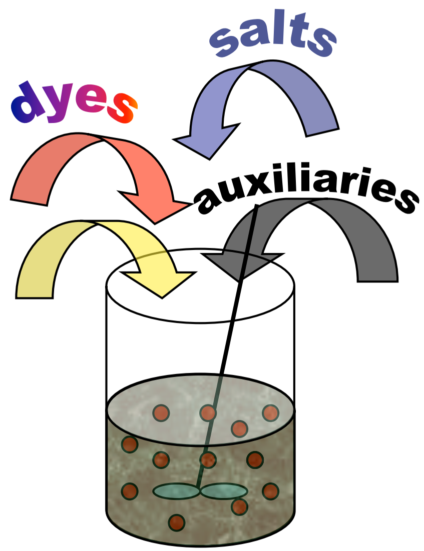
1. They display a multitude of physical and chemical properties that might be exploited in the binding of pollutants.
2. They easily grow and produce high yields of biomass on different media with low nutritional requirements.
3. Many of them are extensively used in large scale industrial fermentation processes representing a potential source of cheap adsorbent materials.
4. Biomass separation from the liquid constitutes a simple operation.
5. Dead biomass can be easily manipulated and subjected to physical and chemical treatments to enhance its performances.

The actual efficacy and applicability of biosorption for industrial wastewater treatments is difficult to assess.

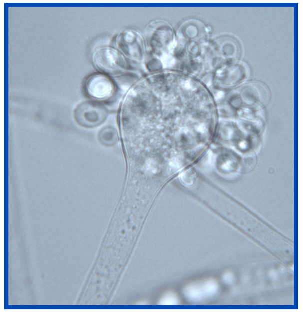
Studies mainly focus on the characterization of processes on single dye solutions at low concentrations.

Not predictive of application to the industrial reality.

Only a few studies about multicomponent solutions mimicking industrial wastewaters or real effluents.



During the last years, at the ***Mycotheca Universitatis Taurinensis* (MUT)**, ***Cunninghamella elegans*** has been selected and patented, for its effectiveness in the biosorption of different industrial dyes and heavy metals.



C. elegans

The decolourisation process has been optimized with respect to:

Media used to grow the fungus: Culture media strongly influenced the cell wall composition, and hence the dyes biosorption yields. Cheaper media (starch and corn steep liquor) achieve the best results;

•Physical pre-treatments: lyophilisation make the biomass robust and stable allowing its conservation and make faster biosorption process irrespective of the particle size;

•Chemical pre-treatments: NaOH and HCl change the biomass affinity for different dyes changing the quickness of the biosorption process, but this benefit does not justify the use of additional chemicals that increase cost and environmental impact of the process.

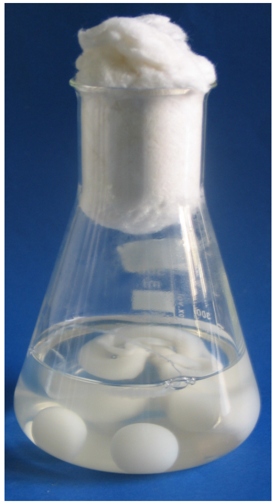
Biomass cultured on starch from cereals and then lyophilised resulted the best!

Aim of this study were to assess the effectiveness of *C. elegans* biomass in biosorption treatments:

compared to a fungal by-product biomass coming from industrial fermentation processes;

considering colour, salts, surfactants and toxicity decrease in different textile spent dye baths and wastewaters in batch and continuous experiments.

C. elegans vs by-product biomass

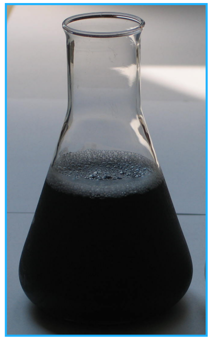


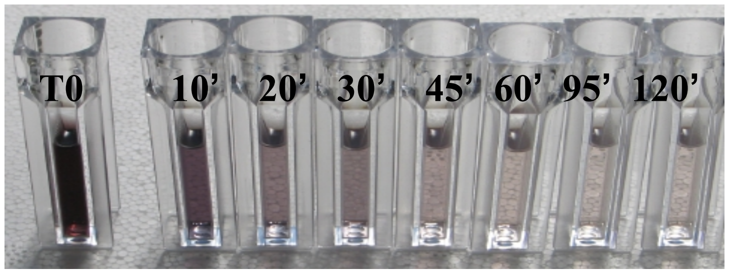
Cunninghamella elegans
was pre-cultured on starch

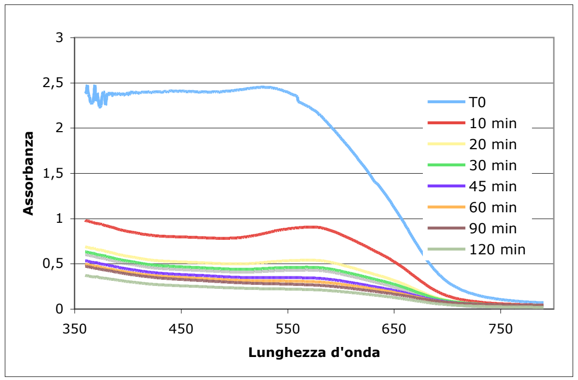
By-product biomass

Acremonium sp.

The two biomasses were homogenized and lyophilized and than put in contact with the effluents (1, 2, 6, 24 h).







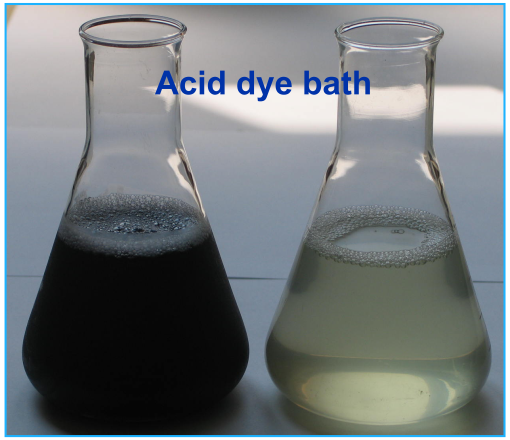
The decolourisation percentage (DP) was determined as the extent of decrease of the visible spectrum area with respect to that of the abiotic control.

9 real spent baths characterized by different dyes and auxiliaries

Effluent	Acronym	Dyes	Salt	pH	Auxiliaries
Real Acid Bath for Polyester 1	**RABP 1**	Mix of 3 dyes at 433 mg l^{-1}	-	5.0	Surfactants, weak acid, fixatives
Real Disperse Bath for Polyamide 1	**RDBP 1**	658 mg l^{-1}	-	9.3	Dispersants, weak acid, strong base
Real Vat Bath for Cotton 1	**RVBC 1**	Mix of 2 dyes at 1424 mg l^{-1}	$NaSO_4$ 20 g l^{-1}	12.7	Weak acid, strong base, glucose
Real Reactive Bath for Cotton 1	**RRBC-1**	Mix of 3 dyes at 542 mg l^{-1}	$NaSO_4$ 77 g l^{-1}	10.9	Weak acid, strong base
Real Reactive Bath for Cotton 2	**RRBC-2**	1 dye at 673 mg l^{-1}	$NaSO_4$ 343 mg l^{-1}	90 g l^{-1}	Ca and Mg sequestering, oil, weak acid, strong base
Real reactive Bath for Cotton - continuous dyeing	**RRBC-3**	Mix of 3 dyes 43 mg l^{-1}	$NaSO_4$ 200 g l^{-1}	10.3	Sodium carbonate
Real reactive Bath for Cotton – washing with cold water	**RRCB-4**	Mix of 3 dyes 34 mg l^{-1}	$NaSO_4$ 200 g l^{-1}	10.0	-
Real reactive Bath for Cotton – neutralization and washing at 40°C	**RRCB-5**	Mix of 3 dyes 98 mg l^{-1}	$NaSO_4$ 200 g l^{-1}	5.9	Acetic acid
Real reactive Bath for Cotton – boiling soaping	**RRCB-6**	Mix of 3 dyes 60 mg l^{-1}	$NaSO_4$ 200 g l^{-1}	7.8	Surfactants-

C. elegans vs *A. strictum* in spent dye baths treatment

WW	Species	Decolourisation percentage (avarange ± st. dev.)			
		1 hour	2 hours	6 hours	24 hours
RAP	*C. elegans*	82.6±0.4	84.4±0.2	85.4±0.3	88.7±0.1*
	A. strictum	81.3±0.4	84.9±0.5	83.4±0.3	81.1±2.8
RDP	*C. elegans*	30.2±6.3	30.1±3.8	24.8±1.1	26.7±2.0
	A. strictum	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0
RVC	*C. elegans*	27.5±2.1	29.6±2.5	20.0±5.1	23.2±0.4*
	A. strictum	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0
RRC1	*C. elegans*	48.0±2.4	54.4±1.3	60.4±8.5	66.0±0.6*
	A. strictum	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0
RRC2	*C. elegans*	42.3±1.7	44.3±1.6	45.4±2.1	28.3±1.7*
	A. strictum	16.7±3.1	20.4±0.3	0.0±0.0	0.0±0.0*
RRC3	*C. elegans*	75.8±2.1	79.2±0.6	78.2±2.3	88.0±0.7*
	A. strictum	0.0±0.0	0.0±0.0	0.0±0.0	5.0±3.8*
RRC4	*C. elegans*	76.4±4.3	80.2±6.6	84.6±2.5	90.7±2.4*
	A. strictum	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0
RRC5	*C. elegans*	94.1±0.4	94.6±0.5	94.5±0.2	98.0±0.3*
	A. strictum	70.4±7.1	73.1±4.6	76.3±2.0	63.9±3.4
RRC6	*C. elegans*	93.2±0.6	92.3±1.9	94.7±0.2	95.5±0.8*
	A. strictum	5.9±1.0	6.2±1.2	11.4±5.8	6.2±1.0



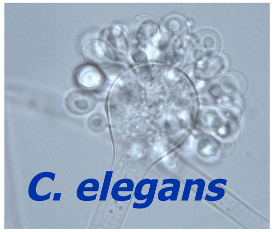
Before **After**

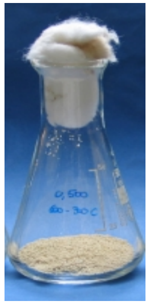
C. elegans **confirmed its effectiveness, but towards vat and disperse dyes.**

A. strictum **was effective only towards acidic baths (RAP and RRC5)**

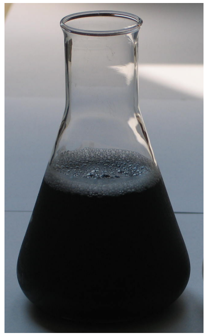
A. strictum **effectiveness lower than *C. elegans.***

Towards a real application: two different approaches





lyophilised



Spent dye baths

(batch and continuous dyeing processes)

40 real samples characterized by different dye classes and concentration, salts, auxiliaries and pH.

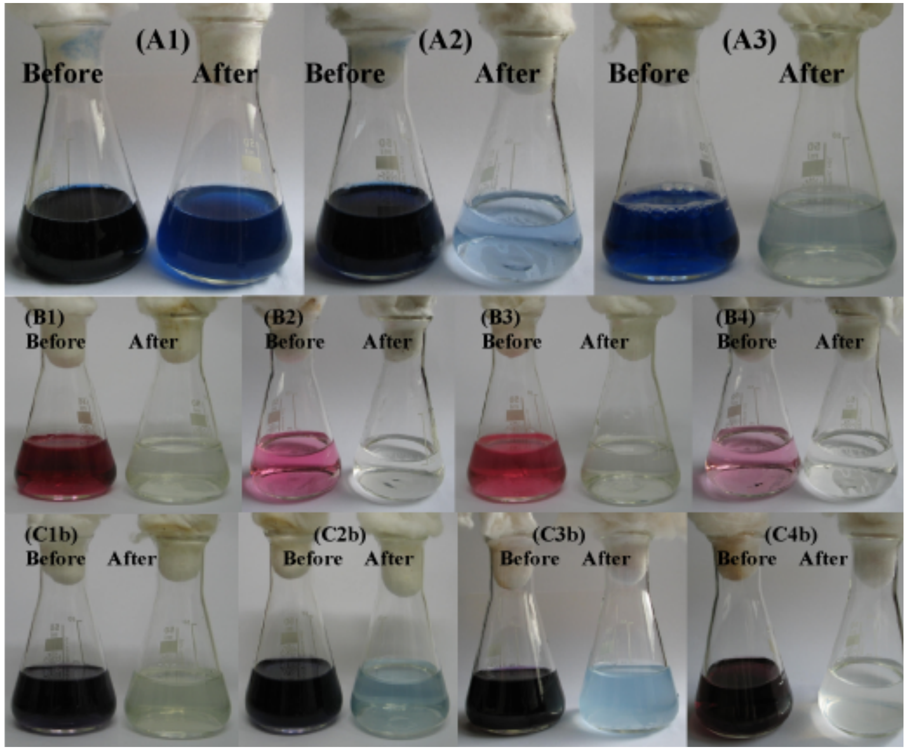
Wastewater treatment plants

(primary, secondary and tertiary treatment)

Colour, COD, toxicity, salts and surfactants

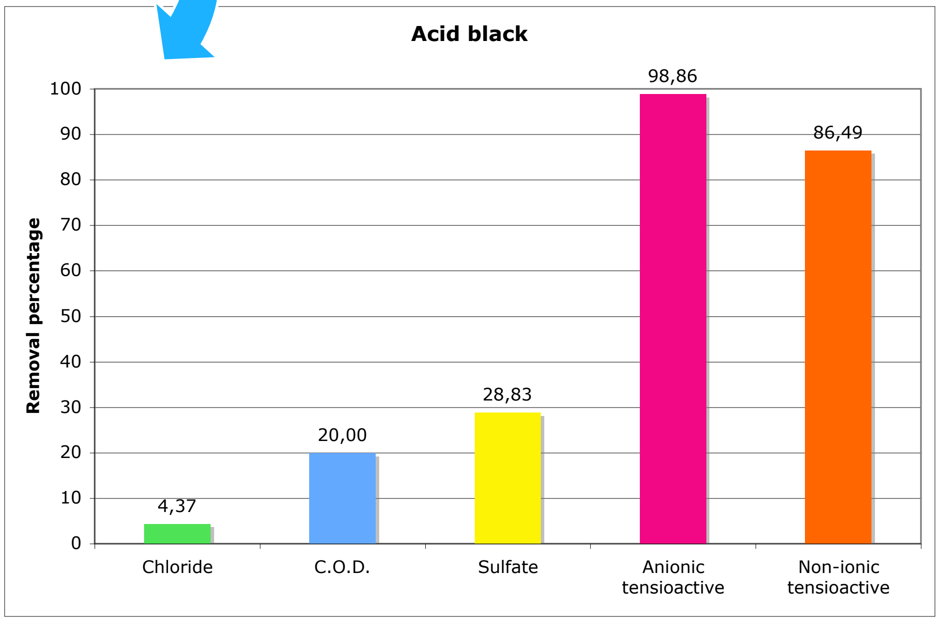
Forniture Tessili Riunite s.p.a., Felli Color s.p.a , Tessitura Enrico Sironi s.a.s, C. Sandroni & C. s.r.l. , Linificio e Canapificio Nazionale s.p.a , Mascioni s.p.a , Cittadini s.p.a , Stazione Sperimentale per la Seta, Centro Tessile Cotoniero e Abbigliamento s.p.a .

Effectiveness of biosorption towards spent dye baths



A **substantial decolourisation** (up to 100%) was achieved within 20 min.

Decrease of important parameters:
•COD up to 68%
•salts up to -57%,
•Surfactants up to 98%.



Effectiveness of biosorption according to the sampling points

Omogenization tank

★

Denitrification tank

Aeration tank

(Activated sludge)

★

3 SAMPLING POINTS (★)

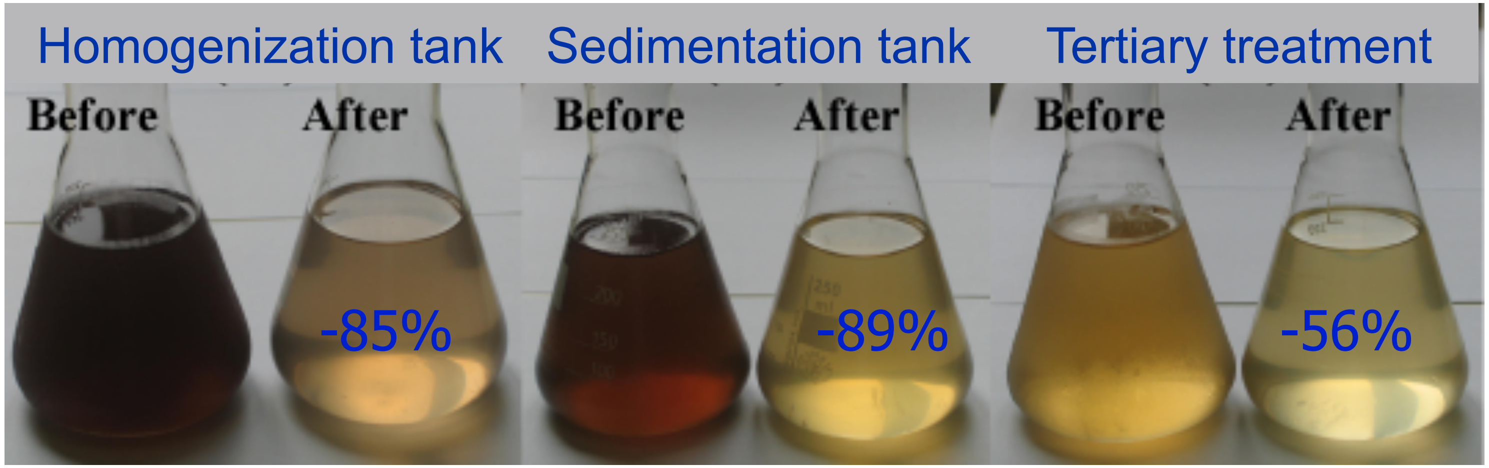
Sedimentation tank

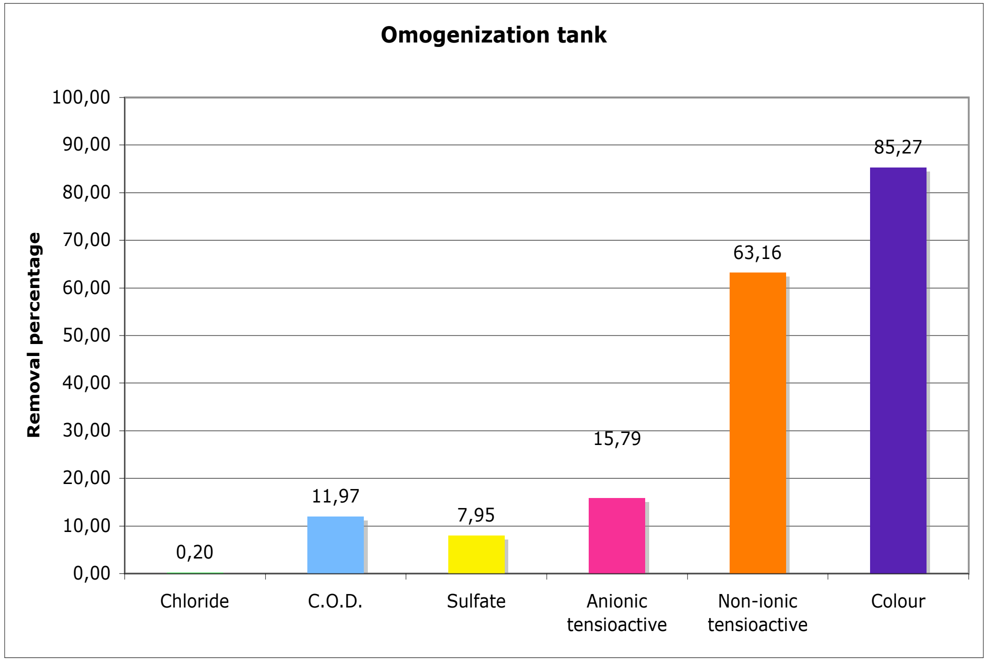
Terziary treatment (Decolourisation)

★

DISCHARGE

Effectiveness of *C. elegans* toward the real industrial effluents

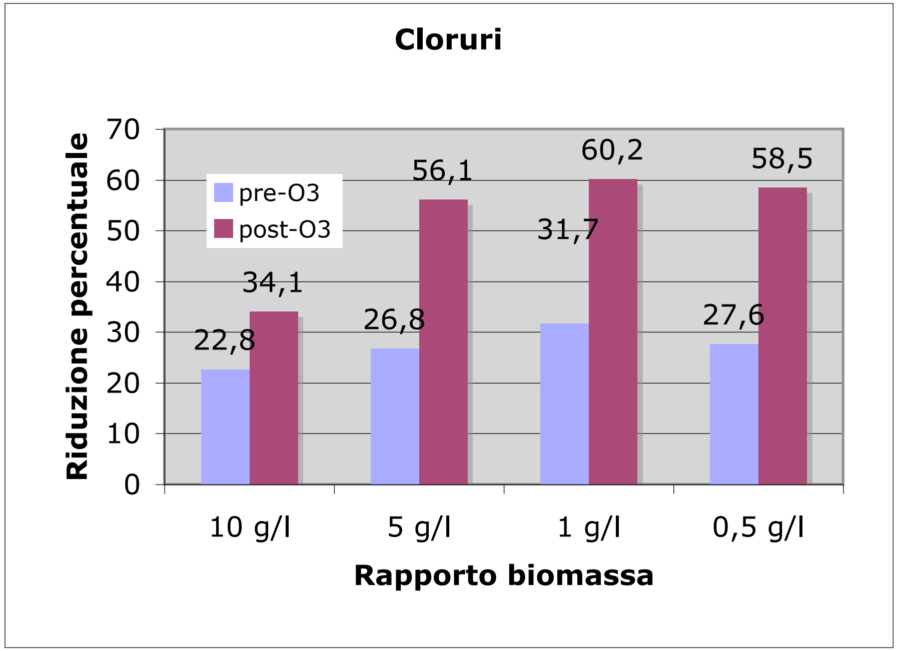


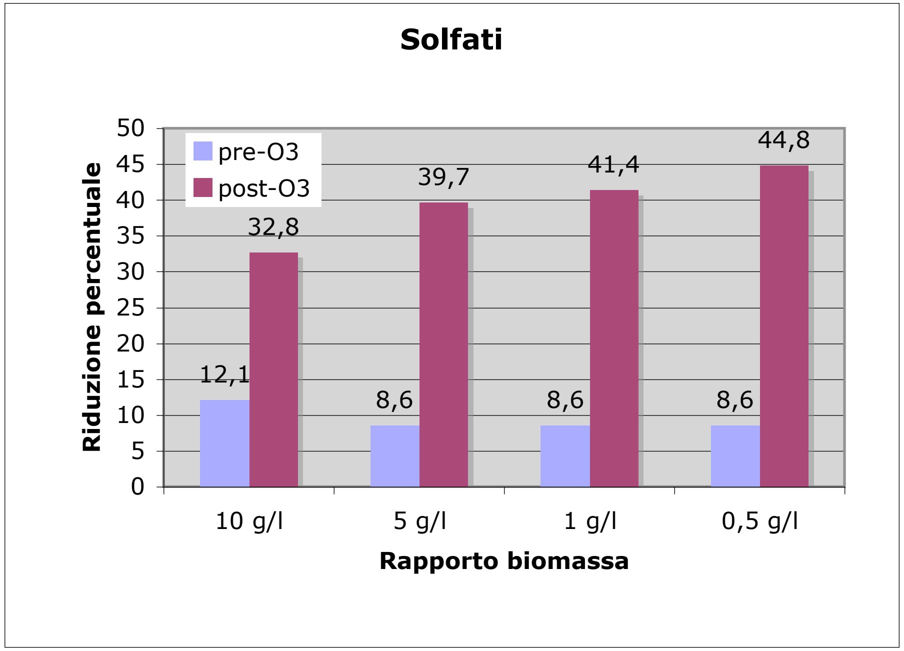


Effective decolourisation also in presence of very low dye concentration

Decrease of COD, salt and tensioactives

Up to now biosorption was considered mainly towards dyes, but the very good results in **salts** and **surfactants** removal open new interesting perspectives!

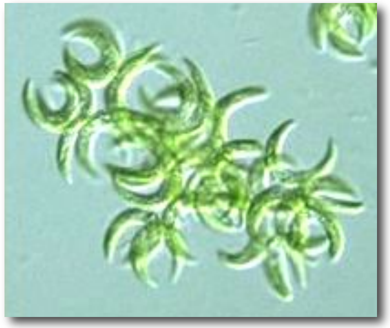




European patent deposition:

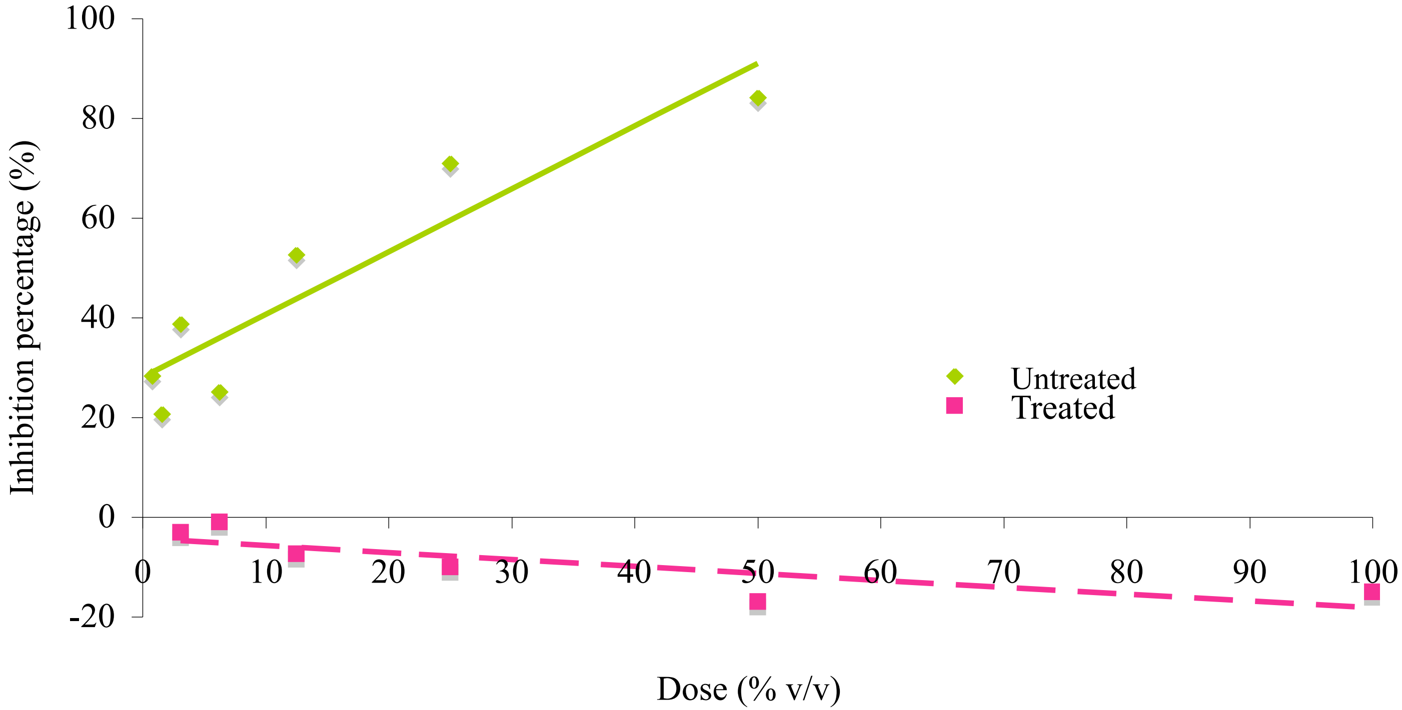
FUNGAL BIOMASS PREPARATION FOR THE TREATMENT OF INDUSTRIAL WASTEWATERS CONTAINING POLLUTANTS
EP10153195.2

Authors: Tigini V., Prigione V., Donelli I., Freddi G., Bertolotto A. and Varese G.C.
Titolare: PAN.ECO S.p.A. (Luxemburg)



ECOTOXICITY: *Pseudokirchneriella subcapitata* was selected, as the **most sensitive** organism towards the wastewaters and it was used **to determine the wastewaters toxicity variation after the biosorption treatment**.

Toxicity **always decreased** after biosorption treatment often under the legal threshold value (EC50)!

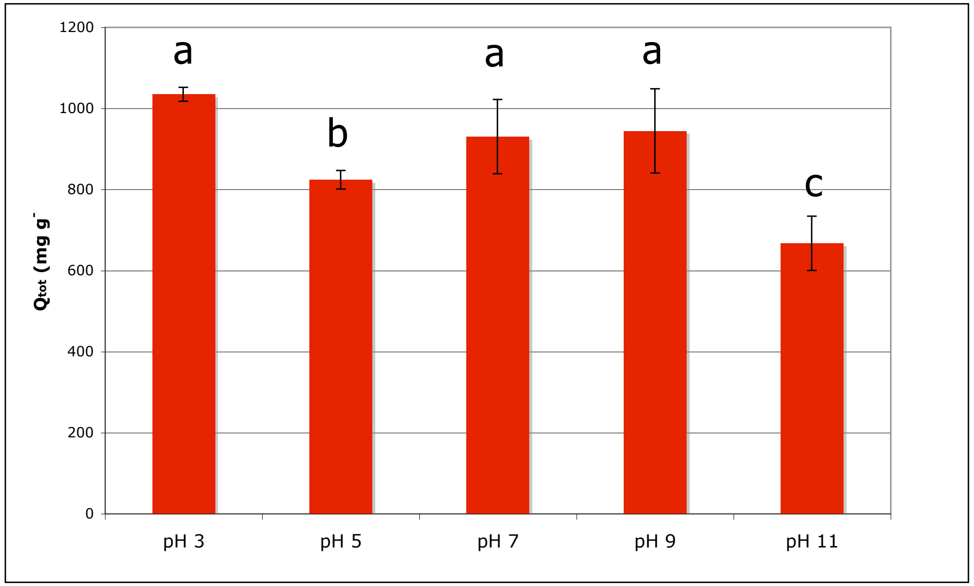


Sample toxicity is proportional to slope and translation of the lines.

NB: *Daphnia magna* resulted insensitive to all textile wastewater tested!

Effect of pH

The literature indicates **pH as one of the most critical abiotic parameter** in regulating the biosorption yields: most of the biosorbent are quite ineffective at high pH values (frequent condition in real wastewaters).



In consecutive feeds, high q_{tot} values (> 600 mg g^{-1}) were obtained from pH 3 to pH 11.

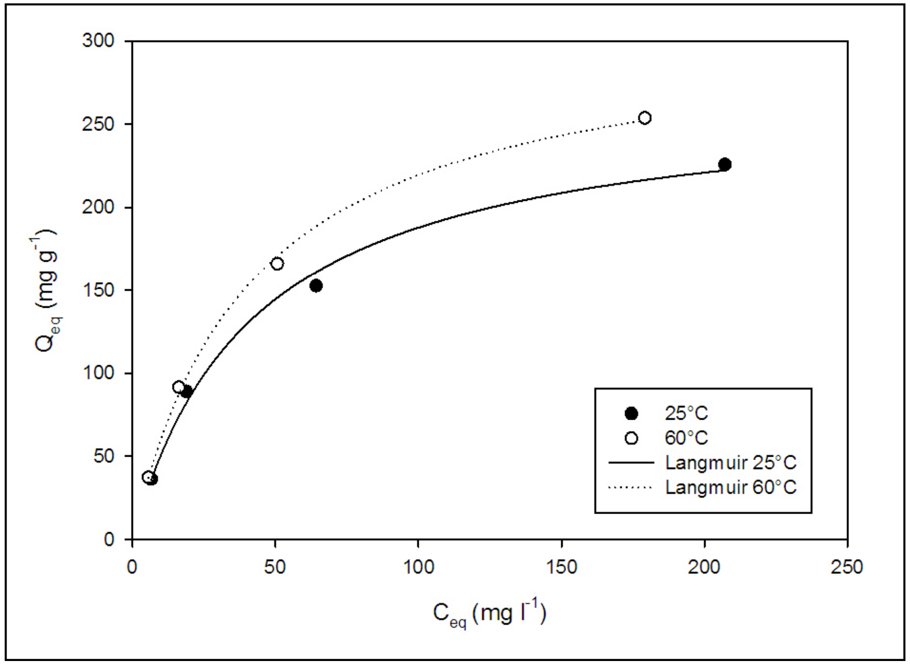
pH is not a limiting factor for the decolourisation yields of *C. elegans* biomass.

Effect of the temperature

Temperature is a very important aspect for a practical application of the method since **wastewaters are generally released at high temperatures**.

C. elegans biomass proved also to be very versatile in a wide range of temperature (25 - 60 °C).

Better results were otained at 60 °C than at 25 °C towards the real acid bath for polyamide!

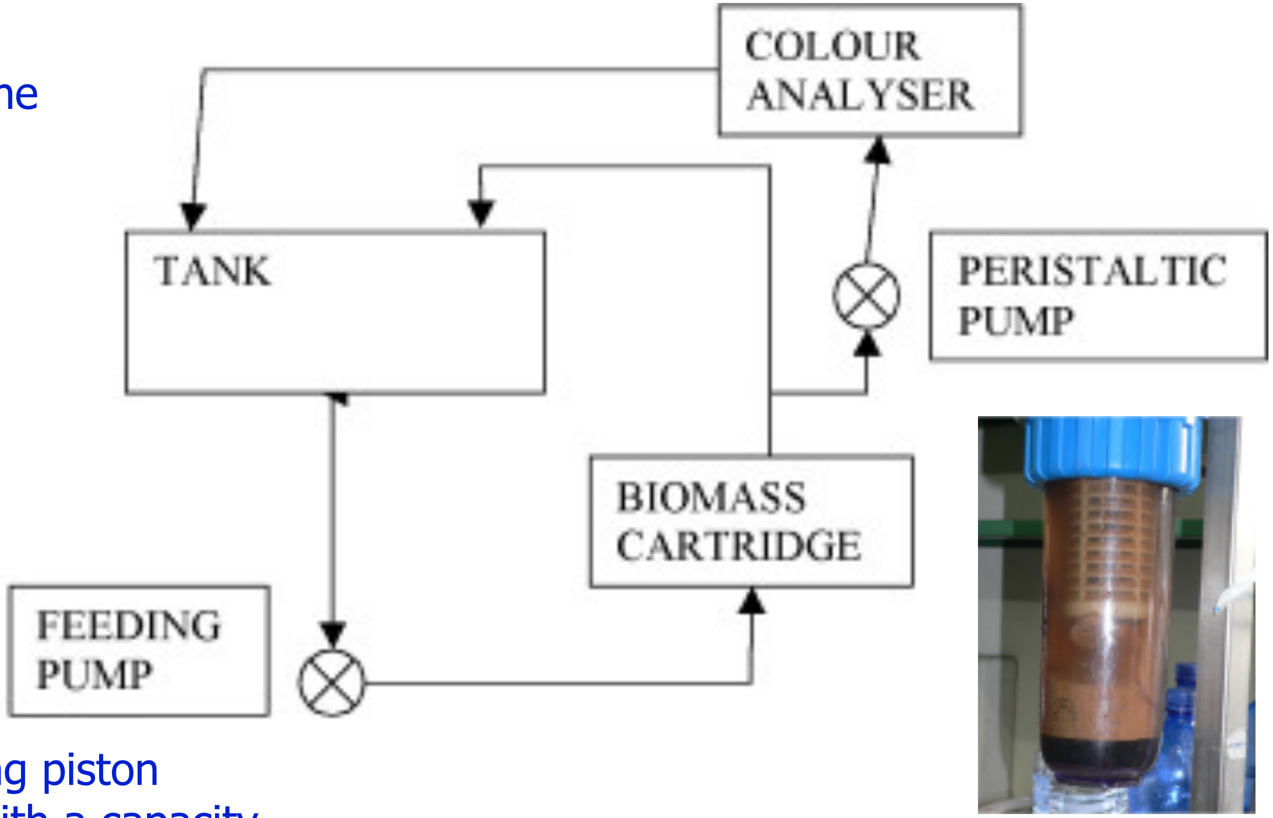


- **Biosorption is a endothermic process**
- ***C. elegans* is effective in true-life conditions**
- **If water could be reused, biosorption would be a power saving treatment.**

Continuous biosorption experiment: the pilot plant

On line **colour analyzer** to continuously check the colour intensity.

Tank (20 L) which feeds the circuit at atmospheric pressure



A metering piston **pump**, with a capacity up to 10 L h^{-1} and a pressure up to 5 bar

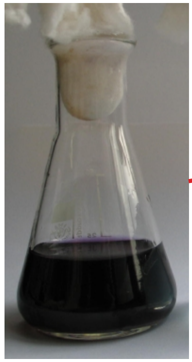
Cartridge in perspex (62 mm diameter x 204 mm height), containing 18 g of the **lyophilised fungal biomass**.

Continuous biosorption experiment: the wastewaters treatment

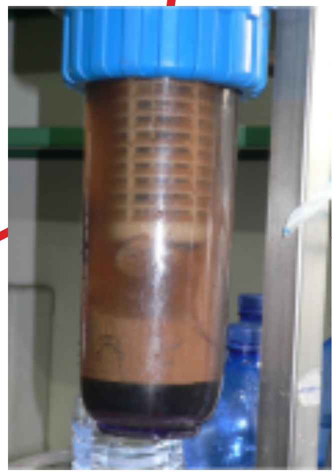
- colour (by spectrophotometer),
- Cl^-,
- SO_4^{2-},
- non-ionic surfactants

were measured at the end of each cycles series.

For each effluent:
- **11 cycles** (150-900 min)



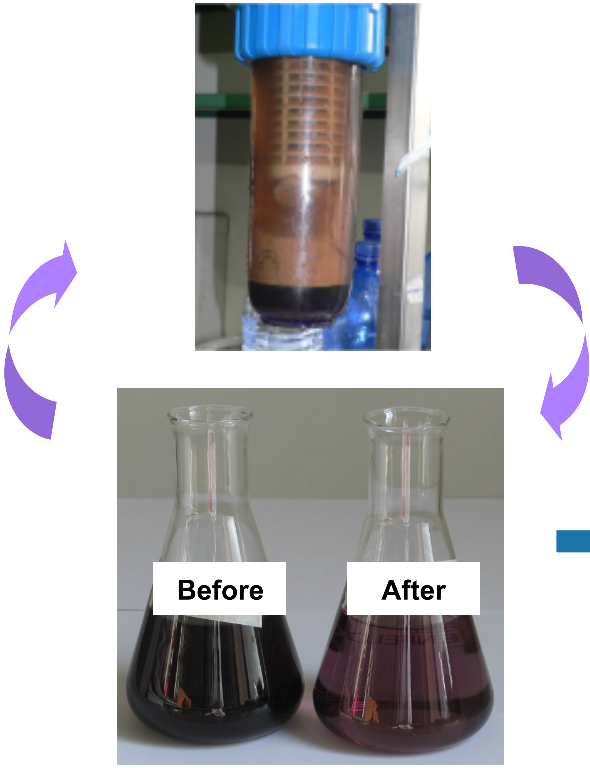
3 L of each effluent:
3 spent dye baths
for wool (A),
cotton (B)
polyester (C)
1 sample from homogenization tank (D).



flow 10 L h^{-1}

Biomass change after each cycles series

Continuous biosorption experiment: results



Sample	Colour	Cl-	SO_4^{2-}	Non-ionic surfactants
A (wool)	-72%	-	-	- 47%
B (cotton)	-54%	-	-20%	- 85%
C (polyester)	-	-15%	-	- 55%
D (omo)	-80%	-	-	- 49%

- *C. elegans* confirmed its effectiveness towards **dyes** (disperse baths was characterized by very low concentration of dyes);
- *C. elegans* confirmed its effectiveness towards **surfactants**;
- Results about salts are **unreliable** because of **colourimetric** analyses are affected by colour samples!

Perspectives: biomass production is in progress

Passing from laboratory scale to industrial scale…

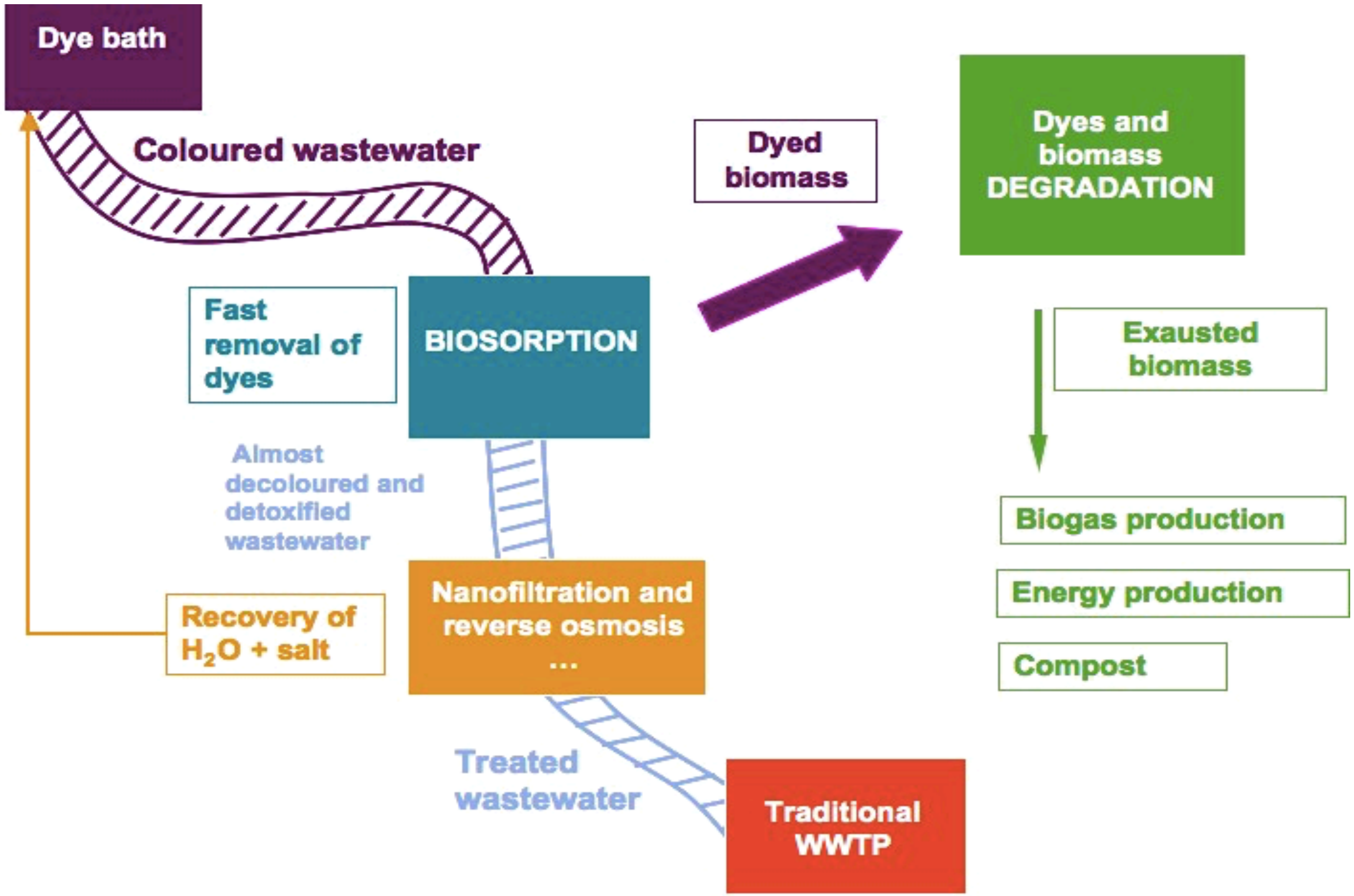
35 g l^{-1} within a week

PURACQUA Project:
Felli Color Spa
EuroD srl
Tosi Spa
Vago Spa
Università Federico II
di Napoli

500 g l^{-1} within 24-48 hours

Biomass production 30 folds higher (Actygea Srl)

Setting up of a pilot plant, which will treat about 1 m^3 d^{-1}



Biosorption is an effective and quick process that can be combined with other physicochemical and biological techniques to reach the 2 main goals: the reuse of water and the complete removal of pollutants.

Acknowledgments

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Puracqua and Biotex Projects

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