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The impact of textile finishing biotechnologies and of the wastewater treatment on environmental quality

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Abstract. The economic development – ecologic equilibrium impact rises numerous and complex problems for the Romanian textile industry, being an important criteria in dwelling upon the research themes related to the environmental protection. This subject, the environment protection, became an essential component of the textile industry development strategy from our country, being the main topic of many researches. The environmental strategy applied can be summarized in the triad: optimization - avoidance - depollution. The following results were obtained during several years of researches and they are detailed in the present paper: pollution studies concerning the polluting factors that are specific for the technologies of finishing textiles; elaboration of modern techniques and technologies of reducing the pollutants' quantity from the effluents resulted during the textile finishing; elaboration of ecologic technological processes by: using enzymes in the finishing processes (cleaning, bleaching, dyeing) meant for yarns and cellulose woven fabrics, dyes and ecologic auxiliaries having reduced power, water and chemical consumption. The main advantages of using the enzymes are associated with less severe reaction conditions, lower processing temperatures, shorter finishing times and the non–toxic and biodegradable products. The new technology used for textile finishing (dyeing), that is presented in this paper, will lead to a minimal negative impact upon the environmental. The quantity of pollutants discharged in wastewaters is minimum and the riscks of contamination are significantly reduced.
Key Words: ecology, enzymes, wastewater treatment, biotechnology, textile industry.

Introduction. Environment protection issues became an essential component of the development strategy the textile industry has, constituting important criteria in the elaboration of different research projects thematic.

Progresses registered on global plan in the synthesis, determination of enzymatic bio-preparations structure and the knowledge of mechanisms by which catalytic processes can take place lead to the enlargement of application scope the biotechnologies have in the textile industrial processes with the aim of elaborating some new technologies for ecological finishing that should assure a sustainable development.

According to Dodu et al (2003) enzymatic bio-preparations constitute an alternative for the classical chemical products used in numerous technological processes.

Experimental research on the finishing biotechnology (pretreatment and dyeing) of the cellulosic textile materials. The classical finishing technologies and biotechnologies for textile finishing were simultaneously experienced in order to compare both mechanical and physico-chemical properties of the textile materials as well as the results in terms of wastewater pollution.

The comparative technological scheme of conventional and organic cellulosic textile materials finishing (Figure 1) and the dyeing process diagram (Figure 2) highlight the advantages of using biotechnology instead of classical technologies.

Results obtained:

- the elaboration of ecologic technological processes by: using catalase type enzymes in the finishing processes (cleaning, bleaching, dyeing) meant for yarns and cellulose woven fabrics, dyes and ecologic auxiliaries having reduced power, water and chemical consumption;
- value reduction of polluting indicators and European Union norms observing;
- technological phases cumulation through bio-technological treatments (Figures 1 and 2).

The comparative results of wastewater quality indicators for both classical technologies and biotechnologies as well as pollution reduction percentage are presented in Table 1 and Figure 3.

The experimental results presented in Table 1 and Figure 3 are obtained at a Romanian textile factory (UCO Ţesătura SRL situated at North Giurgiu Technological and Industrial Park). Both of the processes were tested (the classical one and the ecological process) and for them were takes samples from the wastewater generated. The samples were analyzed and the main quality indicators were determined. The textile factory produces denim cotton fabric. The dyes used for denim fabric are very toxic and in many countries they are forbidden to be used. That is why, this topic is very important and it was studied during several years of research. The results obtained at the Romanian textile company are very good and a significant improvement of the quality indicators can be observed in Figure 3.

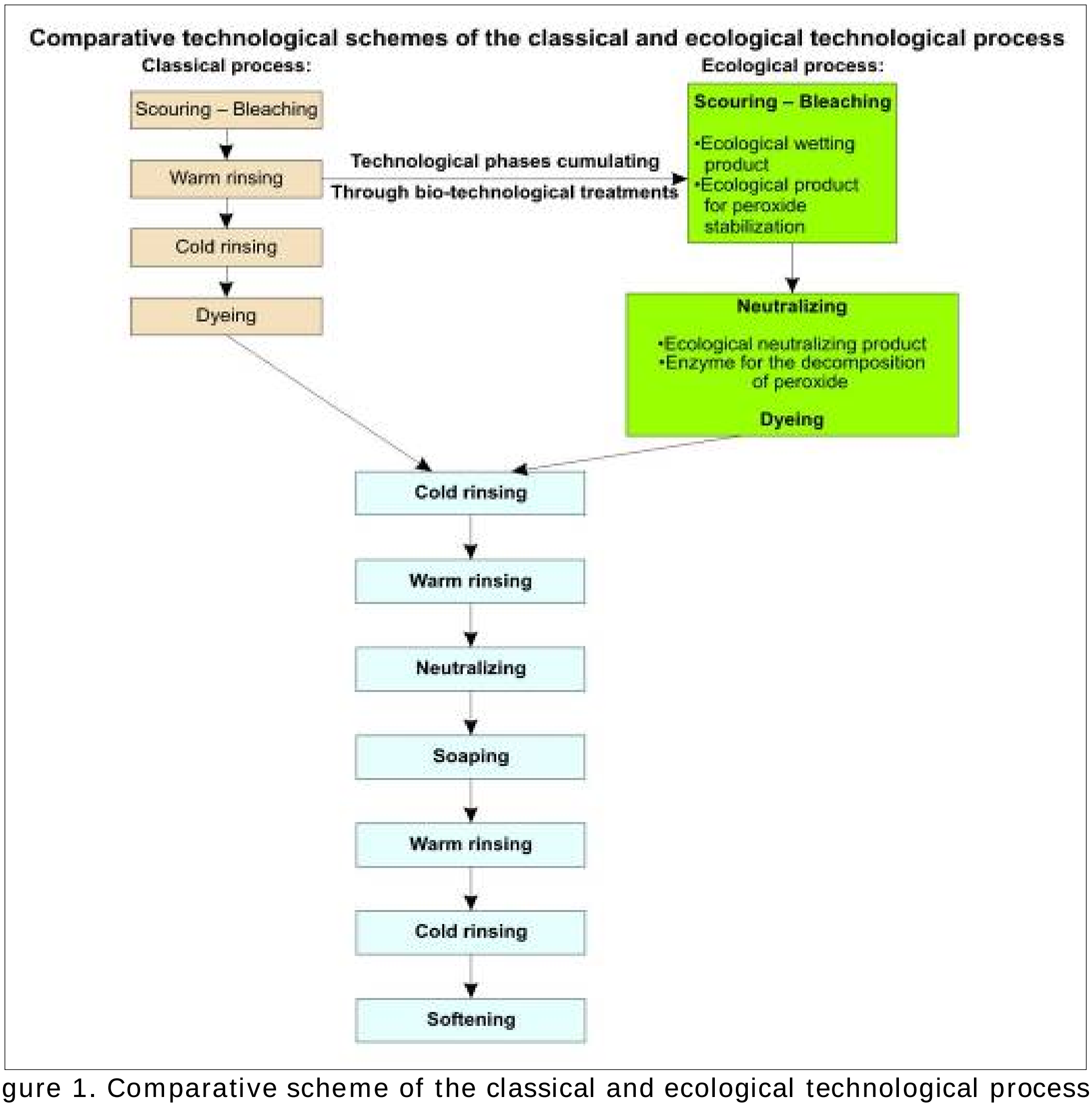

Figure 1. Comparative scheme of the classical and ecological technological process.

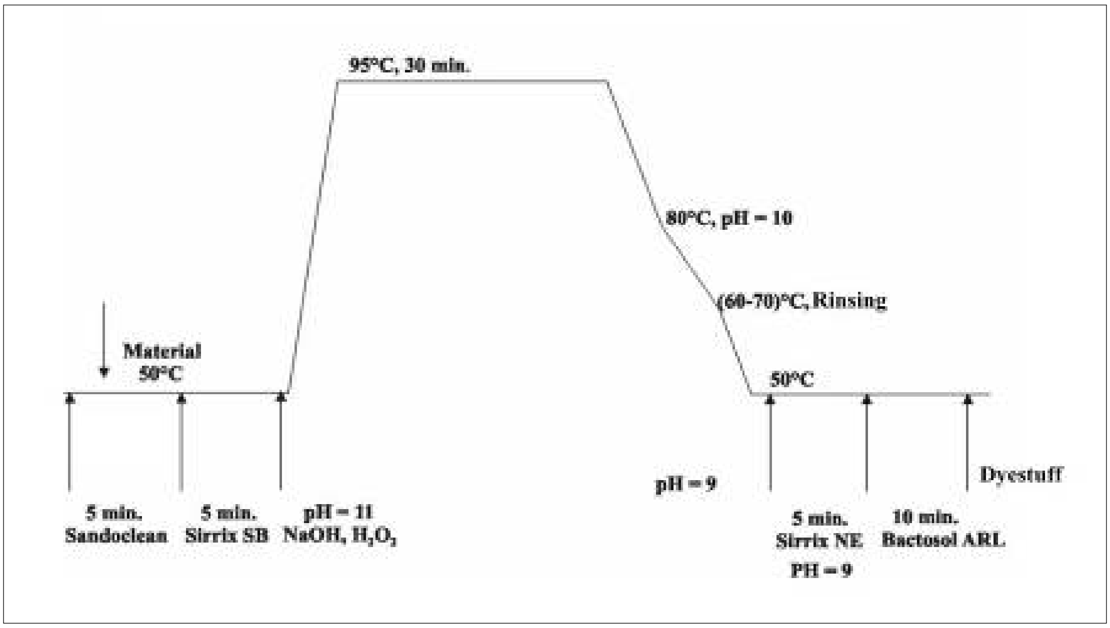

Figure 2. Ecological process diagramme.

Table 1

Comparative analyses of wastewater quality indicators from classical and ecological technological process

Test	*pH*	*COD ($mgO_2\,L^{-1}$)*	*BOD ($mgO_2\,L^{-1}$)*	*Suspended solids ($mg\,L^{-1}$)*	*Sulphates ($mg\,L^{-1}$)*	*Detergents ($mg\,L^{-1}$)*	*Residuum ($mg\,L^{-1}$)*
P1 Wastewater – classical process	12.3	449.82	807.38	167	184.5	6.3	1810
P2 Wastewater – ecological process	7.6	201.9	275.8	11	92.9	5.7	1100
NTPA 002/2005	6.5-8.5	300	500	350	600	25	-
Diminution of P2/P1 (%)	38.2	55.1	65.8	93.4	49.6	9.5	39.2

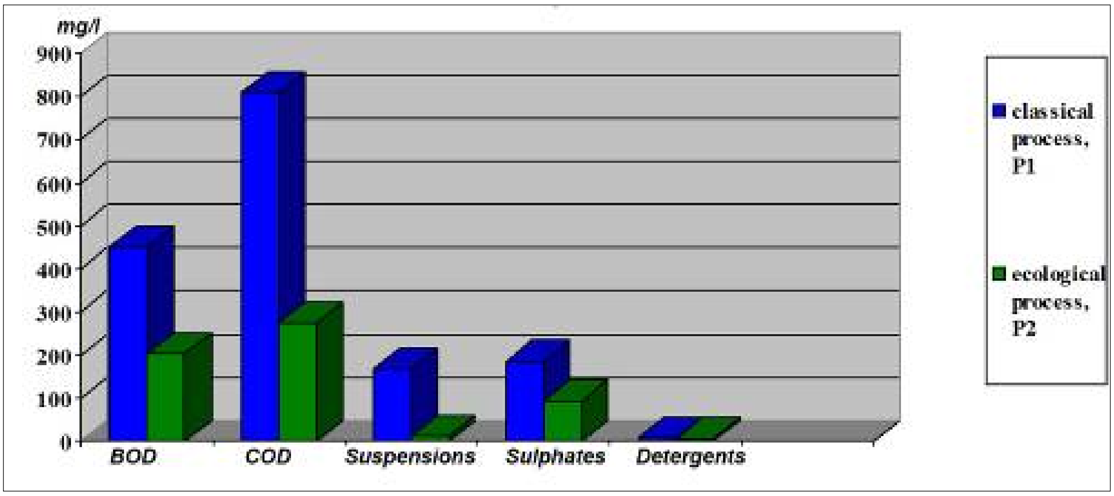

Figure 3. Graphic regarding comparative analyses of wastewater quality indicators from classical and ecological technological process.

The new conceived technology was tested and the following socio-economical effects were obtained:

- reduction of technological phases number (phases cumulating);
- reduction of technological process time by 45 min;

- reduction of technological consumptions/kg textile material by: 56 L water, 0.007 kWh power, 1.02 kg steam, 0.05 kg chemical products;

- reduction of total costs/kg textile material (water, power, steam, chemical products) by 0.293 Euro/kg textile material;

- dying quality enhancement (dye fastness enhancement);

- value reduction of quality indicators for wastewaters (pH, COD, BOD, waterborne, sulphates, detergents), by 30-70%;

- cost reduction for wastewaters de-pollution by 2-4 Euro/L wastewater.

New ecological sulfur dyes dyeing methods for denim type textiles

The consumption of water used for dyeing. During the last years, the water consumption used in dyeing has decreased significantly, depending on the type of dyeing machine/system/process. For example, a reduction of the water consumption of up to 25-40 L kg^{-1} cotton is possible when dyeing with reactive and sulfur dyes. Lange (1997) specifies that during the last years the water consumption values were situated between 100 and 150 liters/cotton kg, values that gradually decreased with the jet dyeing machines development and dyeing systems at low hidromodule.

In Figure 4 the total consumption of water needed for dyeing with sulfur dyes, used also in technological processes of textile SMEs, is presented. This consumption is determined for the rinsing/washing process that follows bleaching and dyeing. Hidromodule correlation with the total water consumption is not linear (Table 2).

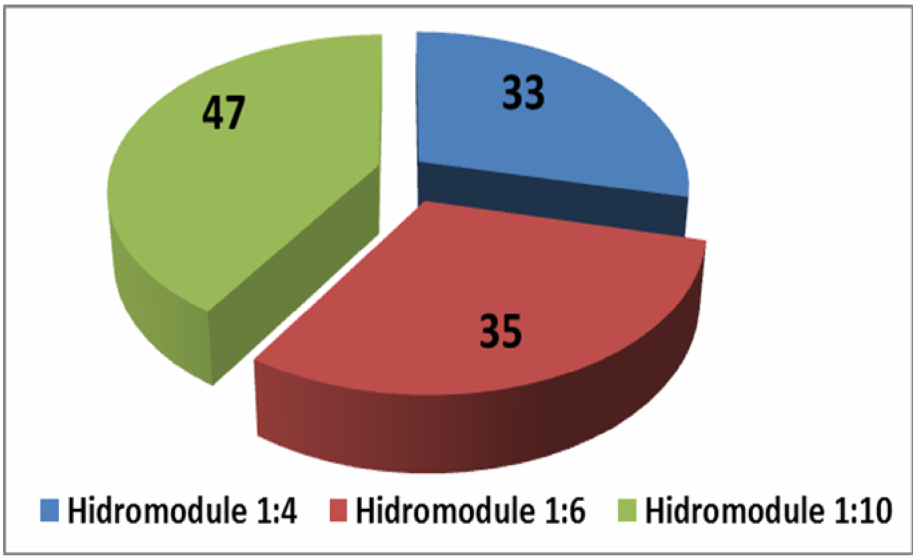

Figure 4. Water consumption needed for rinsing, bleaching and dyeing [L kg^{-1}].

Table 2

Hidromodule influence upon the total water consumption

Hidromodule	*Bleaching (L kg^{-1})*	*Rinsing (L kg^{-1})*	*Dyeing (L kg^{-1})*	*Rinsing (L kg^{-1})*	*Total (L kg^{-1})*
1:4	4	5	2	22	33
1:6	6	6	3	20	35
1:10	10	10	7	20	47

All textile dying processes require a very high consumption of water in order to remove unfixed dye and dye fiber hydrolyzate. Besides the high water consumption problem, waste water from dyeing contamination is the main problem the textile industry faces. For this reason, a continuous and versatile dyeing process, for sulfur dyes called "PAD-OX" was developed, that is characterized by: minimum water consumption, low volume of wastewater, "zero" dye in wastewater.

The continuous dyeing process "PAD-OX" is adaptable for the semi-continuous process in which dyes are fixed by oxidation/fixation without prewash. According to Pricop et al (2013), the process allows 100% dye fixation, requiring only a subsequent rinsing after fixation.

It is a short-time process, environmental friendly, and compared with the classic process (foulard pattern - storage with vinyl-sulphonic reactive dyes or vaporization foulard pattern – vaporizing with sulfur dyes) leads to a decrease in water consumption by aprox. 90%.

Sulphur dyes are appreciated for their excellent washing durability. Sulfur dyes are also resistant to common bleaching treatments with hydrogen peroxide, sodium hypochlorite and perborate. Their main disadvantage is the limited color range, the sulfur dyes being preferred for darker and mate tones.

Conventionally, sulfur dyes are solubilized through dyes reduction in the presence of soda ash or sodium sulphide at boiling temperature. They are applied to cotton materials in the form of reduced sulfur dye. The insolubilisation of the sulfur dye to its original shape after painting is properly made by oxidation dye treatments.

Sodium sulphide is highly toxic and presents a high degree of pollution due to sulfur dioxide resulting from the reaction of dye reduction.

Sodium sulphide was replaced with sugar or molasses, in which case there was a slight increase in BOD and less odor than using sodium sulfide as a reducing agent.

PAD-OX ecological process of dyeing with sulfur dyes experienced and recommended for use in industrial textile production. "PAD-OX" dyeing with sulfur dyes is a process characterized by minimal water consumption, lower quantities of wastewater and "zero" dye contained in wastewater.

The method can be applied to a continuous line formed by a classic foulard and 3 to 4 fixing baths a final rinse tub.

From the chemical point of view, the key of the process are the reactive quinone groups of the dye molecule and the sulfur dye molecule size (quasi polymer), which favors the color-lock in the fiber.

Technological phases are as follows:

- phase 1: the foulard impregnation with dye solution;
- phase 2: migration - ensures diffusion of the dye into the fiber;
- phase 3: setting - insolubilisation of the dye inside the fiber and the development with help from 3 products:
  - acid - prevents dispersion of the dye in the fleet and ensure pH for oxidation,
  - oxidant - to reveal the quinone groups to achieve the final shade,
  - fixing agent - reacts with thiol groups of the dye and with the fiber, locking the dye through ionic bonds;
- phase 4: rinse – removal of salts formed at the end of the process and the neutralization of the fabric.

The success of this process is due solely to DIRESUL RDT dyes.

The recipe for PAD-OX process is as follows:

- dyeing bath:

x g L^{-1} sulphur dye DIRESUL RDT,
7-15 g L^{-1} REDUCTOR D (reducing system),
7-15 g L^{-1} NaOH 50%,
2-3 g L^{-1} SANDOZINE EH liq (weting agent),
2-3 g L^{-1} LADIQUEST 1097 N liq (dispersant/sequestrant)

- fixing bath:

15-25 g L^{-1} DIRESUL OXIDANT BRI liq,
15-25 g L^{-1} acetic acid 80%,
15-25 g L^{-1} DIREFIX SD liq (fixing agent),
2-5 g L^{-1} EKALINE F liq (dispersing agent),
20-30 g L^{-1} crystallized sodium sulphate.

Just like with other dyeing systems in which dye is adsorbed by the fiber and then developed into a separate bath, the utilization of neutral electrolyte (sodium sulfate crystallized) prevents dye desorption of fiber in the developing bath. In this particular case, dye desorption in fixing bath leads to formation of salts with the used cationic agent. For this reason, sodium sulfate is added.

Dyeing strength when using PAD-OX process are comparable to those obtained by the classical sulfur dyes, except for abrasion resistance values which are with about ½ point lower. This parameter can be improved by using an acrylic resin.

Benefits of using PAD–OX process: flexibility and simplicity; very good reproducibility; 100% dye fixation; ecological process; for low/high productivity; reduced dyes shade; good resistance of painting; reduced consumption of reducing agent - consumption decreased by about 40%; reduced staining residual fleet - savings in wastewater treatment; low consumption of water - saving aprox. 90% water; reduce pollutants in water with 15 to 25%; reduction of the amount of sludge - by 10-20%.

In order for the main wastewater quality indicators to be determined, samples were taken and analyzes were performed (Table 3) for the wastewater treatment plant situated at Giurgiu Nord Industrial and Technology Park, where the analyzed textile factory discharges its wastewaters.

Table 3

Characterization of wastewater quality indicators generated by denim textile finishing processes (dyeing with sulfur dyes)

No.	*Parameter*	*Admissible values according to NTPA 002/2005*	*Standard*	*Sampling place C. UCO ŢESĂTURA GIURGIU*		
				P1	*P2*	*Ecological efficiency (%)*
1	pH	6.5-8.5 pH unit	SR ISO 10523-97	12.14	8.1	33
2	Suspended solids	350 mg L^{-1}	STAS 6953-81	962	330	68
3	BOD	300 mgO_2 L^{-1}	SR EN 1899-1/2003	4,424.6	410	91
4	COD	500 mgO_2 L^{-1}	SR ISO 6060/96	7,742.8	610	92
5	NH_4^+	30 mg L^{-1}	SR ISO 71501-2001	1.94	1.14	41
6	Sulfur and hydrogen sulfide	1.0 mg L^{-1}	SR ISO 10530-97	1.94	0.9	54
7	Sulphates	2 mg L^{-1}	STAS 8601/70	128.64	3.4	97
8	Free residual chloride	0.1 mg L^{-1}	STAS 7167-92	1.48	0.9	39
9	Detergents	25 mg L^{-1}	SR EN ISO 7393-1/2002	120	35	71
10	Residuum			2,384	350	85

P1 - classical dyeing with sulfur dyes; P2 - ecological dyeing with DIRESUL dyes using PAD–Ox procedure.

In Figures 5–14 are presented several comparatives graphics for the main quality indicators that characterize the degree of wastewater pollution (legend for Figures 5-14: P1 - classical dyeing with sulfur dyes; P2 - ecological dyeing with DIRESUL dyes using PAD–Ox procedure). In the mentioned graphics are specified the admissible values mentioned in the current legislation (NTPA 002/2002) as well the results obtained using classical dyeing with sulfur dyes as well as the results obtained using PADOX procedure. An improvement of the quality indicators can be easily observed and in Figure 15 is presented the efficiency for the ecological procedure related to the classical dyeing.

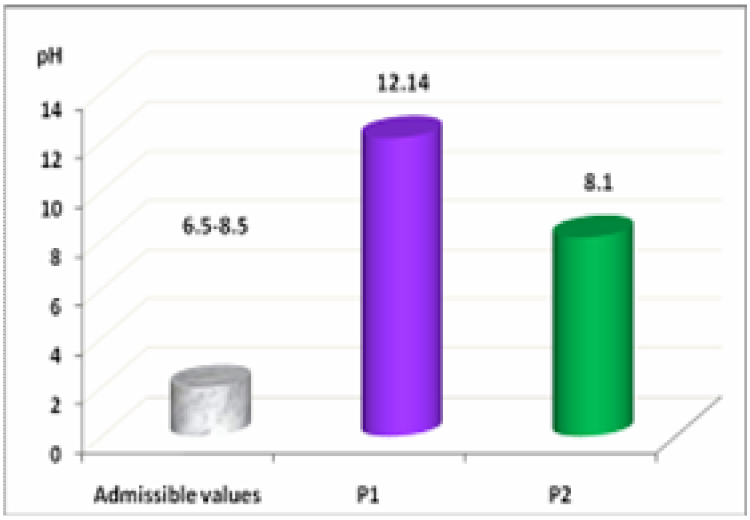

Figure 5. Comparative graphic for ”pH”.

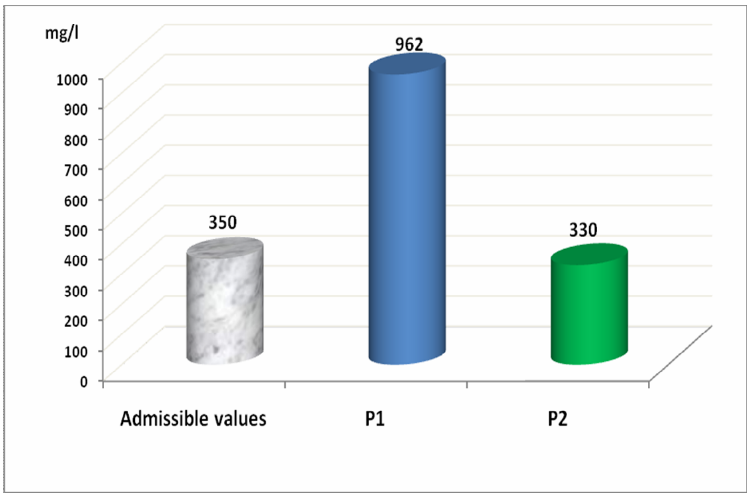

Figure 6. Comparative graphic for ”Suspended solids”.

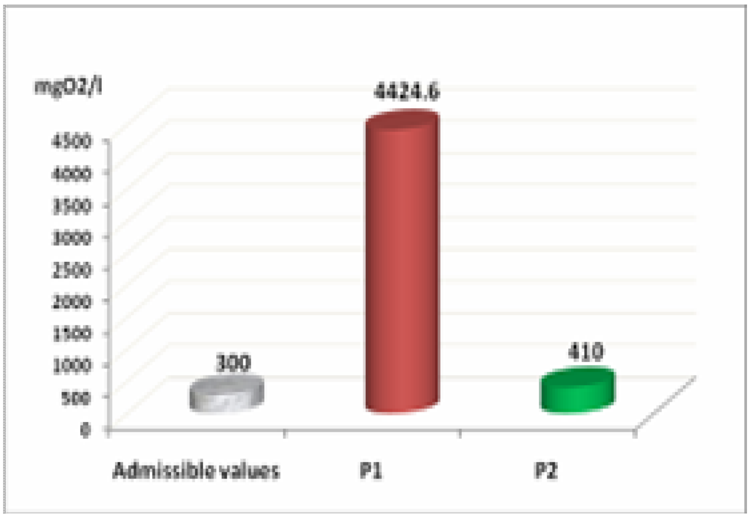

Figure 7. Comparative graphic for ”BOD”.

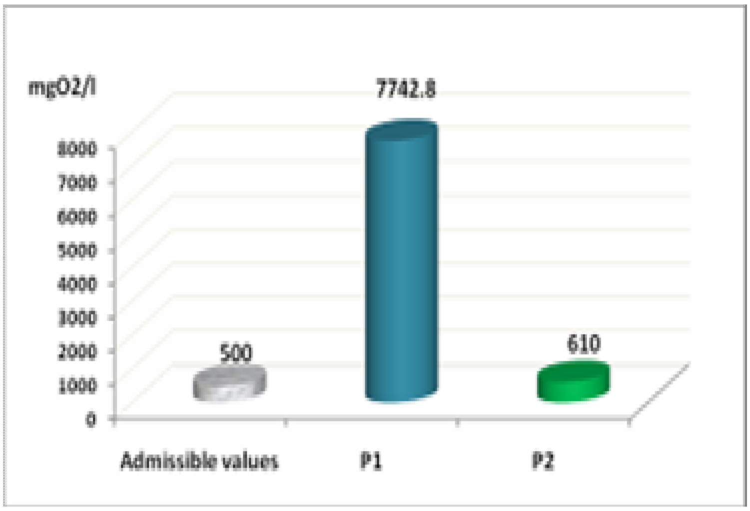

Figure 8. Comparative graphic for ”COD”.

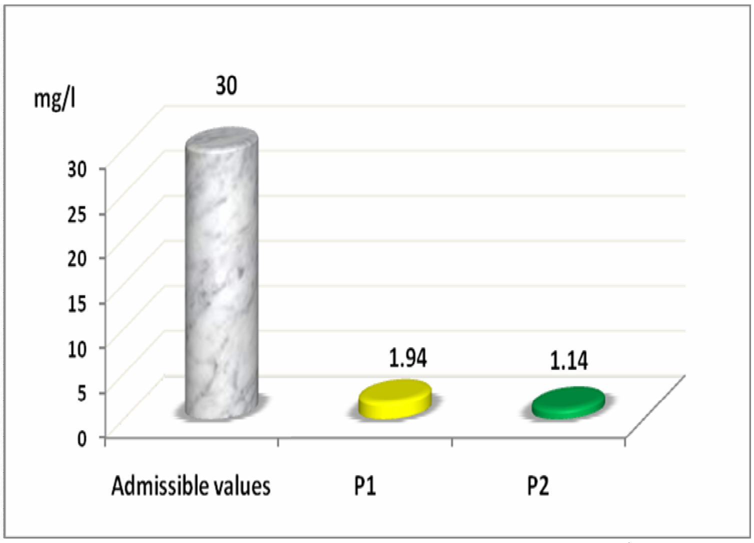

Figure 9. Comparative graphic for ”NH_4^+”.

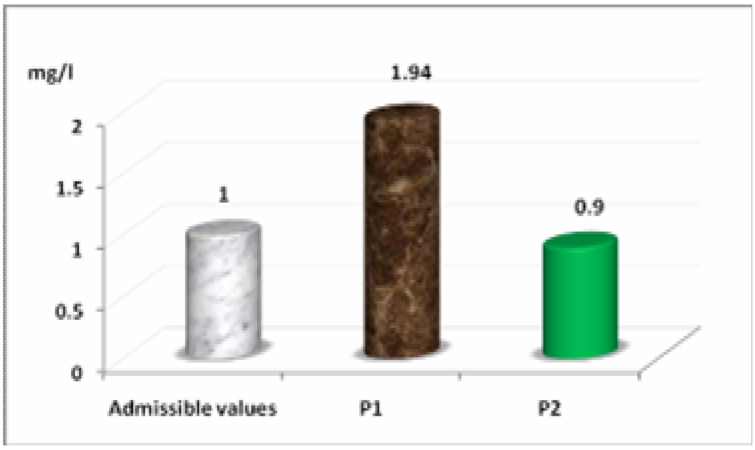

Figure 10. Comparative graphic for ”Sulfur and hydrogen sulfide”.

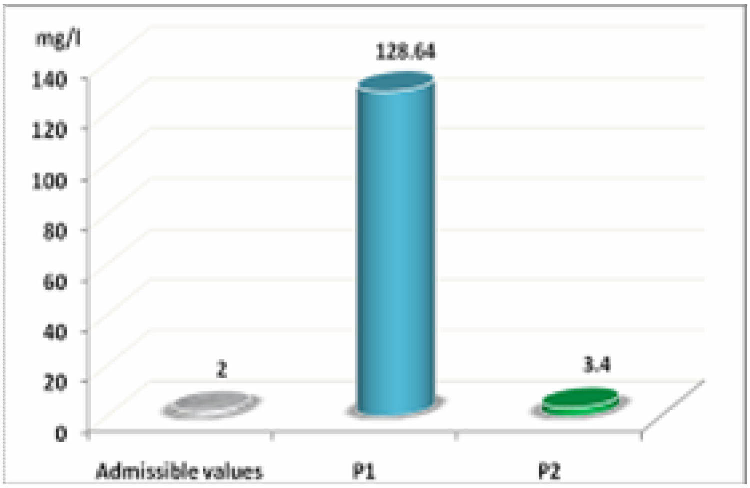

Figure 11. Comparative graphic for ”Sulphates”.

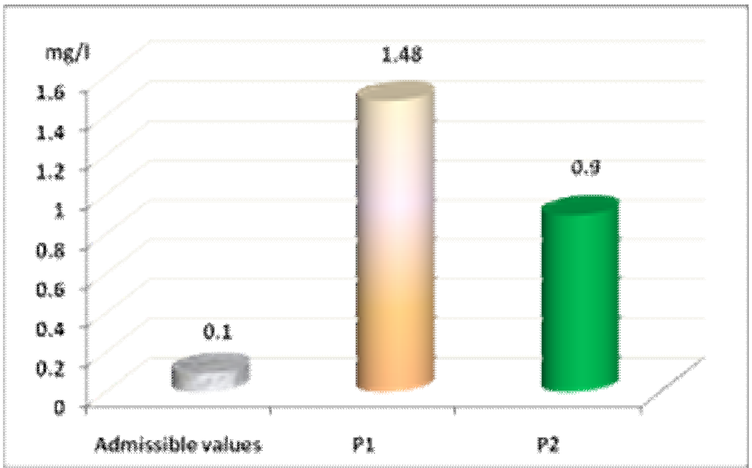

Figure 12. Comparative graphic for ”Free residual chloride”.

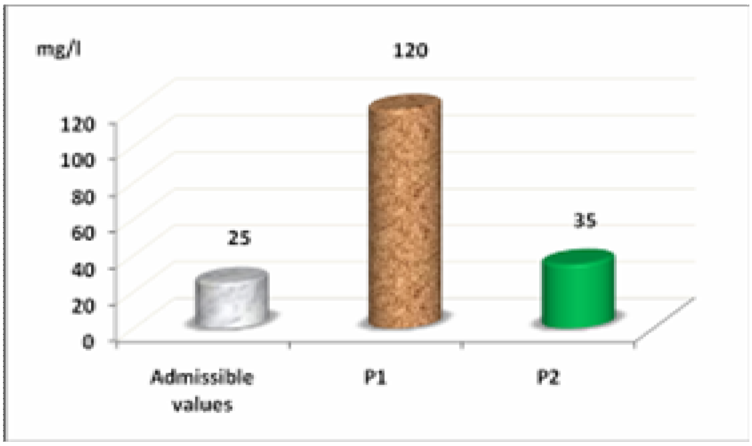

Figure 13. Comparative graphic for ”Detergents”.

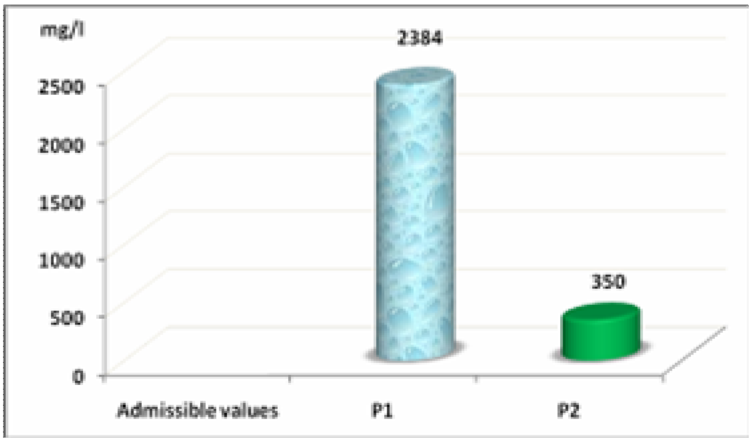

Figure 14. Comparative graphic for "Residuum".

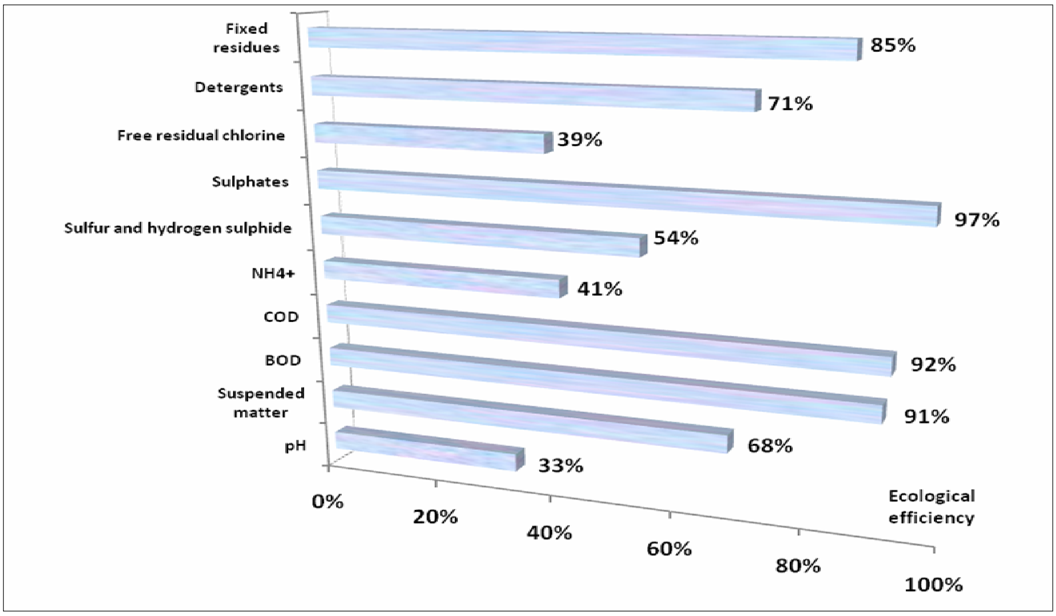

Figure 15. Efficiency diagram for the ecological procedure related to the classical dyeing.

Conclusions. Especially in the textile industry for dyeing and finishing processes, the commonly "raw material" used is water, a resource that has become almost exhausted, yet so necessary. That is why the water must be rationally used to ensure a sustainable development. Several conclusions resulted from the research activities:

- re-finishing and ecological processes must be realized using the best available techniques;
- replacement of dyes with low biodegradability with ecological dyes;
- water consumption reduction and establishing solutions for its reuse in industrial processes.

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