Monitoring and Degradation of Some Organic Pollutants from Waste Waters Resulting From Textile Industry

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Abstract

In this paper some organic pollutants from waste waters resulting from dyeing of polyacrylic fibres were identified, analyzed and degraded. Disperse and cationic dyes used for the dyeing of fibres are non-toxic in accordance with the results of the toxicological tests. So, these dyes can be used in the dyeing process respecting the interdiction of ETAD. These dyes, synthesized for the first time by the authors, are identified by spectral methods, HPLC and can be degraded from waste waters by oxidative procedures with hydrogen peroxide or ozone on a heterogeneous catalyst system and with hydrogen peroxide by the Photo-Fenton advanced oxidation process. Finally, a comparative study is performed. The UV absorber used for protection of dyed fibres is analyzed by HPLC and degraded by oxidative methods. The surfactants used in the washing stages of fibres are identified by spectral analyses, HPLC and are biodegraded by biological methods or using sorbents. Also, some parameters of the surfactants, e.g., surface tension (method Wilhemy Plate), wetting power (Draves method) and foaming power (method Ross Miles), are calculated.

Keywords: pollutant, waste water, monitoring, spectral analyses, cationic dye, surfactant, degradation

1. Introduction

The textile industry represents one of the most important and complicated technological chains. The textile technological chain begins with fabrication or collecting of crude fibres and follows the steps: pre-treatment of fibres, dyeing process, printing, finishing and covering, including washing and drying. From the textile industry results a large volume of waste waters which contain organic (dye, additives, surfactant, etc.) and inorganic (heavy metals, complexing agents) pollutants.

The polluted emissions resulting from textile industry are variable and depend on textile material composition, conditions of technological process, reagents used in the treatment of fibres or textile materials, dyes and additives added in bath of dyeing, etc. If the textile fibres are natural, wool for example, then the residual waters resulting from the dyeing process are polluted by some toxic organic pollutants as pesticides, fats, antibiotics, a.o.

An important problem is the presence of dyes in waste waters resulting from the dyeing process of synthetic fibres [1, 2]. It is well known that the fixation efficiency of dyes on fibre is between 60 and 90% [3]. The organic dyes are very complex chemical structures, being sometime considerably toxic and they are interdicted to be used in the dyeing process of fibres in accordance with ETAD (Ecological and Toxicological Agency of Dyes). Many dyes are very stable and resistant to chemical agents and light. Their structure, which is based on aromatic groups and heterocycles, leads to slow biodegradation. The presence of dyes in residual waters, resulting from the dyeing process, modifies the colour of waters and leads to environmental problems [4]:

1. Modification of the illumination grade of the aquatic medium which leads to the diminution of photosynthesis process and auto-purification capacity of waters.

2. They may be decomposed to toxic organic compounds – e.g., aliphatic amines which lead to cancerous effects.

The European studies [1, 5] have demonstrated that 40% of the pollutants in residual waters from textile industry are attributed to substances which pre-existed in the initial materials used in the finishing process: processing agents, impurities and associated materials from fibres, glue agents (starch, starch derivatives, polyacrylate, etc.). Approximately 50% of the pollutants are: inorganic salts, complexing agents, heavy metal ions, chlorine and products which liberate chlorine as NaClO, surfactants (utilized in washing operations of dyed fibres, etc.), „carrier" substances (trichlorobenzene and *ortho*-phenyl phenol), organic acids, organic solvents, *UV* absorber, dyes and pigments (Fig.1). Also, in residual waters are present suspended solids as: lint, sand, clay, dust, organic and mineral matters, etc. So, 90% of the organic and inorganic matters used in textile processing are found in residual waters and only 10% are eliminated in air.
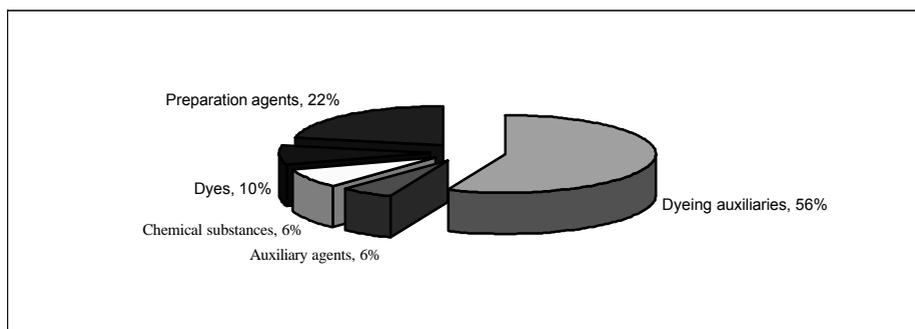
Fig. 1. Substances used in the dyeing process of natural or synthetic fibres

In many scientific papers [4, 6-8] concerning environment and textile industry, dyeing processes utilizing auxiliary substances and other additives in small quantities, without "carrier" reagents, non-toxic, stable and degradable dyes, anionic or non-ionic surfactants (cationic surfactants are toxic, persistent and non-biodegradable), etc., have been examined. The problem of non-toxic and biodegradable dyes synthesis is very important for research workers. By physicochemical analyses [2, 9] of waste waters the pollutants in waters can be identified and quantified, but no safe evaluation of pollutants impact concerning aquatic flora and fauna from surface water (rivers, lakes, seas) can be made. In this situation ecotoxicologic biotests on aquatic organisms have been applied which permit the estimation of acute, sub-acute and chronic toxicity of pollutants. Methods frequently applied in waters treatment (precipitation, oxidation, reduction, coagulation – flocculation, ion exchange, filtration, adsorption, electrochemical treatments, inverse osmosis, removal by evaporation, solvent extraction, etc.) are not effective for the total removal of organic and inorganic pollutants. These methods are characterized by incomplete removal of some pollutants, limited tolerance to pH changes and require high consumption of reagents and energy, production of toxic sludge or other waste products that also need treatment before disposal. In these conditions, sorption removal of impurities on solid or liquid materials is an attractive alternative of conventional waste waters treatment technologies because of the following advantages: possibility to use a vast diversity of sorbent materials (natural or synthetic zeolites, lignino-cellulose, activated charcoal, materials with ion exchange properties, active or inactive biomass); reduced matrix effects; increased process sensibility and selectivity, etc. [10-13].

In this paper a discontinuous dyeing process of polyacrylic fibres with two red disperse dyes and two blue cationic dyes (synthesized for the first time by the authors) is presented. After dyeing, the residual waters are controlled. The organic pollutants are identified and analyzed by spectral analyses, HPLC and other physicochemical procedures. Finally, degradation methods for some organic pollutants in waste waters resulting from the dyeing process are proposed.

2. Experimental

2.1. Reagents and materials

The reagents used in this study are listed in Table 1. The fibres used for dyeing are *polyacrylic fibres* (type Melana 2.0 den), treated with cationic agents with surface properties for reducing the accumulation tendency of impurities on the surface of the fibre. For the removal of impurities it is necessary that the fibre can be wetted by the washing solution. It is also necessary that the fibre possesses high surface tension and the washing solution has low surface tension.

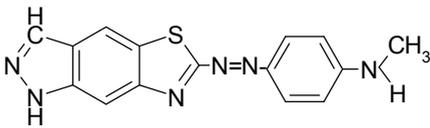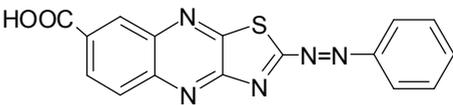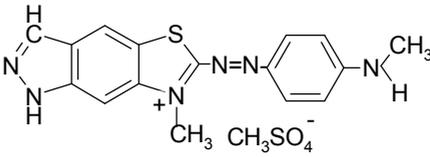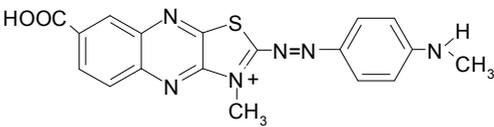**Table 1.** Dyestuff, chemical agents and dyeing technique for polyacrylic fibres

Dyestuff	Chemical and auxiliaries / typical application conditions	Technique
Red disperse dyes and Blue cationic dyes obtained by original synthesis; these dyes are very stable, non-toxic and unknown in specialty literature (synthesized for the first time by the authors, Table 2).	- Acetic acid (*p*H 3.5-4.0), solution 2%. - Sodium sulphate calcinated, solution 10% - Standardization agent for shade type ammonium quaternary salt with lateral chain at alkyl C_{12}-C_{14} (optional) agent retard. - As surfactants a mixture of non-ionic (70% ethoxylated fatty alcohol) and anionic (about 30% sodium alkyl-sulfonates as sodium dodecylbenzensulfonate, alkyl sulphate and linear alkyl benzensulfonates) surfactants are utilized for washing fibres before dyeing and after dyeing	Discontinuous

2.2. Dyeing process of polyacrylic fibres

The affinity of cationic dyes to polyacrylic fibres is the result of the anionic character of the latter. The fixation mechanism of cationic dyes on the polyacrylic fibre in the first step is ionic. In the same time the cationic dyes are dissolved in the polyacrylic fibre; the fibre with terminal anionic groups can be considered as an electrolyte. Actually, the dyeing process takes

place in four steps: (i) migration of dye from solution to the external surface of fibre; (ii) adsorption of cation of dye on the surface of fibre; (iii) diffusion of dye inside the fibre; (iv) formation of electrovalent bonds between cation of dye and anion of fibre.

Table 2. Dyes used for the dyeing of polyacrylic fibres

Dye	Structure of dye	Characteristics of dye
Red disperse dye [14, 15] derivatives of compact condensed system 2-aminothiazolo[4,5-f] indazole [16] applied on Melana polyacrylic fibres and treated with 2-(2'-hydroxy-5'-methyl-3'-sulfophenyl)-benzotriazole *UV* absorber		Colour: Red λ_{max}=488 nm (1,2723) ε_{max}=27621
Red disperse dye [17] derivatives of compact condensed system 2-aminothiazolo[4,5-b]quinoxaline-6 -carboxylic acid [18, 19] applied on Melana polyacrylic fibres and treated with 2-(2'-hydroxy-5'-methyl-3'-sulfophenyl)-benzotriazole *UV* absorber [8]		Colour: Red λ_{max}= 517 nm (1,2431) ε_{max}=29716
Blue cationic dye [20, 21], obtained by quaternization of red disperse azo thiazolo-indazole dye, applied on Melana polyacrylic fibres and treated with 2-(2'-hydroxy-5'-methyl-3'-sulfophenyl) - benzotriazole *UV* absorber		Colour: Blue λ_{max}= 555 nm (1,1202) ε_{max}= 20731
Blue-violet cationic dye [17, 22, 23] obtained by quaternization of red disperse azo thiazolo-quinoxaline dye, applied on Melana polyacrylic fibres, treated with 2-(2'-hydroxy-5'-methyl-3'-sulfophenyl)-benzotriazole *UV* absorber		Colour: Blue-violet λ_{max}=543 nm (1,0561) ε_{max}=18540

The synthesized dyes (Table 2) were used for dyeing polyacrylic fibres. The polyacrylic fibre was scoured at 60^0C for 30 minutes and dried under vacuum for 48 hours at room temperature before dyeing. The scouring process consists of washing in hot water (40 – 80^0C) in presence of anionic surfactant. In general, the detergent emulsifies the mineral oils and

disperses the undissolved pigments. The choice of the surfactants may vary depending on the type of fibre. A mixture of anionic and non-ionic surfactant is commonly used (Table 1). An important factor in the selection of surfactant is its effectiveness in heavy conditions.

Dyeing with cationic dyes can be performed at temperatures below 100^0C without carriers. So, the dyebath was prepared at room temperature with cationic dye (2.0% aqueous solution), acetic acid 1% solution and sodium sulphate 10% solution for adjusting the *p*H at 3.8 – 4; the fleet ratio in the dyebath was 1:40. The dyebath temperature was raised to 60^0C, 70^oC and 100^0C and then held constant during the whole dyeing process. The dyed polyacrylic fibre was rinsed first in cold water and then in boiling water to remove unfixed dye, then again with cold water, and finally, it was dried at room temperature.

2.3. Physicochemical analyses

The dyes from the waste waters are analyzed by *VIS* spectroscopy and by visualization of colour of residual waters. The *VIS* electronic spectra were performed with *Specord 250 UV-VIS* spectrophotometer with double monochromator, variable spectral resolution and cooled double detection and PC system, in quartz cells (l=1cm) for c ~$2·10^{-7}$ *M* dyes. The characteristic absorbance was presented depending on the maximum wavelengths.

The presence of surfactant was detected by spectrometric methods using *Specord 250 UV-VIS* spectrophotometer and determination of surface tension - in accordance with ISO standards.

The determinations of surfactants and dyes were made using a *high performance liquid chromatograph Perkin Elmer 200*, equipped with: quaternary pump; vacuum degasser for solvents; auto-sampler (for the automated injection in the chromatographic column of a previously selected quantity of sample and for automated washing of the syringe); column oven for thermostating the chromatographic column; UV detector type *Diode Array* and alternative with fluorescence, with the possibility of simultaneous spectra acquisition; PC system. The used reagents (Table 3): acetonitrile of HPLC grade (*Riedel de Haen*); water of HPLC grade (*Fluka*); CH_2Cl_2 of HPLC grade (*Fluka*); methanol of HPLC grade (*Fluka*); ammonium formiate of HPLC grade (*Aldrich*). The columns were considered to be the most appropriate because they allow retention times long enough for an efficient separation and do not present the colmation phenomenon for the heterocyclic systems [24, 25].

Table 3. Characteristics of HPLC methods used for determination of dyes and surfactant

Substances	Mobile phase	Column	Flow	Detection	Temp
Red disperse dyes	A: 20 mM ammonium formiate at pH=3 B: acetonitrile Gradient: 30 to 100% B in 30 minutes	Hypersil Gold C18 (5 µm particle size)	1 mL/min.	UV 254 nm λ_{max}=488 nm and λ_{max}= 517nm	25^0C
Blue cationic dyes	A: 0.1 % formic acid B: acetonitrile + 0.1% formic acid	Hypersil Gold (1,9 µm particle size)	0.1 mL/min.	UV 270 nm λ_{max}= 555nm λ_{max}=543 nm	25^0C
Non-ionic surfactants	A: hexane:CH_2Cl_2 = 95:5 B: hexane:CH_2Cl_2:methanol = 50:40:10 (10 µL CH_2Cl_2 containing 20 µg surfactant)	Supelcosil LC-Diol (5 µm particle size)	1 mL/min.	UV 280 nm	35^0C

The surface tension of the mixture of surfactants [26, 27] used in washing process of fibres and for each surfactant was determined on a Kruss tensiometer. The applied method was Wilhemy Plate, for diluted solution (with 0.1% active substance for each surfactant considered witness before the determination of surface tension of mixture from residual waters) at 25^0C.

The wetting time was measured on a diluted solution of the surfactant (0.1% active substance), at 25^0C using Draves method. This method measures the time necessary for the sinking of a bunch of polyacrylic fibres (with standardized weight), inside a cylinder which contains the surfactant solution.

The foaming power was determined on a diluted solution of the surfactant (0.1 % active substance) at 25^0C by the Ross Miles method (ISO 696:1975). The method measures the height of the foam produced by 450 mL solution falling free from a height of 450 mm inside a standardized cylinder containing the same substance.

3. Results and Discussion

3.1. Monitoring of some organic pollutants from waste waters resulting from the dyeing process

The waste waters resulting from the dyeing process of polyacrylic fibres contain (Fig. 1): dye (approximately 10%, the rest being retained on the fibre); surfactants resulting from the washing steps at 60^0C before and after dyeing the fibres; UV absorber used for protection of

dyed fibres, retard agent used for obtaining uniform colour; auxiliary agent and accidental pollutants (from auxiliary processes).

Important specification: the water utilized in the washing of fibres and in other auxiliary processes (washing of dyebath, equipment used in process) is of category II. This water is loaded with mineral substances and other pollutants and is usually analyzed for the identification of possible pollutants. This load of water of category II is present in the residual waters. Usually the waters of category II have certain hardness, which is calculated at 19^0 hardness grade (by usual analysis method).

Another specification: in general, all liquid surfactants contain similar active substances and conditioning agents as EDTA-Na and detergent additives: antifoaming agent, whitening agent, anti-deposition agent, sodium carbonate.

The pH of residual water from the dyeing process is 6.5 - 7.8 and depends on pH of the industrial water (category II) used in the washing process and also of organic and inorganic substances participating in the dyeing of fibres.

The dyes used in the dyeing process are identified and analysed by spectrophotometric UV-VIS methods and the results are presented in Fig. 2. The results of the HPLC analysis of the dyes and *UV* absorber are presented in Fig. 3: *(a)* - the peaks 1 and 2 are unknown, probably due to impurities; 3- excellent peak shapes and resolution for UV absorber; 5 and 6 - excellent peak shapes and good response for azo-thiazolic blue dyes; *(b)* - 1 and 2 - excellent peak shapes and resolution for red disperse dyes.

The absorbance and molar extinction coefficients (ε_{max}) were determined at the maximum wavelengths λ_{max} (Table 2).

(a)   *(b)*

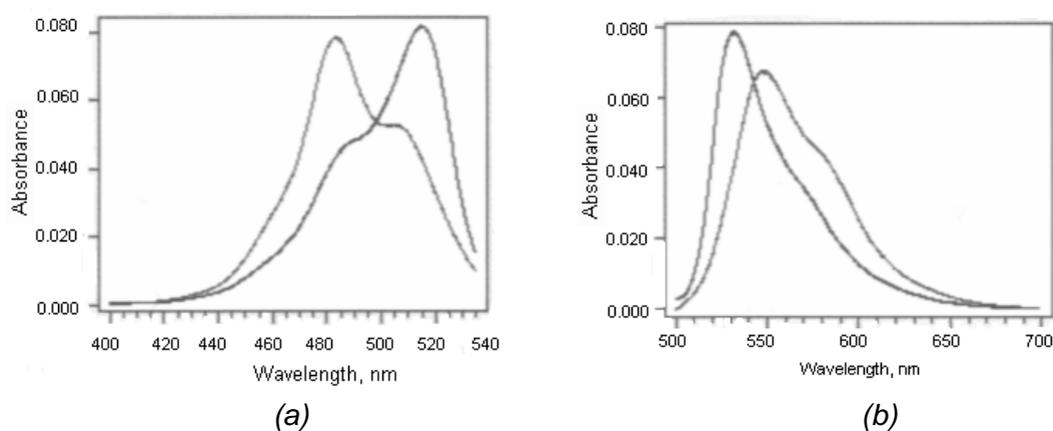**Fig 2 .** Spectrophotometric analyses of dyes in waste waters resulting from dyeing process: (a)-red disperse dyes; (b)-blue cationic dyes.

(a)   *(b)*
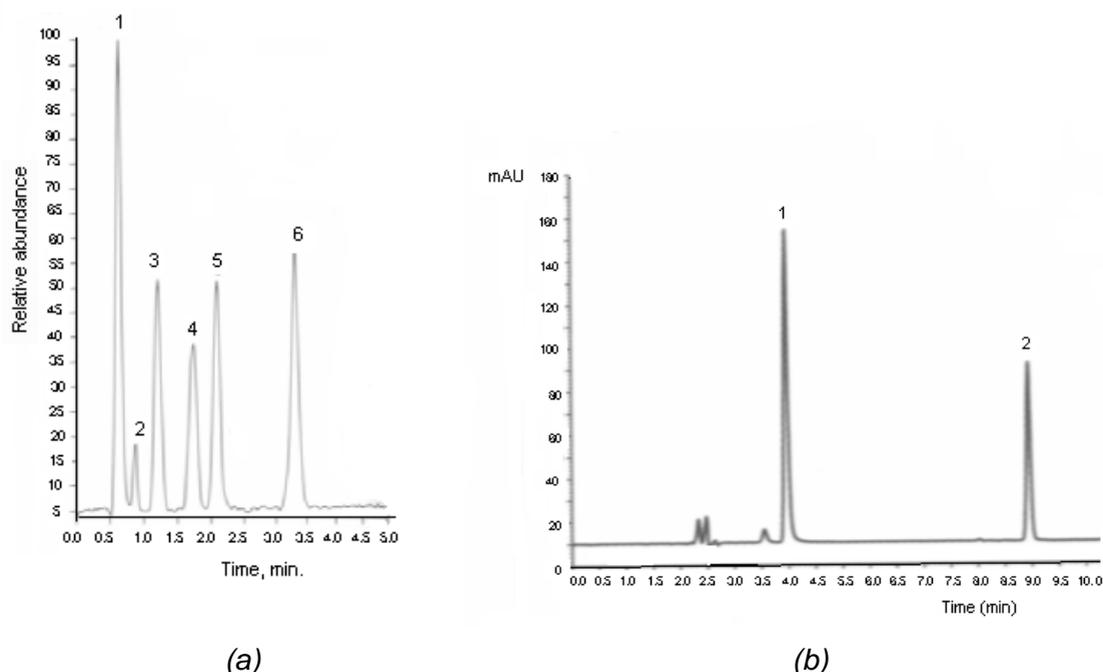
Fig. 3. HPLC/UV chromatograms of organic pollutants identified in waste waters resulting from the dyeing process.

The surfactants are identified by a spectrometric method using Methylene Blue solution, after extraction. Another method for identification of surfactants was the determination of surface tension, wetting power and foaming power. The results are presented in Table 4. Finally, the non-ionic and anionic surfactants used in the washing process of undyed and dyed fibres were analysed and separated from the waste waters by HPLC. In 30 minutes the non-ionic surfactant (70% in the mixture) was separated and the peaks were referred to 9-10 ethoxy groups of ethoxylated fatty alcohol.

Table 4. Surface tension, wetting power and foaming power of surfactants

Mixture of surfactants	Surface tension [mN/m]	Wetting power [s]	Foaming power [cm]
Non-ionic surfactant and anionic surfactant mixture	24.83	10	14.7/14.6
Non-ionic surfactant	25.45	35	16.9/16.8
Anionic surfactant	24.96	16	14.9/14.8

The results show that the wetting power, surface tension and foaming power of the mixture of surfactants are better in comparison with the same parameters of the single surfactants.

The chosen surfactants are 98-99% biodegradable [27, 28]. The utilization of antifoaming agents is not recommendable because they are expensive, foul smelling and are eliminated from waste water only by abiotic process.

3.2. Degradation methods of some organic compounds from waste water resulting from dyeing process

In some cases the classical methods for water purification like coagulation, adsorption on activated charcoal or biological treatments are ineffective, because 20% of the dyes may have remained in the residual waters. It is also known that the removal of dyes by their transfer from the aqueous phase to another phase would require subsequent treating for their degradation.

The oxidative procedures [29] for the degradation of dyes and other organic auxiliaries like *UV* absorber, used in the dyeing process, were examined. In these procedures the pollutant molecules are decomposed in simple biodegradable molecules.

The dyes with structures presented in Table 2 are degraded by oxidative procedures using as oxidant agents hydrogen peroxide (1st method) and ozone (2nd method) on the heterogeneous catalyst system CuO/Al_2O_3. We have chosen this catalyst system because the structures of the cationic dyes contain thiazole ring and piperazine ring, so the heterocycles and their chromophores can be oxidized by hydrogen peroxide and ozone, which in presence of the catalyst can generate OH· radicals. These radicals are highly reactive to the pollutants in the solution.

The studies demonstrated that the CuO/Al_2O_3 system is the best in the degradation process because the decomposition rate of hydrogen peroxide on CuO is great and also, the catalyst/O_3 system is very efficient comparative with the simple ozonization.

The results of the discoloration process of blue dyes (for example) in residual water sample by oxidative procedures are presented in Table 5 and Figures 4 and 5.

Table 5. Results of the discoloration process of dyes in presence of H_2O_2 and O_3 on the catalyst system

Dye	Oxidant	Catalyst [3 g/L]	Reduction of colour [%]	Time [min]	Reduction of CCO [%]	CCO-Cr [mg O_2/L] arithmetical mean	
						initial	final
Cationic dyes	H_2O_2 (1.32 g/L)	CuO/Al_2O_3	99.81	100	40.95	107.09	63.23
	O_3	CuO/Al_2O_3	97.99	100	45.68	140.56	76.35
Disperse dyes	H_2O_2 (1.32 g/L)	CuO/Al_2O_3	99.16	100	40.42	104.65	62.73
	O_3	CuO/Al_2O_3	96.83	100	45.12	140.04	75.98

The chemical consumption of oxygen (CCO) of completely discoloured samples was 40.95% (arithmetical mean) for hydrogen peroxide used as oxidant agent and 45.68% for ozone. The CCO-Cr calculated value of industrial water (category II) is 29.5 mgO_2/L. In Romania the accepted limit value for water from quality class II (O.M. 1146-2003) is 25 mgO_2/L.
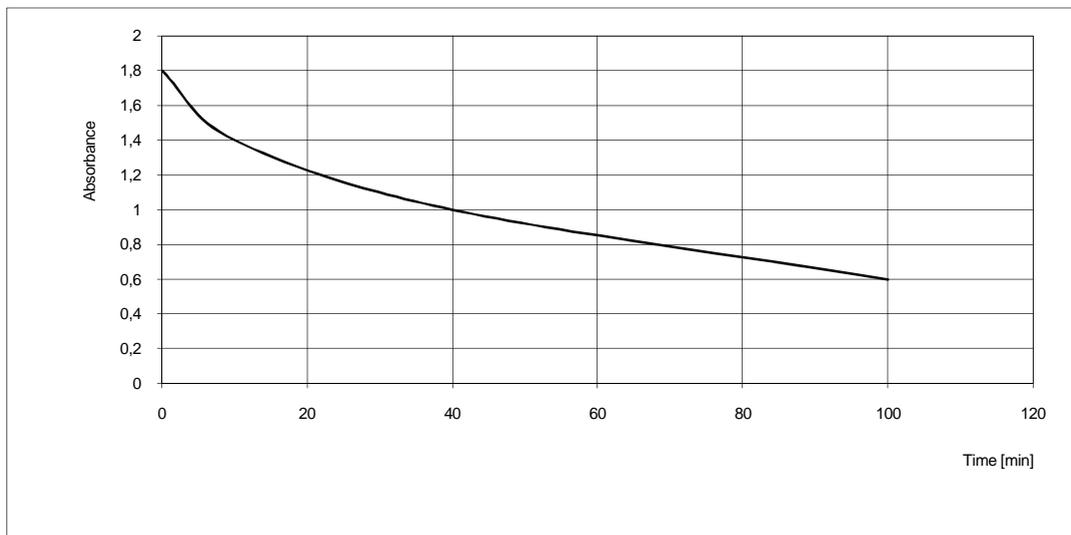

Fig. 4. Reduction of colour of blue cationic dyes (for example) from residual water sample in presence of hydrogen peroxide and catalyst CuO/Al_2O_3
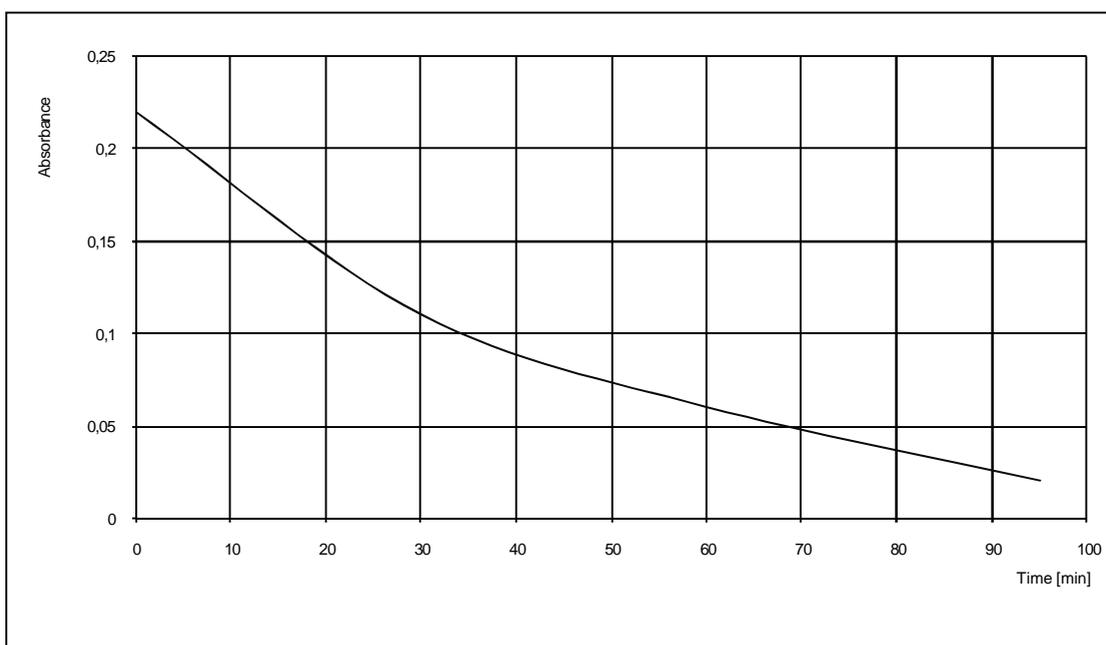

Fig. 5. Reduction of colour of blue cationic dyes (for example) from residual water sample in presence of ozone and catalyst CuO/Al_2O_3

The *p*H of the residual water has an influence on the discoloration process of residual water. So, the *p*H 6.0 - 7.8 of residual water has positive influence on the discoloration process.

The obtained results emphasized that the oxidation procedures with hydrogen peroxide and ozone in presence of the heterogeneous catalyst system CuO/Al_2O_3 lead to fast degradation of dyes.

The Photo-Fenton oxidative procedure for degradation of dyes and *UV* absorber from waste waters was also tested. The Photo-Fenton process was realized in a photo-catalytic reactor equipped with *UV* source from quartz lamp with Hg vapours under pressure. The oxidant was Fenton reactive - hydrogen peroxide solution and catalyst $FeSO_4$ (obtained by dissolution of a defined amount of $FeSO_4 \cdot 7H_2O$). The quantitative evaluation of the oxidative procedure was realized by collecting some samples from residual waters to which MnO_2 was added for the decomposition of the excess of hydrogen peroxide and NaOH 40% solution for precipitation of $Fe(OH)_3$; after filtration CCO was determined by a standardized method (K_2CrO_4 in H_2SO_4 medium). The conclusions are: for residual water sample with pH > 3 (Fig. 6), the oxidative degree decreased because Fe^{3+} precipitated as $Fe(OH)_3$ and the coordination compound $[Fe(OH)(H_2O)_5]^{2+}$ may be formed. So, the generation of HO· and HO_2· radicals is very limited due to the disappearance from solution of active centres associated with $Fe^{2+/3+}$ and to the absorption of UV radiation by $Fe(OH)_3$ and $[Fe(OH)(H_2O)_5]^{2+}$.
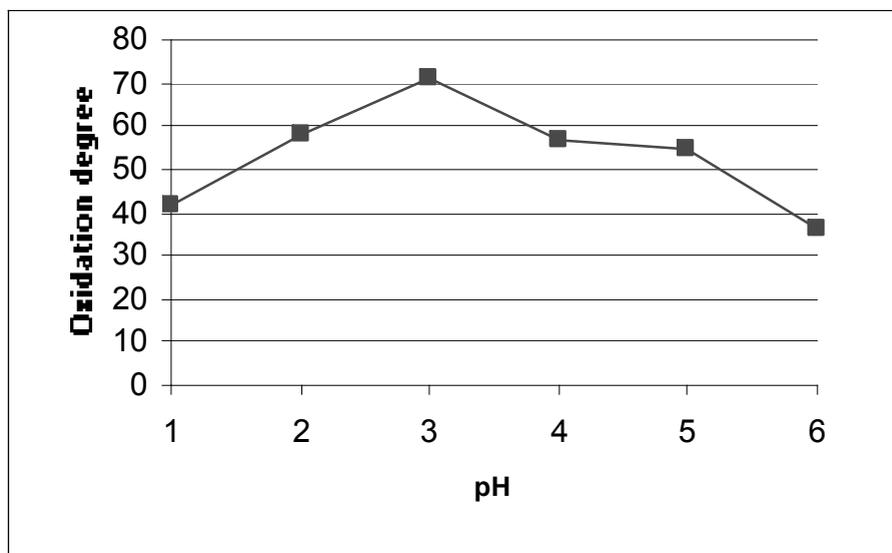

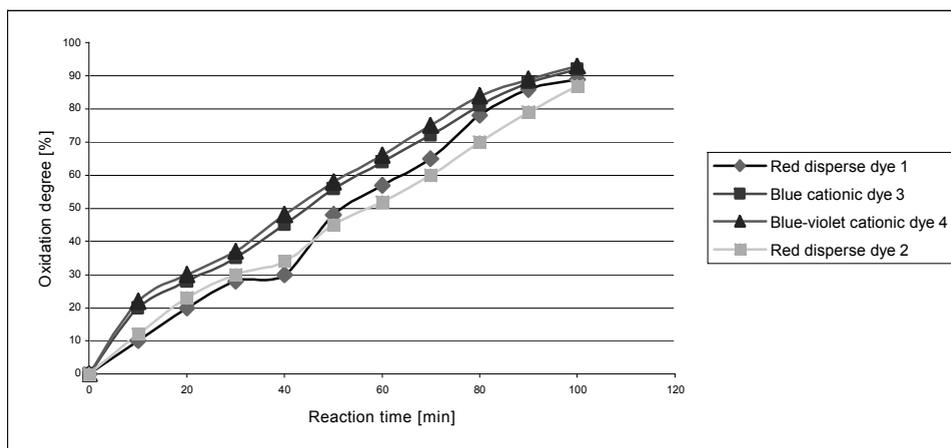**Fig. 6.** Variation of the oxidation degree depending on the initial pH

Fig. 7. Variation of the oxidation degree of dyes with time

Using this advanced oxidative procedure the discoloration (degradation) of dyes in the residual water sample is below 95% in 100 min (Fig. 7); the maximum values of dyes oxidation [%] in 100 min are: 89% for red disperse dye 1; 87% for red disperse dye 2; 92% for blue cationic dye; 93% for blue-violet cationic dye.

The Photo-Fenton procedure (Fe^{2+}/H_2O_2) was abandoned in this case because of the supplementary treatment needed for separating the iron from the residual water (higher cost of the treatment) and the insufficient degradation degree of dyes (below 95% in 100 min).

The 2-(2'-hydroxy-5'-methyl-3'-sulfophenyl)-benzotriazole *UV* absorber used for protection of dyed fibres colour was degraded by advanced oxidative Photo-Fenton procedures using as oxidant agents hydrogen peroxide or ozone on the heterogeneous catalyst system CuO/Al_2O_3. The results are presented in Fig. 8 and Table 6.

Table 6. Results of *UV* absorber degradation using advanced oxidative procedures (AOP)

	Oxidant	Catalyst [3 g/L]	Oxidation degree [%]	Time [min]
UV absorber	H_2O_2 (1.32 g/L)	CuO/Al_2O_3	98.75	100
	O_3	CuO/Al_2O_3	95.55	100
	Photo-Fenton	$FeSO_4$	81.25	100

Advanced oxidative procedures used for degradation of dyes and *UV* absorber were applied. The efficiency of the Photo-Fenton procedure depends on several important factors: nature and initial concentration of organic compounds; organic substrate/hydrogen peroxide ratio; pH of initial solution; concentration of catalyst; time of reaction. In this study, the optimal parameters established for the Photo-Fenton procedure are: concentration of hydrogen peroxide of 50% H_2O_2 for stoichiometric ratio organic compound/hydrogen peroxide;

concentration of $FeSO_4$ catalyst equivalent to 100 mg Fe^{2+}/L; pH of residual water sample = 3.0. However, the oxidation degree of organic compounds using Photo-Fenton procedure is lower in comparison with oxidative procedures using hydrogen peroxide and ozone on the heterogeneous catalyst system CuO/Al_2O_3.
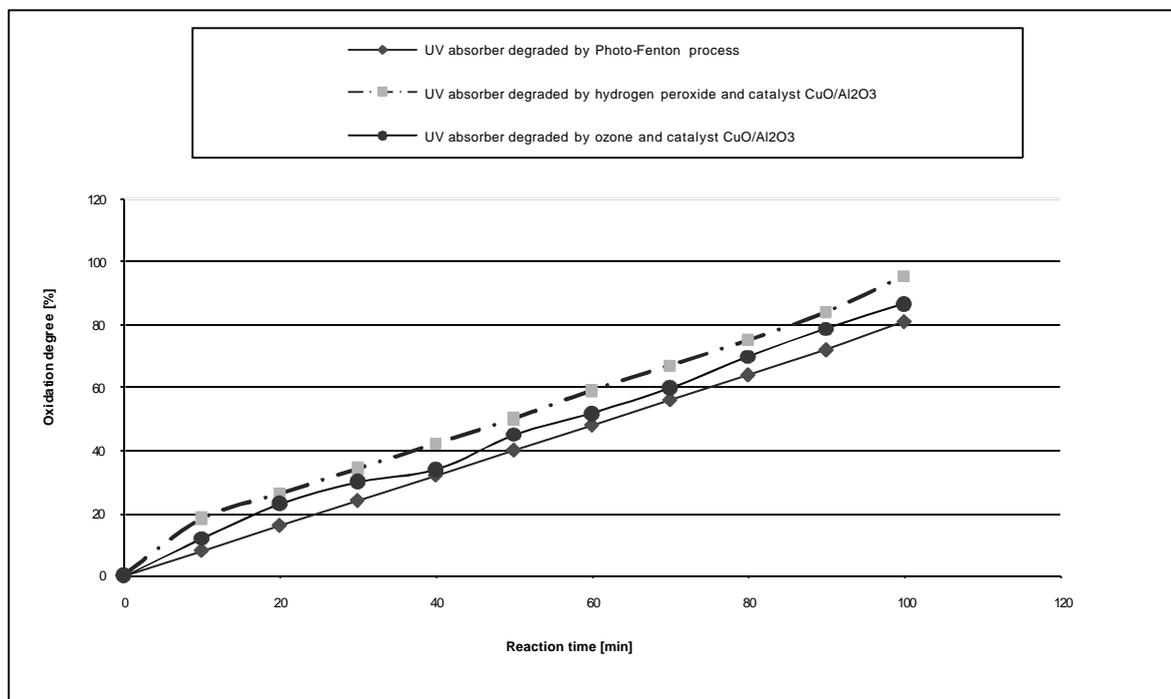

Fig. 8. Variation of the oxidation degree of UV absorber with time by oxidative procedures

Surfactants used in the washing process of undyed and dyed polyacrylic fibres can be biodegraded by using active or inactive biomass which is specially produced or results from industrial fermentative technology. In this work some conventional and unconventional sorbents are tested for the removal of surfactants and dyes. The choice of sorbent was based on requirements for high selectivity and capacity, favourable kinetic features, physicochemical stability, mechanical strength, easy regeneration and low cost [12]. Of interest from this point of view are the synthetic and engineered materials - synthetic resins, functionalized polymers with chelating groups, textile dyes, and activated charcoal. In other to avoid some disadvantages of conventional sorbents based on synthetic polymers (high prices, difficulties in obtaining, pollution produced during their synthesis) and in accordance with the tendency of replacing chemically synthesized compounds, unconventional materials are increasingly used for waste waters analyses and treatment [12, 13]. Unconventional sorbents may be used for removal of surfactants and dyes as synthetic (ashes, different charcoals in the presence or not of biodegradable polymers such as polyelectrolytes) and natural cellulose and/or lignocellulose materials (hemp fibres, cellolignine, hemp fibres), peat and cotton. Higher interest has been induced by the natural sorbents which offer advantages in preconcentration and separation

processes of organic compounds due to their characteristics: non-pollutant materials, easy accessible, not producing toxic residues; low price; possibility of continuous processing; highly hydrophilic (rapid kinetics of the sorption process); tolerance to biological molecules and possibility of functionalization; different shapes; good mechanical resistance; high porosity.

In our research we studied the sorption removal of disperse and cationic dyes and surfactants using the unconventional natural sorbents presented in Table 7.

Table 7. Results of removal process of dyes and surfactants using unconventional natural sorbents

Type of sorbent	Type of organic pollutant/Results	
	Disperse/cationic dye	Surfactant
Hemp fibres	Bath conditions: Azo disperse/cationic dyes (0.05-0.3 g/L); q_0=150.0 mg/g; K_L=0,634 L/g; R= 89.23%	Bath conditions: 0.5 g/L surfactant; q_0=80.6 mg/g; K_L=0,138 L/g
Peat from Poiana Stampei with next characteristics: brown colour; 49 g% organic carbon content; 7.8 g% total proteins; 3.44% ash; pH 3.5; specific area 192 m^2/g	Bath conditions: Azo disperse/cationic dyes (0.3 g/L); q_0=91.0 mg/g; K_L=0,912 L/g; peat dose 20 g/L, R=90%	Bath conditions: 0.5 g/L surfactant; q_0=78.0 mg/g; K_L=0,654 L/g; peat dose 20 g/L, R=56%
Cellolignine – residual product obtained after treating the wood with dilute mineral acid at 150-160^{0}C, with following composition: 45-48% cellulose; 32-35% lignin; 4-8% pentosane and 1-1.5% ash.	Bath conditions: Red disperse dye (2 mg/mL); q_0=90.9 mg/g; K_L=0,909 L/g; R=91% Blue cationic dye (0.05-0.5 g/L); q_0=87.01 mg/g; K_L=0,864 L/g; R=90%	No significant results.
Cotton fibres B26 [13] with specific surface Ssp=31.71 m^2/g	Bath conditions: Red disperse dye (2 mg/mL); q_0=76.5 mg/g; K_L=0,813 L/g; R=83% Blue cationic dye (0.05-0.5 g/L); q_0=89.7 mg/g; K_L=0,920 L/g; R=92%	Bath conditions: 0.5 g/L surfactant; q_0=93.0 mg/g; K_L=0,996 L/g; R=97%

K_L – Langmuir constant;
q_0 – maximum value of sorption capacity;
R% - removal degree of dye/surfactant.

The experimental studies of organic pollutants (dyes and surfactants) removal on the selected sorbents were carried out in batch conditions. After a defined time (usually 24 hours) the phases were separated and the amount of pollutant in the filtrate was measured by a spectrophotometric method. The sorption capacity of the sorbents was evaluated by the amount of absorbed dye/surfactant according to the equation:

$$q = \frac{C_0 - C}{G} V \cdot 10^{-3}$$, mg dye/surfactant/g sorbent

where: C_0 and C are the initial and equilibrium concentration, respectively, of the studied compound in the aqueous system (mg/L), G is the amount of sorbent (g) and V is the volume of the aqueous system (L). The removal degree of dye/surfactant is calculated by the equation:

R% = [(C_0-C)/C_0]·100.

Linear Langmuir and Freundlich [13] models were applied to the sorption isotherm and the characteristic parameters were calculated.

The research indicates a high removal degree for dyes and surfactants in accordance with calculated data (Table 7). The actual tendency is to use non-conventional materials, natural or synthetic ones, agricultural wastes or secondary products from different industries to reduce the overall cost of sorbent preparation, treatment process with no supplementary generation of toxic product. For increasing the treatment efficiency by sorption, combined treatment steps with conventional and unconventional sorbents will be developed.

4. Conclusions

In this paper some organic pollutants from waste waters resulting from dyeing of polyacrylic fibres were identified, analyzed and degraded.

The cationic dyes used for the dyeing of fibres are non-toxic and may be used in the dyeing process respecting the interdiction of ETAD. These dyes, synthesized for the first time by the authors, can be degraded by oxidative procedures with hydrogen peroxide or ozone on a heterogeneous catalyst system. The degradation is almost complete in max 100 min. The Photo-Fenton procedure was tested and the results show that the organic substances from residual waters can be oxidized but this degree is smaller in comparison with the chosen oxidative procedures.

The surfactants which are used in the washing stages of fibres are analyzed by spectral analyses and HPLC. The surface tension, wetting power and foaming power of the surfactants were calculated. The results show that the parameters of the mixture of surfactants are better than those of the single surfactants. The surfactants from the mixture are biodegradable ~ 99% because their linear structures permit easy destruction. Unconventional sorbents are also used for removal of dyes and surfactants.

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