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Abstract

The aim of the study was to evaluate the effectiveness of the technology proposed for low-loaded wastewater treatment enabling multiple reuse of recycled water in a closed circuit. The subject of the study was real textile wastewater produced during the dyeing of cellulose fibres with reactive dyes. Initial wastewater was divided into low- and high-loaded streams. The low-loaded wastewater was subjected to pretreatment at biological, ultrafiltration and ozonation stages. The pretreatment was carried out four times. The reclaimed water was reused in the rinsing and washing operations. Evaluation was made of functional properties of cotton knitted fabric dyed in the process in which the reclaimed water was used. The permissible number of recycling cycles of reclaimed water for selected unit operations (rinsing, washing) was analysed with respect to functional properties of the dyed knitted fabric. In selected cases for all parameters tested, good, acceptable colorfastness was obtained.

Key words: textile wastewater, closed water circuit, dyeing with reactive dyes, colour quality assessment.

The problem of sewage treatment in our country is not completely resolved and is becoming increasingly important due to the need to implement more stringent EU directives which aim at better protection of the natural environment. In the industry there is a large number of small and medium-size private companies engaged in the dyeing and finishing of textiles, in which problems related to wastewater treatment are often not satisfactorily resolved. On the other hand, the prices of water supply and sewage discharge are rapidly increasing. Thus for virtually all textile companies engaged in wet processing, water saving becomes an important issue. An ideal solution would be to obtain such a degree of wastewater purification as to be able to reuse it as reclaimed water in industrial processes, which would dramatically reduce the amount of fresh water used in the processes of wet treatment. The quality of treated wastewater should meet the requirements for processed water, which would lead to closing the water circuit and, at the same time, ensure the minimisation of discharged wastewater.

The treatment of textile wastewater and closing water circuits are not new issues. For many years research in this area has been conducted both globally and in our country [4-11]. However, the development of the textile industry, the introduction of new technologies, raw materials and products as well as increasingly stringent requirements for environmental protection make it necessary to conduct new research and implement more effective methods of treatment. There is a variety of solutions that can be applied,

however the primary criterion is to ensure high treatment efficiency at the lowest possible cost [3,12-16].

The Textile Research Institute (TRI) has significant achievements in the recovery of water from textile wastewater [15-18], and part of the solutions developed have been implemented in industrial practice. Recently the TRI in cooperation with Łódź University of Technology (TUL) have developed an interesting and innovative technological concept of reusing water which involves an integrated biological treatment, ultrafiltration and ozonation. The method makes it possible to reuse up to 40% of wastewater produced in a dyeing plant.

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■ Experimental methods

Subject of research and experimental methods

The object of study was textile wastewater produced during the dyeing of cellulose fibres with reactive dyes. After dyeing, the wastewater was separated into two streams comprising:

- low-loaded wastewater from rinsing after dyeing and washing, except for the first rinsing (stream I),
- high-loaded wastewater from dyeing and washing as well as from the first rinsing (stream II).

■ Introduction

Textile wastewater is troublesome and toxic to the environment. Characteristic features of textile wastewater are intensive colour, high content of chemical compounds, the presence of suspensions, poor biodegradability, high toxicity to aquatic organisms and different pH. Depending on the type and range of products, the composition of wastewater is subject to major changes. For these reasons it is difficult to purify [1-3].

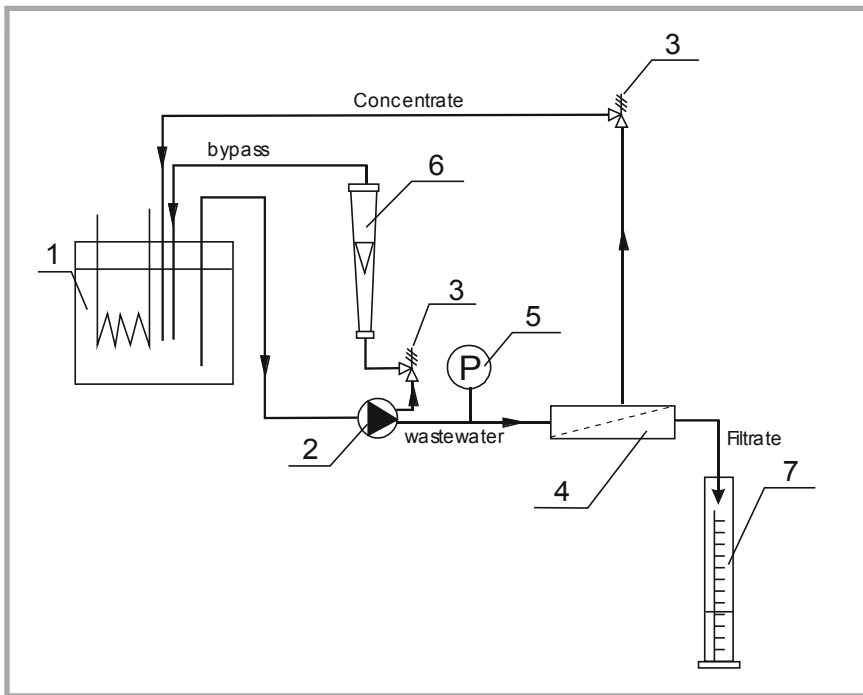


Figure 1. Schematic of ultrafiltration set-up: 1 – thermostat, 2 – pump, 3 – control valves, 4 – pressure chamber with a membrane, 5 – manometer, 6 – rotameter, 7 – measuring cylinder.

The separated low-loaded wastewater (stream I) was subjected to pretreatment during biological operation, ultrafiltration and ozonation. After the last stage of pretreatment (ozonation) the wastewater, as reclaimed water, after dissolution with process water at a 1:1 ratio was used in rinsing and washing after dyeing

(cf. The procedure of textile dyeing in reclaimed water in the *Experimental Methods* section). After the dyeing process, the wastewater was separated once again into two streams comprising low- and high-loaded wastewater. The low-loaded wastewater was pretreated in biological, ultrafiltration and ozonation stages, and

then used as reclaimed water in the dyeing process for washing and rinsing after dyeing. In total, all of the operations described above (separation of low-loaded wastewater – treatment – dyeing) were repeated four times.

Biological treatment

Biological treatment was carried out at the Department of Bioprocess Engineering, Faculty of Process and Environmental Engineering, TUL. The biological degradation of wastewater was conducted in a Biological Aerated Filter (BAF) filled with ceramsite (9 to 13 mm in diameter) as a biofilm support material. The volume of the BAF reactor was 15 dm³. The experimental set-up was described previously in literature [19]. The hydraulic retention time (HRT) was fixed at 72 h.

Ultrafiltration

Ultrafiltration was conducted at the Textile Research Institute in the system shown in *Figure 1*.

Ultrafiltration was carried out by the cross-flow method at a constant liquid flow rate in the system equal to 2 dm³/min at 20-30 °C. Tests were performed at a pressure of 0.5 MPa. The initial wastewater volume was 5 dm³, and the solution was concentrated to 2.5 dm³ (1:2). The membrane used in the experiment was 20 PS flat sheet with a surface area of approximately 314 cm², whose characteristics are summarised in *Table 1*.

Table 1. Parameters of membrane used in the experiment.

Membrane type	Polymer	MCWO, kDa	pH range	Typical LMh/bar	Pressure range, MPa	Producer
Ultrafiltration membrane						
PS 20	polysulfone	20	2-11	900	0.1-1.0	Sepro Membranes Inc. (USA)

Table 2. Hydrodynamic parameters of bubble column depending on liquid volume in the column.

Liquid volume, dm ³	Gas flow rate, dm ³ /min	Ozone concentration, g/Nm ³	ϵ_g	$k_L a, s^{-1}$	$k_L, m/s$	$a, m^2/m^3$
9	4	35.2	$2.810 \cdot 10^{-2}$	$7.73 \cdot 10^{-3}$	$1.88 \cdot 10^{-4}$	41.1
10			$2.337 \cdot 10^{-2}$	$6.49 \cdot 10^{-3}$	$1.91 \cdot 10^{-4}$	34.0
12			$2.474 \cdot 10^{-2}$	$5.25 \cdot 10^{-3}$	$1.45 \cdot 10^{-4}$	36.1
15			$2.475 \cdot 10^{-2}$	$3.94 \cdot 10^{-3}$	$1.09 \cdot 10^{-4}$	36.1

Table 3. Hydrodynamic parameters of bubble column depending on gas flow rate.

Liquid volume, dm ³	Gas flow rate, dm ³ /min	Ozone concentration, g/Nm ³	ϵ_g	$k_L a, s^{-1}$	$k_L, m/s$	$A, m^2/m^3$
9	2	60.0	$1.759 \cdot 10^{-2}$	$4.07 \cdot 10^{-3}$	$1.60 \cdot 10^{-4}$	25.5
	3	45.0	$2.288 \cdot 10^{-2}$	$6.81 \cdot 10^{-3}$	$2.05 \cdot 10^{-4}$	33.3
	4	35.2	$2.810 \cdot 10^{-2}$	$8.27 \cdot 10^{-3}$	$2.01 \cdot 10^{-4}$	41.1
	5	27.5	$3.071 \cdot 10^{-2}$	$7.57 \cdot 10^{-3}$	$1.68 \cdot 10^{-4}$	45.0

Ozonation

Ozonation was carried out at the Textile Research Institute in the system shown in *Figure 2*.

The process of ozonation was carried out at a fractional scale using a TOG-C8X ozone generator (TRIOGEN Ltd, Glasgow, Scotland) owned by TRI, in a glass bubble column with a chamber volume of about 20 liters equipped with an ozone concentration sensor (BMT Messtechnik, Berlin, Germany). The ozone generator had the following parameters: the range of ozone generation – up to 8 g O₃/h, and gas flow rate from 2 to 5 dm³/min. Tests of ozonation were carried out with 9 dm³ of wastewater in the reactor.

The basic parameters characterising operations of the bubble column were determined: the nature of liquid and

gas flow, gas hold-up (ϵ_G), interfacial specific surface area (a), volumetric mass transfer coefficient ($k_L a$), and mass transfer coefficient on the liquid side (k_L). These parameters are given in **Tables 2 and 3**.

In the purification of the low-loaded wastewater stream with ozone the following parameters were used:

- ozone dose: 420 mg O₃/dm³,
- gas flow rate: 3 dm³/min,
- ozone concentration in inlet gas: 42 g/Nm³,
- reaction time: 30 min.

Analytical control of wastewater

The colour of the wastewater was determined on the basis of absorbance measurements by the spectrophotometric method at three wavelengths: 436, 525 and 620 nm using a Jasco spectrophotometer (Jasco, Japan) according to the DIN-38404/1 Standard. Determination of COD and TOC of the wastewater was conducted on the basis of the HACH LANGE Standard [20]. The conductance and pH was measured by a S47-K Seven-Multi pH/conductometer (Mettler-Toledo, Switzerland). The pH was measured using an InLab[®] RoutinPro electrode, while the electrolytic conductance was measured by an InLab[®] 731 electrode.

Procedure of textile dyeing in the reclaimed water

Cotton knitted fabric (knitted fabric 100% CO) was selected for dyeing with the following reactive dyes: Synozol Yellow KHL, Synozol Red KHL and Synozol Blue KHL (Kisco Int., Turkey). The colour intensity applied was 1% (weight of the dye was 1% of the fibre weight). In addition to the dye, in the dyeing process, sodium chloride in an amount of 40 g/dm³ and sodium carbonate in an amount of 15 g/dm³ was used. The liquor ratio was 1:10. The technological process was conducted on REDKROME laboratory dyeing apparatus (UGOLINI, Italy) using the following operations:

- dyeing,
- first rinsing after dyeing carried out in water at 80 °C for 10 minutes,
- second rinsing after dyeing carried out in water at 40 °C for 10 minutes,
- washing for 15 minutes at 98 °C in a bath using Periwet WLW washing agent (Dr. Petry GmbH, Germany) in an amount of 2 g/ ³,
- rinsing after washing carried out in water at 80 °C for 10 minutes,

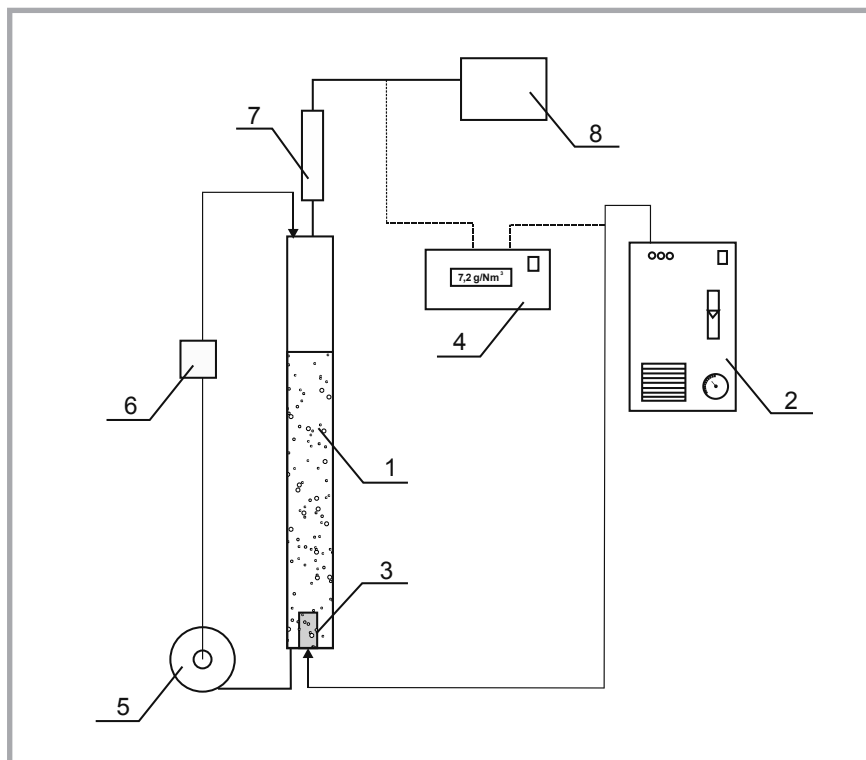


Figure 2. Schematic of ozonation set-up: 1 – bubbling column, 2 – ozonator with oxygen concentrator, 3 – ozone diffuser, 4 – ozone meter in gas phase, 5 – peristaltic pump, 6 – sampling point, 7 – scrubber with silica gel, 8 – ozone destructor.

- rinsing and acidification for a period of 10 minutes at 40 °C using acetic acid in an amount ensuring a bath pH of about 4,
- rinsing after acidification in water at 40 °C for 10 minutes.

Estimation of the functional properties of products

The quality of colour obtained was estimated on the basis of analysis of the relative color intensity based on colour measurements using a Datacolor 650 spectrophotometer (Datacolor Int.) and Datacolor Tools software. The criterion for assessing colour quality was the difference in the colour of samples dyed with the use of water reclaimed from wastewater and samples dyed using clean process water. The colour of the samples was measured according to PN-EN ISO 105-J01:2002., and colour differences were determined according to PN-EN ISO 105-J03. To compare the quality of colours obtained using various water media, an acceptable threshold value of the total colour difference LAB Delta E equal to 1.5 between the colour of the textile sample dyed in clean water (pattern) and that of the sample dyed in water reclaimed from wastewater (sample) was determined.

- Additionally tests of colorfastness to
- washing at 40 °C C1S according to PN-EN ISO 105-C06: 2010 met. A1S,
 - acidic and alkaline sweat according to PN-EN ISO 105-E04: 2013,
 - dry and wet friction according to PN-EN ISO 105-X12: 2005
- were performed.

Results and discussion

The water circulation applied is shown schematically in **Figure 3**, while **Table 4** gives detailed results of physicochemical analyses of initial wastewater and that after subsequent stages of treatment for each water cycle.

Figure 4 shows a comparison of physicochemical parameters of water reclaimed from wastewater (COD, TOC, absorbance at 525 nm) for each subsequent water cycle.

Data given in **Table 4** indicate that in the case of biological treatment, ultrafiltration and ozonation, regardless of the number of cycles, the purification efficiency was high, reaching 95.5%-97.2% for COD, 93.9%-95.9% for TOC and 92.6%-98.9% for colour (absorbance 525 nm). Concentrations of pollutants in the reclaimed

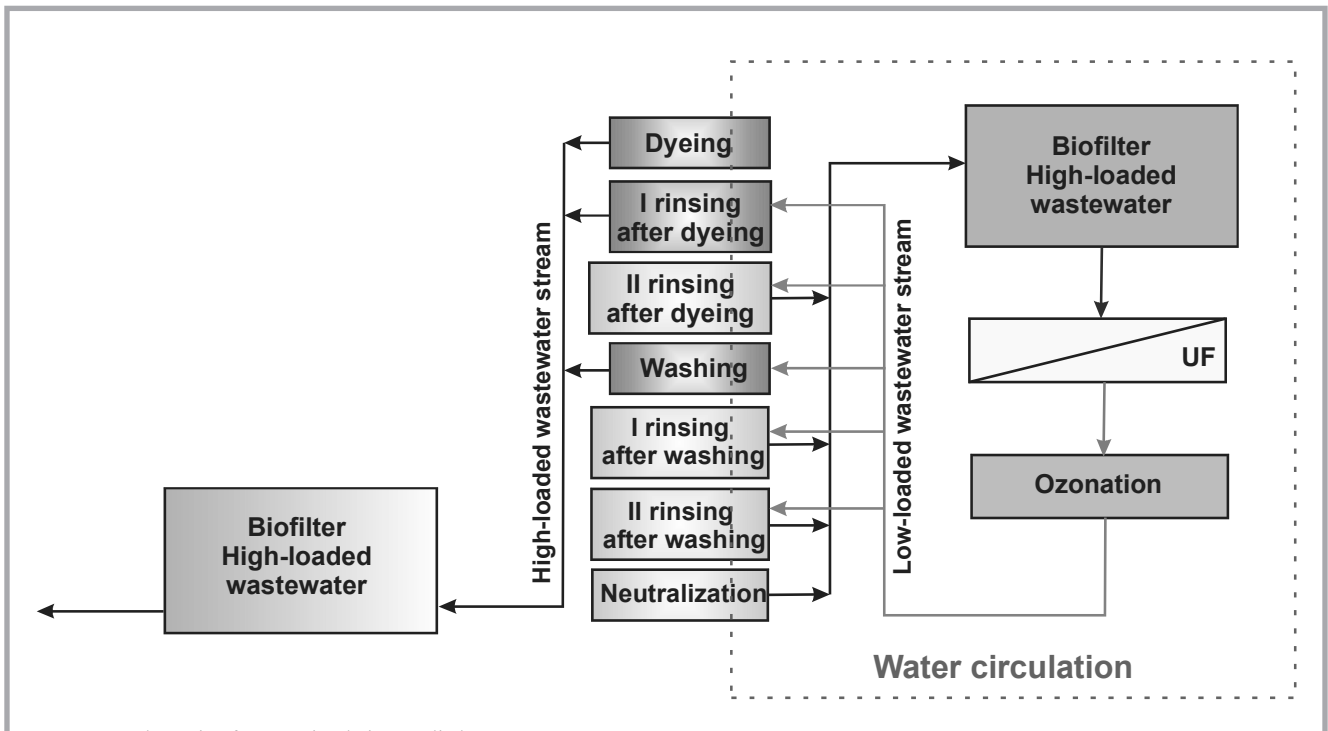


Figure 3. Schematic of water circulation applied.

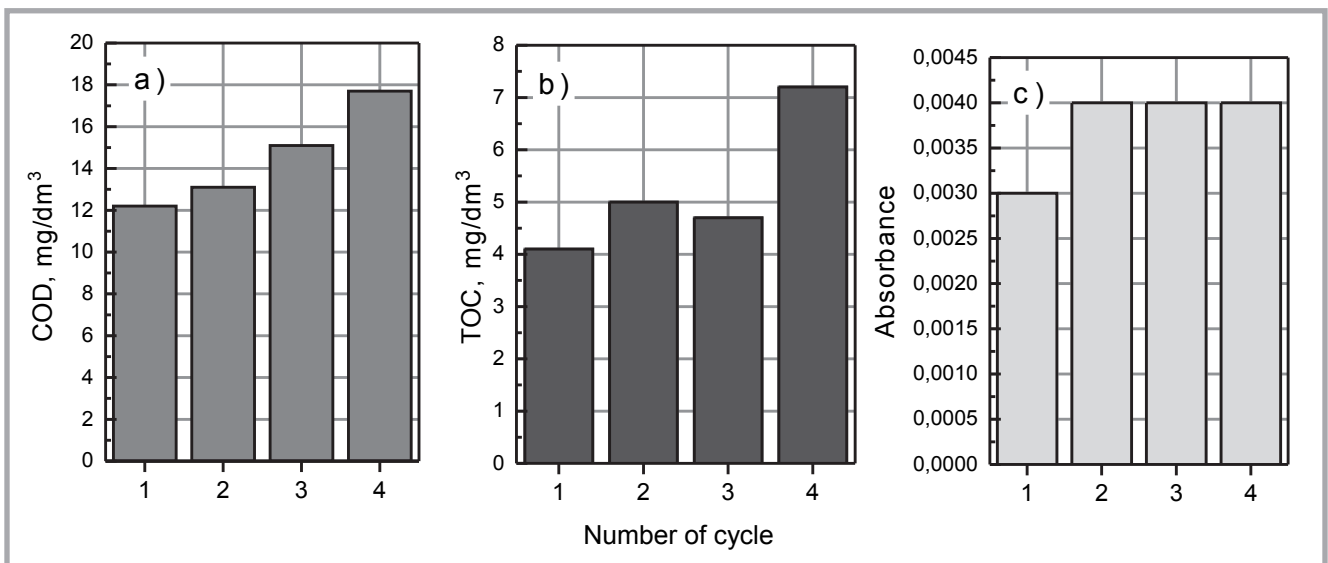


Figure 4. Comparison of physicochemical parameters of water reclaimed from wastewater: a) COD, b) TOC, c) absorbance at 525 nm, for each subsequent water cycle.

water were similar and very low (Figure 4), ranging from 12 mg O₂/dm³ to 18 mg O₂/dm³ in the case of COD, from 4 mg/dm³ to 7 mg/dm³ for TOC and from 0.003 to 0.004 for absorbance (525 nm).

Water reclaimed from the wastewater was then used in the dyeing of knitted fabric from cotton fibres in washing and rinsing operations. The knitted fabric dyed was evaluated from the point of view of its functional properties, determining the

total color difference (LAB Delta E) between the color of the samples of fabric dyed in the process water (pattern) and those dyed with water reclaimed from the wastewater in rinsing and washing operations using selected reactive Synozol dyes. Figure 5 shows LAB Delta E values obtained for knitted fabric samples from cotton fibres subjected to dyeing with the use of selected dyes and reclaimed water for subsequent water cycles compared to the acceptable value (LAB Delta E = 1.5).

As follows from the data above, only in some samples, mainly those dyed with Blue KHL, the value of LAB Delta E in cycles II, III and IV was unacceptable. In most samples it was within acceptable limits, not exceeding the value of 1.5.

The reason for variation in the DE index is the different chemical structure of the reactive dyes used, and hence their varied sensitivity to remaining residual impurities in the water. It has been known

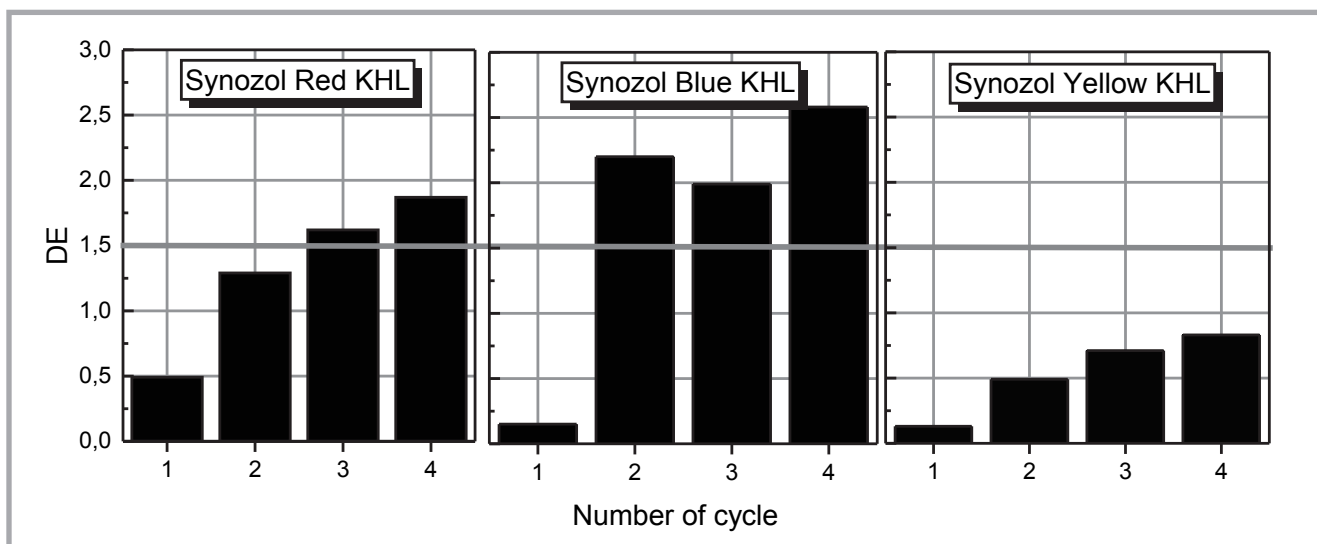


Figure 5. Values of LAB Delta E for knitted fabric from cotton fibres dyed with selected dyes with the use of reclaimed water in washing and rinsing operations for four water cycles. Dye concentration in the bath was 1 wt.% in relation to fabric weight.

Table 4. Pollutant concentration in wastewater before and after pretreatment for subsequent water cycles. *Note:* * low-loaded wastewater stream from three rinsing operations and final neutralization; in all operations process water was used; ** low-loaded wastewater stream from three rinsing operations and final neutralization; in the rinsing and washing operations the water reclaimed from the wastewater was applied, while in other operations process water was used.

	COD	TOC	Absorbance			Conductance	pH
	mg O ₂ /dm ³	mg/dm ³	436 nm	525 nm	620 nm	mS	—
Water cycle I							
Initial wastewater before treatment*	305	66.9	0.155	0.146	0.123	1.006	9.07
Wastewater after biological treatment	53.5	14.1	0.049	0.043	0.027	1.063	8.61
Wastewater after ultrafiltration	20.3	6.10	0.010	0.010	0.005	1.027	8.79
Wastewater after ozonation (reclaimed water)	12.2	4.1	0.005	0.003	0.002	0.980	8.54
Water cycle II							
Initial wastewater before treatment**	476	105.9	0.061	0.054	0.040	1.279	9.17
Initial wastewater after biological treatment	46.1	14.4	0.038	0.034	0.017	1.251	8.11
Wastewater after ultrafiltration	19.1	5.4	0.008	0.008	0.004	1.197	8.50
Wastewater after ozonation (reclaimed water)	13.1	5.0	0.006	0.004	0.003	1.216	8.68
Water cycle III							
Initial wastewater before treatment**	444	115	0.071	0.062	0.050	1.221	9.31
Wastewater after biological treatment	57.8	14.9	0.040	0.036	0.020	1.287	8.48
Wastewater after ultrafiltration	31.9	8.0	0.010	0.011	0.005	1.264	8.33
Wastewater after ozonation (reclaimed water)	15.1	4.7	0.005	0.004	0.002	1.225	8.67
Water cycle IV							
Initial wastewater before treatment**	391	125	0.097	0.090	0.074	1.141	7.31
Wastewater after biological treatment	36.7	11.7	0.036	0.036	0.023	1.235	8.34
Wastewater after ultrafiltration	21.1	7.7	0.010	0.011	0.006	1.094	8.45
Wastewater after ozonation (reclaimed water)	17.7	7.2	0.002	0.004	0.001	1.219	8.67

from previous experiments that residual pollutants, especially the products of dye oxidation with ozone, have an effect on coloring operations in purified, recovered water. In addition, according to literature data and dyeing practice, it is known that this may occur in the case of reactive blue dyes.

Table 5 gives examples of the colorfastness of knitted fabric samples from cotton fibres dyed with Synozol Yellow

KHL using reclaimed water for four water cycles.

As follows from the data presented above, when knitted fabric from cotton fibres was dyed with Synozol Yellow KHL using reclaimed water in washing and rinsing operations for each water cycle, good and very good colorfastness was obtained, like in the case of knitted fabric from cotton fibres, where in all unit operations, including rinsing

and washing, only process water was applied. When reactive Synozol Red KHL and Synozol Blue KHL dyes were used, the colorfastness was also good or very good.

Economic analysis will be the goal of further work aimed at commercializing the results of the research. Previous experience and analyzes indicate the economic viability of the implementation of wastewater treatment technologies with

Table 5. Colorfastness of knitted fabric samples from cotton fibres dyed with Synazol Yellow KHL using reclaimed water for four water cycles.

Tested parameter		No. of water cycle			
		I	II	III	IV
Colorfastness to alkaline sweat	Change in sample color	4-5	4-5	5	5
	Soiling of accompanying white fabric – cotton	5	5	5	5
	Soiling of accompanying white fabric – wool	5	5	5	5
Colorfastness to acidic sweat	Change in sample color	4-5	4-5	5	5
	Soiling of accompanying white fabric – cotton	5	5	5	5
	Soiling of accompanying white fabric – wool	5	5	5	5
Colorfastness to dry rubbing	Soiling of rubbing white cotton fabric – wale	5	5	4-5	5
	Soiling of rubbing white cotton fabric – row	5	5	4-5	5
Colorfastness to wet rubbing	Soiling of rubbing white cotton fabric – wale	4	4-5	4	4
	Soiling of rubbing white cotton fabric – row	4	4	4	4
Colorfastness to washing 40 °C	Change in sample color	4-5	4-5	5	5
	Soiling of accompanying white fabric – cotton	5	5	5	5
	Soiling of accompanying white fabric – wool	5	5	5	5

simultaneous recovery of at least 40-50% of water.

Conclusions

The study leads to the following conclusions:

- the treatment method applied, including biological pretreatment, ultrafiltration and ozonation, is very effective, making it possible to reclaim water with a low concentration of pollutants;
- the reclaimed water can be successfully used in washing and rinsing operations after dyeing,
- the functional properties of products from cotton fibres after the dying process conducted with the use of reclaimed water do not differ from those where process water was exclusively used in all operations.



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