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Ecological Aspect of Preliminary Treatments of Flax Fibre

Abstract
The present paper discusses the results of testing effluent quality in various variants of flax fibre preliminary treatment with the use of different bleaching agents, especially such which enhance the efficiency of the fibre chemical treatment process. Hydrogen peroxide and per-acetic acid are recommended as alternative bleaching agents instead of chlorine compounds. An improvement of chlorine-free bleaching methods effectiveness is aimed at by the use of compounds, which may lead to an efficient decrease in the effluent load with toxic chemicals.

Key words: *flax fibres, bleaching, hydrogen peroxide, per-acetic acid, chlorine-free bleaching, ecology aspects.*

Introduction

Practically all the chemical compounds used in the fibre manufacturing and finishing processes are harmful to humans and the environment. These compounds are mostly discharged as industrial effluents into water reservoirs, but they can also pollute air or combine permanently with textiles. They can penetrate the human body through the skin, the respiratory system and the alimentary canal. Their effects can result in various skin diseases, allergies and other illnesses, while polluting or damaging the environment at the same time.

The product ecology concerning environment-friendly goods may be considered on a broad basis as a complex issue, or by taking its three different aspects into consideration separately:
- *production ecology* - including the assessment of all important factors for the environment arising in the product manufacturing process,
- *human ecology* - including all ecological and sanitary factors which are of importance during the use of textile products, especially concerning adverse effects on human health,
- *utilisation ecology* - including all environmental problems associated with the disposal of waste product [1-6].

The chemical treatment of flax fibre, which requires the process to be performed with quite a high content of chemicals, is an environmentally dangerous treatment. Particularly harmful are the organic chlorine compounds whose total content is regarded as parameter AOX (adsorbable organic halogens). The presence of these compounds in effluents from textile plants and in textile raw materials is subject to strict inspection in different countries [1-3]. Especially high AOX values were found in a bleaching bath using chlorine compounds discharged into wastewater. In this connection, chlorine-free bleaching technologies have become an object of intensive interest for finishing technologists [7-11]. Therefore, the present paper focuses on the first of the above-mentioned aspects, testing the quality of effluents from the flax fibre treatments.

Experimental

Effluent quality testing

The analysis of effluent quality was carried out for the following variants of flax fibre treatment [12] on a laboratory scale, using the bath ratio of 50:1:
- after an alkaline boiling-off (sample 1),
- after bleaching with chlorine compounds (samples 3, 3A, 4, 5),
- after chlorine-free bleaching, using hydrogen peroxide 35% (samples 2, 6, 7, 10) and per-acetic acid 15% (samples 20, 24) as bleaching agents,
- after bleaching processes supported by an enzymatic treatment (samples 8, 9, 11, 12, 18, 19, 23, 25, 26, 27, 28).

In all the treatment variants, comparative tests of the degree of effluent pollution were performed. The effluent quality was assessed by analysing the indicators [13], presented in Table 1. In addition, dyebaths after dyeing with reactive dyes were analysed for AOX (Table 8).

Materials

Fibre

Flax roving with a sliver weight of 750 tex and the following quantitative chemical compositions was used in the examinations:
- hemicellulose content 16%,
- lignin content 4.5%,
- pectin content 1.5%.

The polymerisation degree of cellulose was 3510.

Chemicals used in the alkaline boiling-off process

The alkaline boiling-off process was carried out with the use of the following chemical agents:
- sodium hydroxide,
- sodium carbonate,
- Pretepon G from ORGANIKA S.A. [14],
- Sultafon UNS from Stockhausen [15],
- Sulfokyl TL 893 from THOR [16],
- Sulveol NSE from THOR [16].

Table 1. *The parameters of effluents assessed and test methods used (*after 5 and 14 days, respectively).*

Parameter tested	Testing method
Colour	Polish Standard PN-74/C-04558
pH value	Potentiometric method by PN-87/P-04732 pH-meter type N517, from Mera Tronik
COD (Chemical Oxygen Demand): - the dichromate method - the permanganate method	 PN-74/C-04578.03 PN-85/C-04578.02
$BOD_{5,\ 14}$ (Biochemical Oxygen Demands)*	The dilution method by PN-84/C-4578.05, and auxiliary standard PN-72/C-04545.02 determination of dissolved oxygen by Winkler's method
Suspension content	PN-72/C-04559.02
Chloride content	PN-75/C-04617.02
AOX (Absorbable Organic Halogens)	ISO 9562:1989, using an AOX analyser EOX/TS, model ECS 3000 from EUROGLAS

Chemicals used in the acid treatment

The boiling-off process was followed by the acid treatment with the use of the following chemical agents:

- sulphuring acid,
- Solopol BLS conc., from Stockhausen [15].

Chemicals used for bleaching

The bleaching process was carried out with the use of the following chemical agents (all standard commercial products):

- hydrogen peroxide 35%,
- sodium hypochlorite,
- sodium chlorite 40%,
- peracetic acid 15%,
- sodium nitrate,
- sodium hydroxide,
- water glass,
- Pretepon G,
- Solopol BLS conc.,
- Sultafon UNS,
- magnesium sulphate.

Enzymatic agents used in the treatment

The enzymatic treatment was carried out with the use of two cellulolytic enzymatic agents and one pectinolytic enzymatic agent:

- Tiozym CEL from Ciba Geigy A.G. [17],
- Cellulosoft Ultra L from Novo Nordisk [18],
- BioPrep L from Novo Nordisk [18].

Table 2. *Allowable effluence parameters from flax fibre plants.*

Parameters investigated	Unit	Allowable value
Reaction	pH	9.0
BOD_5	mg O_2/dm^3	up to 700
COD permanganate method	mg O_2/dm^3	-
COD dichromate method	mg O_2/dm^3	up to 1000
AOX	mg Cl/dm^3	up to 0.01
Colour-threshold number	-	50
Chloride	mg Cl/dm^3	400

Table 3. *Results of the quality testing of effluents after conventional bleaching [20]. Sample 1 - after alkaline boiling-off; sample 2 - chlorine-free bleaching method - peroxide method; samples 3, 3A - hypochlorite methods (sample 3 - sodium hypochlorite concentration 2 g/l; sample 3A - sodium hypochlorite concentration 5 g/l); sample 4 - chlorite method; sample 5 - chlorite and peroxide method.*

Parameters investigated	Unit	Sample 1	Sample 2	Sample 3	Sample 3A	Sample 4	Sample 5
Reaction	pH	9.5	10	10.5	9	3.5	6.7
AOX	mg Cl/dm^3	< 0.01	< 0.01	125.45	278.3	34.13	27.3
BOD_5	mg O_2/dm^3	510	680	620	1100	880	780
COD permanganate method	mg O_2/dm^3	1480	760	890	420	920	840
COD dichromate method	mg O_2/dm^3	8268	2544	3180	3803	4850	3697
Suspension	mg/dm^3	780	380	417	1072	510	445
Colour-threshold number	-	400	60	80	68	74	78
Chloride	mg Cl/dm^3	-	-	2045	4625	615	505

Table 4. *Results of the quality testing of effluents after peroxide bleaching with the use of auxiliary agents Stockhausen and THOR [12]. Sample 6 - with common auxiliary agents; sample 7 - with Stockhausen auxiliary agents; sample 10 - with THOR auxiliary agents.*

Parameters investigated	Unit	Sample 6	Sample 7	Sample 10
Reaction	pH	6.8	6.8	9.8
AOX	mg Cl/dm^3	< 0.01	< 0.01	2.8
BOD_5	mg O_2/dm^3	700	720	1952 BZT_{14} 660
COD permanganate method	mg O_2/dm^3	780	810	2397.6
COD dichromate method	mg O_2/dm^3	2671	2770	8199
Suspension	mg/dm^3	400	780	800
Colour-threshold number	-	60	284	248
Chloride	mg/dm^3	-	-	57

Table 5. *Results of the quality testing of effluents after bleaching with per-acetic acid [20]. Sample 20 as sample 24 - the difference only in bath ratio during the fibre treatment.*

Parameters investigated	Unit	Sample 20 bath ratio 50:1	Sample 24 bath ratio 20:1
Reaction	pH	8.5	9.3
AOX	mg Cl/dm^3	9	8.8
BOD_5	mg O_2/dm^3	5226 BOD_{14} 5707	5794 BOD_{14} 6230
COD permanganate method	mg O_2/dm^3	350	470
COD dichromate method	mg O_2/dm^3	15820	17385
Suspension	mg/dm^3	412	435
Colour-threshold number	-	48	61
Chloride	mg/dm^3	170	168

Results

The quality of effluents resulted from the prescribed variants of preliminary treatment and bleaching was tested, and the results obtained are given in Tables 3-8. The allowable parameter values of effluents are given in Table 2 [19].

Results Description

Based on the analysis of the effluent parameters, depending on the variant of preliminary treatment and the bleaching process used, one can state the following:

- In the alkaline boiling-off treatment, the effluents become strongly coloured, showing an alkaline character and a high content of suspended solids, while the AOX parameter is very good, with COD and BOD remaining at a medium level (Table 3, sample 1).
- The use of sodium hypochlorite in the bleaching process brings about a severe increase in AOX, COD and BOD. The bath shows an alkaline character. The increase in the sodium hypochlorite concentration is accompanied by considerably increased values of the tested parameters (Table 3, samples 3 and 3a).
- The use of sodium chlorite in the bleaching process results in a less severe increase in AOX, but COD is clearly increased and the effluents show an acidic character (Table 3, sample 4).
- The combination of sodium chlorite and hydrogen peroxide in the bleaching process have an advantageous effect on the values of AOX and COD (Table 3, sample 5).

Table 6. Results of the quality testing of effluents after peroxide bleaching aided with cellulolytic enzymes. Sample 8, 9, 11, 12 - peroxide bleaching method (8, 9 - Tinozym CEL treated before and after bleaching respectively; 11, 12 - Cellulosoft Ultra L treated before and after bleaching respectively); sample 23 as sample 11 - the difference in bleaching bath ratio (20:1); sample 18, 19, 25 - per-acetic acid bleaching method (18, 19 - Cellulosoft Ultra L treated before bleaching - the difference in pH; sample 25 - Cellulosoft Ultra L, treated after bleaching in the same conditions as sample 18.

Parameters investigated	Unit	Sample 8	Sample 9	Sample 11	Sample 12	Sample 18	Sample 19	Sample 23	Sample 25
pH - value	-	8.5	8.5	10.2	10.1	8.9	6.2	7.4	7.9
AOX	mg Cl/dm^3	< 0.01	< 0.01	< 0.01	< 0.01	9.3	8.1	< 0.01	9.1
BOD_5	mg O_2/dm^3	734	742	700	1551	2834	2141	760	3115
COD permanganate method	mg O_2/dm^3	901.3	910.8	640	720	430	510	690	730
COD dichromate method	mg O_2/dm^3	3082	3115	2355	4864	11234	9881	2578	12180
Suspension	mg/dm^3	408	408	181	151	175	188	193	179
Colour-threshold number	-	48	51	50	48	51	56	51	53
Chloride	mg/dm^3	-	-	-	-	174	155	-	76

- The hydrogen peroxide treatment with the use of auxiliary agents from THOR considerably increases the examined parameters of effluents, as compared to the parameters of the peroxide bleaching with the use of chemicals used so far (Table 4, samples 6, 7, and 10).
- The bleaching with hydrogen peroxide aided with cellulolytic enzymes results in the lowest pollution of effluents in the variants where the enzymatic treatment preceded the bleaching process (Table 6, samples 8, 9, 11, 12, 18, 19, 23 and 25).
- The use of the pectinolytic enzyme in peroxide bleaching causes the COD and BOD to increase, as compared to the effluent parameters obtained in the fibre treatment with cellulolytic enzymes (Table 7, samples 26, 27 and 28).
- The use of peracetic acid as a bleaching agent, both with the liquor ratio 50:1 and 20:1, results in a considerable increase in the values of COD and BOD, and a significant increase in AOX over the allowable value (Table 5, samples 20 and 24).
- In the case of effluences after the dyeing process, the AOX parameter is significantly greater than the allowable value presented in Table 2.

The analysis of the test results indicates that from the point of view of the effluent parameters under consideration, the most optimal variant of fibre treatment is the peroxide bleaching aided with cellulolytic enzymes.

Summary

Based on the data given in Tables 3-8 concerning the degree of effluent pollution, one may present the following statements:

- The effluents from the bleaching processes performed with the use of hydrogen peroxide, both by the conventional method and with the use of enzymatic agents, contain no absorbable organic halogens (AOX<0.01).
- The effluents from the conventional bleaching with sodium hyperchlorite are characterised by high AOX; the increase in the bleaching agent concentration up to 5 g/dm^3 of active chlorine causes the AOX to increase up to 278.3 mgCl/dm^3 (allowable value: 0.01 mgCl/dm^3).
- The effluents from the peroxide bleaching with the use of cellulolytic enzyme before the actual bleaching process are characterised by the lowest degree of pollution, as compared to those in the remaining treatment variant under investigation.
- The use of pectinolytic enzyme in the peroxide bleaching causes the BOD and COD to increase, as compared to those of the effluents from the treatment with cellulolytic enzymes. The reaction of the effluent obtained is more alkaline than that of the effluents from the treatment with the cellulolytic enzyme Tinozym CEL.
- The effluents resulting from the fibre treatments with the examined enzymatic agents differ considerably in the suspended solid content. A high suspension content in effluents takes place after the treatment with Tinozym CEL, which indicates an intensive fibre separation and removal

Table 7. Results of the quality testing of effluents after peroxide bleaching aide with pectinolytic enzymes [12]. Sample 26 Bio Prep L treated before bleaching; 27 - Bio Prep L treated after bleaching; 28 - treated in the same conditions as sample 26 but missing out the stage of boiling-off.

Parameters investigated	Unit	Sample 26	Sample 27	Sample 28
Reaction	pH	9.9	10.25	9.2
AOX	mg Cl/dm^3	< 0.01	< 0.01	< 0.01
BOD_5	mg O_2/dm^3	990	890	1080
COD permanganate method	mg O_2/dm^3	640	600	840
COD dichromate method	mg O_2/dm^3	3426	3253	3712
Suspension	mg/dm^3	245	248	720
Colour-threshold number	-	52	51	59
Chloride	mg/dm^3	-	-	-

Table 8. Values of AOX parameter for dyebaths [12].

Dyestuffs	Auxiliary agents	AOX mgCl/dm^3
Helakthine Red F-2B	40 g/l NaCl 10 g/l Na_2CO_3 0.5 g/l Rokafenol N-8	5.34
Sumifix Supra Brillant Red 3BF	40 g/l NaCl 10 g/l Na_2CO_3 0.5 g/l Rokafenol N-8	3.13
Helakthine Scarlet DE-2G	45 g/l NaCl 10 g/l Na_2CO_3 2 g/l Nitrol S	9.52

of non-cellulose substances. The lowest suspended solid content is shown by the effluents after the peroxide bleaching with the use of Cellulosoft Ultra L.

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