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Influence of Bleaching Stages and Dyeing Process on Changes in a Selected Heavy Metal Content in Flax Fibres

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Abstract

Raw flax fibres consist of over 70% cellulose, over 20% hemicelluloses, pectins and lignins, 2.5% wax and fat, and 3% proteins. Non-cellulosic substances constitute a glue connecting elementary fibres. Because of the huge content of hydrophobic substances, raw flax fibres are difficult to wet by water. There is a necessity of removing hydrophobic substances from fibres before further chemical treatments. Classical bleaching of flax woven fabric is a long-running process that includes four stages, each starting from the scouring process in an alkaline bath. In order to obtain full whiteness, there is a necessity of carrying out four full stages of scouring and bleaching. The results of changes in a selected heavy metal content in flax fibres after a particular bleaching stage and dyeing process were shown. The content of heavy metals in flax fibres was determined using the qualitative (ICP-MS) and semi-qualitative (LA-ICP-ToF-MS) methods. Also changes in the content of extractable elements to artificial acid sweat was determined. The content of selected metals in flax fibres fell with a decrease in non-cellulosic polysaccharide content in the fibres. The important influence of dye fixation on the extractable copper content was also shown.

Key words: flax, heavy metals content, ICP measurements, bleaching, dyeing.

Introduction

During the cultivation and processing of fibres, a huge amount of chemical substances are used (plant protection products, bleaching agents, dyes, auxiliaries etc.), some of which may have harmful or have a toxic effect on the environment. The main pollutants of textiles are formaldehyde, heavy metals, allergic dyes, finishing agents (softener, flame retardants, water repellent etc.), dyes cleaving carcinogenic amines, pesticides, carriers, pentachlorophenol, biocides etc. Their presence in textiles is restricted or acceptable in a limited amount only by the law and/or ecological textile labelling requirements [1, 2]. Heavy metals (including cadmium, chromium, nickel, arsenic and beryllium) are an important group of carcinogens for human [3]. Besides the health hazard, the presence of heavy metal in textiles may lead to some difficulties in the finishing process. It is well known that ferric, copper and manganese ions present on cellulosic fibres or in water used for treatment may cause the catalytic decomposition of hydrogen peroxide, contributing to the chemical damage of cellulosic fibres after the bleaching process. Also ferric ions are easily oxidised to form deposits on fabric, causing its yellowing. Cadmium and magnesium ions create insoluble salts with direct and reactive dyes as well as with soap and some surfactants [4, 5]. It is reported that heavy metals present on a cotton substrate can catalyse an organic reaction leading to the binding of an organic compound to the cotton [6].

Metal-complex dyes are an important class of synthetic dyes due to their excellent light fastness and washing fastness. The most important metal-complex dyes used in the textile industry are copper, chromium and cobalt complexes [7, 8]. Numerous dyes for wool, leather or nylon belong to the group of metal-complex dyes [4]. Moreover some direct and reactive dyes are of the metal-complex type [7, 8]. However, there is no possibility to replace metal-complex dyes with other ones due to the loss of some important shades like turquoise, brilliant green, violet, blue and navy shades [6]. Furthermore heavy metal compounds (such as lead, copper, manganese, zinc and arsenic) used as catalysts during the synthesis of dyes may contaminate commercial products [7, 8]. Raw textile materials, especially natural fibres, are often contaminated with heavy metals [9, 10]. Flax and hemp may absorb heavy metals from the environment due to the presence of pectins, lignins and hemicellulose, mainly in seeds and roots [11, 12]. Also the presence in fibres of dyes containing hydroxyl, amine or carboxylic groups in the (o,o') position to the azo- group results in the chelating of metal ions [7, 8, 13].

In this work, changes in the heavy metal content in flax fibres after particular stages of bleaching and dyeing processes were shown. The measurement was carried out using the quantitative ICP analysis. The content of heavy metal was measured in the mass of flax fibres as well as in an extract after artificial acid sweat treatment. Also the relative heavy

Table 1. Description of samples.

Sample	Description of sample
0	Raw, desized flax fabric
B-I	Bleach flax fabric after first stage
B-II	Bleach flax fabric after scouring in second stage
B-III	Bleach flax fabric after second stage
B-III	Bleach flax fabric after scouring in third stage
B-III	Bleach flax fabric after third stage
B-IV	Bleach flax fabric after scouring in fourth stage
B-IV	Bleach flax fabric after fourth stage
D-1	Dyed flax fabric – 0.5% (o.w.f.) dye
D-1f	Dyed, fixed flax fabric – 0.5% (o.w.f.) dye
D-2	Dyed flax fabric – 1.5% (o.w.f.) dye
D-2f	Dyed, fixed flax fabric – 1.5% (o.w.f.) dye
D-3	Dyed flax fabric – 5% (o.w.f.) dye
D-3f	Dyed, fixed flax fabric – 5% (o.w.f.) dye

metal content in the raw and bleached flax fabric was measured using semi-quantitative (LA-ICP-MS) analysis. The progress of the removal of non-cellulosic substances from flax fibres after a particular bleaching stage was controlled by the Ruthenium Red dyeing method.

Materials and methods

Raw, desized flax woven fabric of plain weave was supplied by LEN S.A., Kamienna Góra, Poland. The sodium hydroxide, sodium carbonate, hydrochloric acid, water-glass and hydrogen peroxide used, products of POCH, were of a high purity grade. C.I. Direct Blue 86, a product of 'ZACHEM Dyes', Poland was used without further purification.

Scouring and bleaching of flax fabric

The classical process of bleaching flax woven fabric, comprising four stages, was carried out. All scouring and bleaching processes were performed using a laboratory jigger type LJ 500 TM, product of Ernst Benz, Switzerland. The first stage included the following: scouring; hot, warm and cold rinsing; acidification in diluted hydrochloric acid (2 g·dm⁻³ HCl) for 30 minutes at an ambient temperature, and neutralisation (in a bath containing 4 g·dm⁻³ sodium hydroxide). From stage two to four included scouring; hot, warm and cold rinsing, and bleaching. The scouring process in the first stage was performed for 120 minutes, in a bath containing 9 g·dm⁻³ of sodium carbonate and 0.5 g·dm⁻³ of sodium hydroxide at a temperature of 90 °C. From the second to the fourth

stage scouring processes were carried out in milder conditions, in a bath containing 6 g·dm⁻³ of sodium carbonate (bath temperature 80 °C, 60 minutes). All bleaching processes were performed for 180 minutes at a temperature of 80 °C. The bleaching bath contained 11 cm³·dm⁻³ of hydrogen peroxide solution (25%, w/v), 4 cm³·dm⁻³ of water-glass and 1 g·dm⁻³ of sodium hydroxide. After each bleaching process the fabric was rinsed in hot and warm water.

Determination of residual pectin content

The residual pectin content in flax fabric after every bleaching stage was determined by staining with Ruthenium Red dye (Sigma Aldrich). Ruthenium Red is a dye which selectively binds to carboxylic groups in pectins [14]. The method developed by Novonordisk and described by Klug-Santner et al. [15] was used. A sample of raw flax fabric (assumed as 100% residual pectin control), samples after particular bleaching stages and a sample after four bleaching stages (assumed as 0% residual pectin control) were dyed together in a bath containing 0.2 g·dm⁻³ of Ruthenium Red, 1 g·dm⁻³ of ammonium chloride, 2.8 cm³·dm⁻³ of ammonium hydroxide solution (25%, w/v) and 1 g·dm⁻³ of Malripal O 13/40 (wetting agent, a product of Sasol, Germany GmbH). The dyeing process was performed for 15 minutes at an ambient temperature and liquor ratio of 50:1. After the dyeing process was carried out the samples were rinsed in distilled water, washed at a temperature of 90 °C in a bath containing 1 g·dm⁻³ of Malripal O 13/100 (washing agent, a product of Sasol, Germany GmbH), rinsed and dried at ambient temperature. The residual pectin content in the flax fabric was determined on the basis of reflectance measurements at 540 nm, using a Spectraflash SP 300 Datacolor spectrometer, a product of Datacolor, Switzerland. From the K/S values determined, the residual pectin content was calculated by using controls. The amount of Ruthenium Red linked to the pectin products, estimated as K/S, is directly proportional to the residual pectin content in the fabric [14].

Dyeing with C.I. Direct Blue 86

Flax woven fabric after four stages of the bleaching process was used for the dyeing experiments. The fabric samples were dyed in a BFA-12 Mathis Labomat laboratory dyeing machine, manufac-

tured and granted to us by Werner Mathis AG Textile Machines, Switzerland, in a dyebath containing 0.5%, 1.5% and 5% (o.w.f.) dye and 50:1 liquor ratio. The dyebath contained 5 g·dm⁻³ of sodium chloride and 0.5 g·dm⁻³ of sodium carbonate. A well-known dyeing method with direct dyes was used. All the fabric samples were wetted out in cold water before the dyeing process was carried out. After the dyeing process the samples were rinsed in warm and cold water. Half of each sample was fixed in a bath containing of 5 g·dm⁻³ Zetosal DN 45 (a cationic agent used to improve fastness properties, a product of Zschimmer & Schwarz Inc., Germany) and 1 cm³·dm⁻³ of acetic acid solution (30%, w/v) for 30 minutes at a temperature of 40 °C. Next the samples were dried at ambient temperature.

Heavy metal content determination

The content of heavy metals was determined in the fibre mass and in extracts of artificial acid sweat. Analysis of the heavy metal content in the fibre mass of fabric after the bleaching process was performed using an Inductively Coupled Plasma-Mass Spectrometer with a Time of Flight Analyser (ICP-ToF-MS) - Optimass 8000, GBC Scientific Equipment. In the scope of the dyed fabric, the content of heavy metals was determined using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), X-Series, Thermo Electron Corporation. For each sample, three repetitions were made. Mono- and multi-elemental ICP-MS class standards (Merck) were used. Before the analysis, the fabric was mineralised in closed Teflon vials with 5 cm³ of spectrally pure concentrated nitric acid (Baker) and placed in a microwave oven system, Milistone MLS-1200 MEGA. Optimisation of the mass spectrometer was performed using the multi-elemental ICP-MS class standard (Merck) of 10 ng·cm⁻³ concentration, containing elements in the range of light, medium and heavy mass. The analytical quality of the results obtained were checked by determination of elements in the Certificate Reference Material (IAEA-V-10) Trace Elements in Hay.

To compare the results of heavy metal content in bleach fabric, the semi-quantitative LA-ICP-ToF-MS (Laser Ablation Inductively Coupled Plasma Time of Flight Mass Spectrometry) method was used on Optimass 8000, GBC Scien-

tific Equipment. This is a non-destructive method, where the action of a high-energy laser beam results in the evaporation and removal of material in the form of neutral atoms and molecules as well as positive and negative ions from the surface of the measured object exposed to radiation. Optimisation of the mass spectrometer with a laser ablation beam was performed using a Certificate Reference Materials NIST 610 glass.

Analysis of the heavy metal content in artificial acid sweat extracts was performed using Inductively Coupled Plasma-Mass Spectrometry ICP-MS, X-Series; Thermo Electron Corporation. Before the analysis, the fabric was shaken for 2 hours in artificial acid sweat (according to PN-EN-ISO 105-E04:1999) at a temperature of 40 °C. Before analysis, the extracts were diluted with distilled water in a 1:1 ratio. The standards also contained artificial acid sweat in the same ratio as in the analytical sample. The results obtained were checked using Atomic Absorption Spectroscopy AAS SOLAAR M6, Unicam Atomic Absorption.

Results and discussion

In order to evaluate the changes in the heavy metal content of flax fabric after the bleaching stage and dyeing processes, ICP analysis of solutions prepared by microwave decomposition or acid sweat extraction was performed. Also the relative heavy metal isotope intensity on the surface of flax fabric was measured using the semi-quantitative (LA-ICP-ToF-MS) method. The results of the heavy metal content in the mass of flax fibres after the bleaching stages and dyeing processes (described in *Table 1*) are shown in *Tables 2* and *4*. The results of the relative heavy metal isotope intensity on the surface of bleached flax fibres are shown in *Table 3*.

Raw flax fabric is characterised by a high concentration of manganese, barium and strontium (*Table 2*). The results are comparable with those reported in our previous work [10]. Moreover a high concentration of chromium was noticed. Angelova et al. found that flax crops can accumulate a high level of heavy metals (lead, copper, zinc and cadmium) and can be used as culture for the removal of heavy metals from soil [12]. For cadmium, manganese, barium and strontium, the decreasing tendency in their content with the progress of the bleaching stage

Table 2. Residual pectin content and the changes in the content of heavy metals in the mass of flax fibres after bleaching stages as received from ICP-ToF-MS measurements; n.d. not detected, R% remission from sample at 540 nm, K/S Kubelka-Munk factor (the K/S factor is proportional to the concentration of colour substances in the fibre).

Sample	Residual pectin content (PC)			Heavy metals content (mg·kg ⁻¹)										
	R%	K/S	PC%	As	Pb	Cd	Cr	Co	Cu	Ni	Zn	Mn	Ba	Sr
0	16.51	2.111	100	n.d.	0.28	0.11	5.90	0.04	1.21	0.55	4.98	14.6	10.9	32.1
B-I	16.69	2.079	95		0.28	0.09	8.39	0.05	3.51	0.58	7.40	12.7	10.4	27.2
B-IIs	17.54	1.938	72		0.46	n.d.	9.23	0.03	5.96	0.42	5.46	1.29	2.73	3.51
B-II	18.90	1.740	39		0.15		6.97	0.02	5.68	0.28	4.55	0.32	2.74	3.25
B-IIIs	20.05	1.594	15		0.16		5.67	0.02	2.04	0.53	4.34	0.30	2.53	3.52
B-III	20.46	1.546	7		0.11		4.77	0.02	1.52	0.28	2.93	0.20	3.78	4.66
B-IVs	20.74	1.515	2		0.11		4.85	0.03	1.66	0.28	4.81	0.23	5.65	5.83
B-IV	20.84	1.503	0		0.16		5.36	0.01	1.07	0.23	2.74	0.19	5.49	8.63

Table 3. Intensity and relative intensity of heavy metals isotopes presence on the surface of flax fibres after bleaching stages as received from LA-ICP-ToF-MS measurements; ¹ intensity of heavy metals isotopes, ² relative intensity of heavy metals isotopes in %.

Sample	Intensity and relative intensity of heavy metals isotopes										
	As ⁷⁵	Pb ²⁰⁶⁺²⁰⁷⁺²⁰⁸	Cd ¹¹⁴	Cr ¹¹⁴	Co ⁵⁹	Cu ⁶⁵	Ni ⁶⁰	Zn ⁶⁶	Mn ⁵⁵	Ba ¹³⁵	Sr ⁸⁸
0 ¹	311.5	15192	295.7	103806	820	5909	2671	11294	40366	5487	192631
B-I ²	99.5	94.1	38.4	101.3	133.3	62.2	95.7	251.5	124.7	147.1	180.6
B-IIs ²	81.2	43.4	56.1	98.7	73.6	54.0	101.3	47.5	15.8	32.2	12.9
B-II ²	94.8	51.7	44.3	106.8	92.9	58.9	101.4	39.6	12.6	31.7	13.6
B-IIIs ²	86.0	62.4	49.0	105.8	150.8	45.0	111.2	206.8	10.1	29.2	11.4
B-III ²	83.4	31.7	34.4	98.0	93.2	40.8	88.0	33.4	6.7	25.5	10.2
B-IVs ²	86.3	31.1	35.8	97.6	74.6	57.6	84.8	89.5	7.5	88.1	49.6
B-IV ²	86.7	31.1	33.0	105.0	115.6	44.8	89.3	40.1	7.7	49.2	35.1

Table 4. Content of heavy metals in the mass of dyed flax fibres as received from ICP-MS measurements; n.d. not detected.

Sample	Heavy metals content, mg·kg ⁻¹							
	Sb	As	Pb	Cd	Cr	Co	Cu	Ni
D-1	-	n.d.	n.d.	n.d.	0.20	0.005	22.46	0.29
D-1f			0.26		1.91	0.025	24.69	1.15
D-2			n.d.		0.21	0.003	38.62	0.25
D-2f			0.15		1.81	0.009	42.24	0.36
D-3			n.d.		0.93	0.013	114.31	0.81
D-3f			0.48		0.008	122.06	0.83	

was noticed. It is hard to find a tendency in the change in cobalt content after the bleaching stages. In the case of nickel and zinc, there is observed an increase in their content after the first bleaching stage, and a rise in that of chromium, lead and copper after the second bleaching stage. This may be possibly connected to the huge amount of non-cellulosic polysaccharides present in the fibres (*Table 2*) and to the sorption of heavy metals from the bleaching baths [17 - 19]. It is known that metal ions can be absorbed by carboxylic, hydroxyl and carbonyl groups (present in hemicelluloses, pectin and lignin products) [18]. Retted flax fibres consist of 64 - 74% cellulose, 16 - 19% hemicellulose, 2 - 3% lignins, 1.8 - 3% pectins and 1.5 - 1.7% fat and waxes [19]. Williams et al. mentioned that the absorption capacity of linseed straw fibres for copper, nickel and cadmium ions may be connected with the

presence and orientation of pectic materials [18]. Also a number of researches have noted the sorption capacity of pectic substances to divalent heavy metals, but it is hard to compare these results with those due to the different treatment condition, source and structure of pectic substances [20, 21]. Lee et al. [22] found that heavy metal sorption by lignocellulosic fibres (kenaf, coconut, spruce, sugarcane) does not correlate with the lignin content in fibres, but all raw fibres with a lignin content greater than 10% readily absorb heavy metals. Hence lignin may play some role in their sorption. On the other hand, Nawirska found that the lignin fraction extracted from some fruit pomace has a poor capacity to bind heavy metals [11]. Pejic et al. did not find a simple correlation between the lignin and hemicellulose content in short hemp fibres and their uptake capacities for cadmium, lead and zinc ions, but the total up-

Table 5. Content of heavy metals extracted to the artificial acid sweat from dyed flax fibres as received from ICP-MS measurements; n.d. not detected.

Sample	Heavy metals content, mg·kg ⁻¹							
	Sb	As	Pb	Cd	Cr	Co	Cu	Ni
acid sweat	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.005	n.d.
B-IV	0.007	n.d.	0.010	0.002	0.071	0.011	0.861	0.21
D-1	0.034	0.034	0.020	0.003	0.130	0.030	4.910	0.29
D-1f	0.010	0.010	0.050	0.005	0.030	0.011	1.554	0.17
D-2	0.030	0.030	0.030	0.005	0.300	0.030	8.220	0.56
D-2f	0.010	0.010	0.120	0.020	0.120	0.020	1.142	0.27
D-3	0.040	0.040	0.008	0.005	0.243	0.025	13.13	0.49
D-3f	0.030	0.026	0.050	0.012	0.097	0.024	2.290	0.39

take capacity for cadmium and zinc ions increased with the lignin and hemicelluloses content reduction [13]. Kongdee et al. observed that copper and zinc ions showed an increased binding capacity for cellulose substrates (bleached cotton, viscose, lyocell) in an alkaline bath [23].

The content of nickel, zinc, chromium, lead and copper in bleached flax fibres decreased with the progress of non-cellulosic substance removal (Figures 2 & 3). Arsenic was not detected in the mass of all the bleached flax fabric. The content of a selected heavy metal in the mass of flax fibres after the fourth bleaching

stage (except chromium) did not exceed the allowable level for group I (goods for babies) according to Oeko-Tex Standard 100 requirements, referring to the content of heavy metals to artificial acid sweat, which may be lower than in the fibre mass.

The data obtained from the semi-quantitative (LA-ICP-ToF-MS) analysis revealed (Table 3) that the mass spectrum consists of the same elements as was found by the quantitative analysis (ICP-ToF-MS) – data not shown. The changes in cadmium, manganese, barium and strontium participation on the surface of

flax fibres estimated by the semi-quantitative method coincide well with those estimated by quantitative analysis. There is no tendency of a decrease in chromium, arsenic and nickel content after consecutive proceeding of the bleaching stage. It is hard to find any tendency in lead and cobalt participation in conjunction with the process of non-cellulosic substance removal.

The results of heavy metal content in the mass of fabric and extracted to artificial acid sweat from dyed fabric are shown in Tables 5. As was expected, a relatively huge amount of copper is present in the mass of all the dyed fabric – unfixed and fixed (Table 5). The direct dye used belongs to the group of copper metal-complex dyes (Figure 1). The amount of copper extracted to an artificial acid sweat solution increased with an increase in the dyeing strength. However, the quantity of copper extracted to artificial acid sweat amounted to from ca. 12% for sample D-3 to ca. 22% for sample D-1 of the total amount of copper in the mass of flax fabric. An important influence of the dye fixation process on the decrease in

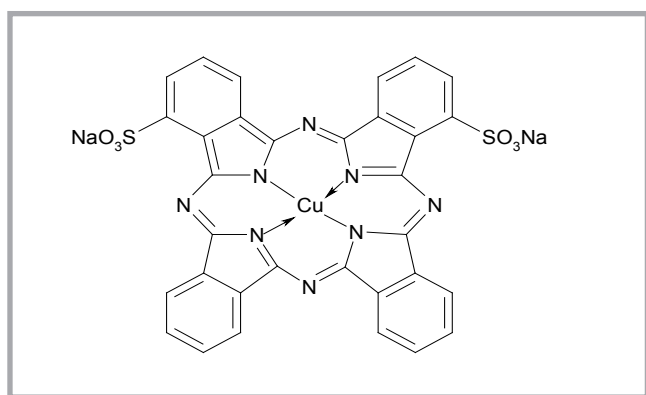


Figure 1. Molecular structure of C.I. Direct Blue 86 [24].

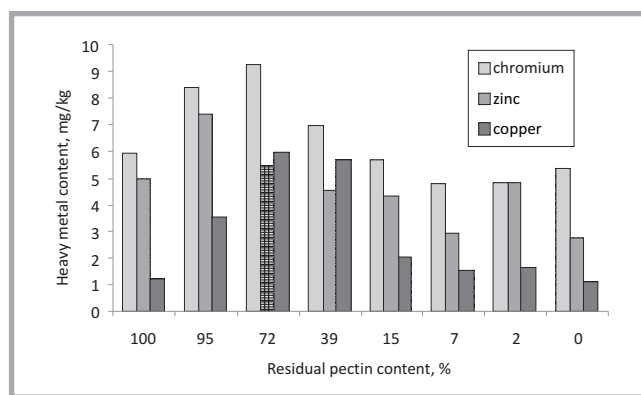


Figure 2. Changes in chromium, zinc and copper content in the mass of bleached flax fibres vs. residual pectin content.

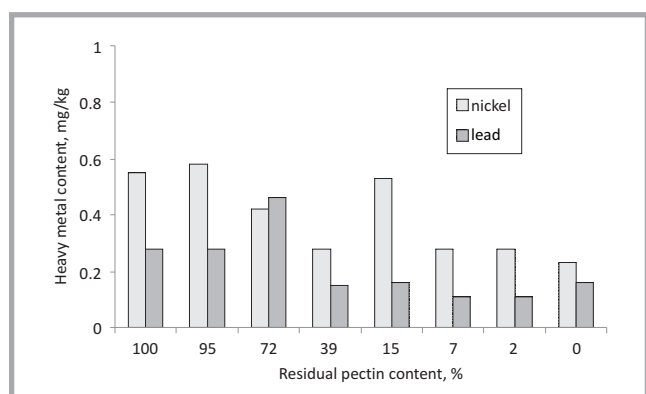


Figure 3. Changes in nickel and lead content in the mass of bleached flax fibres vs. residual pectin content.

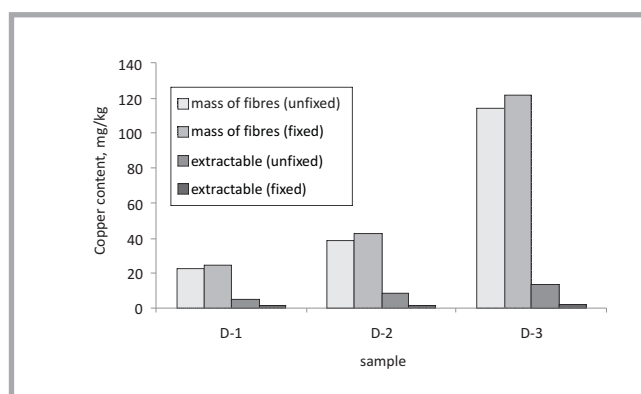


Figure 4. Copper content in the mass of dyed flax fibres and extractable copper content in the mass of dyed flax fibres.

copper content in the artificial acid sweat extracts was observed (**Figure 4**), which is connected with an increase in colour fastness to washing after the fixation of dyes. The quantity of extractable copper from the fixed samples did not exceed 7% of the total copper in the mass of flax fabric. All the dyed flax fabric (unfixed and fixed) meet the requirements for group I (goods for babies) of Oeko-Tex Standard 100.

Conclusion

It is very important that daily wear textiles (especially textiles for babies and those in direct contact with human skin) do not contain compounds (including heavy metals) having possibly harmful or toxic effects. Also the heavy metals present in natural fibres may contribute to some difficulties, especially in bleaching and dyeing processes.

Our results revealed that flax fabric, probably due to the presence of a high amount of non-cellulosic polysaccharides, may accumulate nickel, zinc, chromium, lead and copper from scouring and bleaching baths. Their content in the mass of fibres decreases with the process of removal of non-cellulosic substances from fibres within the bleaching stages. Flax fabric can be bleached from 1/4 (first bleaching stage only) to 4/4 whiteness (full whiteness - all bleaching stages). Thus an assessment of the influence of the bleaching process on the heavy metal content change in flax fabrics may depend on the non-cellulosic substance content.

Manganese, barium, chromium and strontium were also detected in the raw fabric. However, their content in flax fabric are significantly reduced after all bleaching stages. The content of heavy metal in the mass of flax fibres (except chromium) does not exceed the permissible level for Group I of Oeko-Tex Standard 100.

Semi-quantitative, non-destructive LA-ICP-ToF-MS analysis can be successfully applied as a fast and simple method for assessment of relative changes in the heavy metal content of flax fibres after manufacturing processes as compared to the quantitative (destructive) ICP-ToF-MS method.

The use of copper-complex direct dyes causes an increased copper content in the mass of fibres. Nevertheless, a cop-

per amount below 22% in fibres for unfixed dyeing and below 7% for fixed dyeing were extractable by an artificial acid sweat solution, proving the significance of the fixing process in fabric dyeing. It can be noted that all unfixed and fixed dyed flax fabrics meet the requirements of Oeko-Tex Standard 100 for Group I and can be used for manufacturing safe textile goods for babies.



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