Impact of metal ions concentration on effects of fluorescent whitening agents for cellulose substrates

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Received December 12, 2020

UDC 677.017.855
Original scientific paper

The influence of metal ions, iron and copper, in the concentration range of 1, 5, 10 and 30 ppm added to the solution of fluorescent whitening agent (FWA) in concentrations of 0.08, 0.12 and 0.25% for processing cellulose substrates at room temperature was investigated. The properties of cellulose substrates were monitored through optical and protective effects, where the fluorescence spectra, degree of whiteness and UPF (Ultraviolet Protection Factor) values were analysed. The analysed optical and protective phenomena differ for treated cellulosic substrates, fabric and filter paper. FWAs increase the whiteness and UV protection of the material. It was found that the metal ion added in different concentrations affects the reduction and quenching of fluorescence and the reduction of the whiteness of cellulose substrates. The influence of metal ions on UPF depends on the substrate, the type and concentration of the metal ion, and the concentration of the FWA to which they were added.
Ključne riječi: *metal ions, fluorescent whitening agent, UPF, fluorescence quenching, whiteness of cellulose substrates*

1. Introduction

The whiteness is often associated with the concept of purity and freshness, so since ancient times, efforts have been made to achieve as much whiteness as possible, especially on textile materials. The degree of whiteness, W, for an ideally white surface is 100, while higher values than 100 are obtained on samples treated with fluorescent compounds. FWA are a special type of fluorescent compounds that are used simultaneously or in separate processes in combination with chemical whiteners to achieve high whiteness. Fluorescence belongs to the photoluminescence group; this phenomenon of cold light is caused by electromagnetic radiation [1, 2]. A luminescent substance absorbs electromagnetic radiation, is excited by photons that hit electrons, and they move to a higher energy level. Electrons, returning from the higher state to the ground state, emit visible light in the blue region, with a bathochromic shift, which is observed as luminescent radiation [3, 4].

FWAs are colourless or slightly coloured organic compounds that have at least seven conjugated double bonds [5]. They are actually a special type of dye that contains a fluorescent system instead of the chromophore, which is characteristic of dyes. Like dyes, they have a certain affinity for the individual substrates for which they are intended [6]. Classic FWAs also have a certain UV protective effect on fabrics made of cotton and its blends [7]. Ultraviolet (UV) radiation, which is harmful to health, partly reaches the Earth, and long-term and unprotected exposure to solar radiation can be harmful to health, it can cause a decrease in the immune system, allergies, herpes, as well as potential possibilities of malignant skin diseases, which are increasingly common [8]. One of the possible measures to prevent skin cancer is the use of protective clothing [9]. UV protection factor, UPF (Ultraviolet Protection Factor) stands for protective action, is a quantity that describes how much UV radiation (UV-A and UV-B) is blocked by the textile material. It is based on the instrumental definition of the protective properties of the fabric and the determination of transient UV radiation (transmission) through the examined sample. Criteria and classification of the protective effect of textiles according to AS/NZS 4399:1996 UPF can be in the range from 0 to 1000, and is marked with grades 0 to 50 (50+). Already from a UPF of 15 the textile is considered to have a protective effect. Clothing that provides excellent UV protection has a rating of 40, 45, 50 or 50+, (for clothing with the highest protection ability) [10].

It has been proven that metals in textile processing baths affect the stability of FWAs, especially the stilbene type used in this research [2]. Textiles washed in the presence of higher concentrations of metal ions have significant differences in tint change compared to normally washed textiles [11]. According to research, with the addition of iron ions of the minimum conc. $c=1\cdot10^{-6}$ M, the fluorescence intensity of the solution decreases. By increasing the concentration of metal ions, the fluorescence further decreases, and at the highest concentration of metal ions, $c=5\cdot10^{-4}$ M, the fluorescence intensity of the solution is significantly lower, while only the highest concentration of copper ions leads to a decrease in the fluorescence intensity of the solution [12]. A study of the influence of iron and copper ions on the effect of optical whitening s was carried out by monitoring the whiteness of cotton fabric processed in a laboratory apparatus [13].

In this research, two cellulose substrates, a cotton fabric and a cellulose filter, were investigated by monitoring the influence of metal ions, iron and copper, in conc. of 1, 5, 10 and 30 ppm on the optical and protective phenomena obtained by the effect of the stilbene derivative applied in conc. 0.08, 0.12 and 0.25%.

2. Experimental part

2.1. Materials

Two cellulose substrates are standard pre-bleached cotton fabric (T) from the supplier wfk - Cleaning Technology Institute, Germany and filter paper (F) label 3w, manufactured by Filtrak, Germany, tab.1.

Tab.1 Properties of cellulose substrates

Cotton fabric (T)
- 100 % cotton - mass per unit area: 175.6 g/m2 - embroidery: canvas - thread density: warp: 25 cm-1 weft: 25 cm-1 - yarn fineness: warp: 29.5 tex weft: 29.5 tex - W_{CIE} = 64.6
Filter paper (F)
- 100 % cellulose - mass per unit area: 65 g/m2 - diameter: 7.5 cm - W_{CIE} = 39.9

The selected FWA is the commercial product Tinopal DMS-X, Ciba, stilbene derivative, 4,4'-bis-(triazinylamino)stilbene-2,2'-disulfonate, molecular weight 924.93 g/mol [14], whose structure is shown in Fig.1.

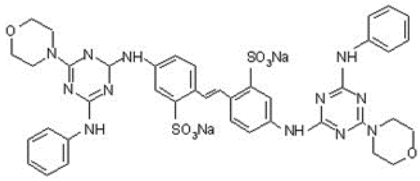


Fig.1 Stilbene derivative, 4,4'-bis-(triazinylamino)stilbene-2,2'-disulfonate [14]

FWA was prepared in different concentrations, 0.08, 0.12 and 0.25% with distilled water.

Solutions of metal ions were prepared in concentrations of 1.0, 5.0, 10.0 and 30.0 ppm, where standard solutions of iron (Fe) and copper (Cu) with a concentration of 100 mg/dm³ (100 ppm) were used.

2.2. Procedure

Selected cellulose substrates, cotton fabric (T) weighing 0.8 g and filter paper (F) weighing 0.3 g were treated in solutions of different concentrations of FWA without (0) and with the addition of Fe and Cu metal ions of the specified concentrations (1, 5, 10 and 30 ppm) by the exhaustion procedure. This procedure was carried out by placing the substrate in previously prepared solutions, volume 20 mL in Petri dishes. During a total time of 30 minutes, the substrates were gently moved, and after 15 minutes they were also turned to the other side. After the procedure, the cellulose substrates were hanged and air-dried in a closed space.

2.3. Methods

The characterization of the cellulose substrates before and after the exhaustion procedure was carried out using the methods of fluorimetry, remission spectrophotometry and UV-Vis spectrophotometry.

2.3.1. Fluorimetry

The measurement of the fluorescence intensity of the material was carried out on a fluorimeter F-7000, Hitachi, with a scanning speed of 240 nm/min, a measuring range of 400-600 nm and a power supply of 250 V. During the measurement, the samples were placed in a chamber where the secondary fluorescent light falls on the photocell in front of which it is placed filter for absorption of primary UV radiation. The results are expressed through relative fluorescence intensity (Φrel).

2.3.2. Remission spectrophotometry

The materials were measured on a Spectraflash SF 600+ CT emission spectrophotometer, tt. Datacolor, with aperture size 20 mm, standard illumination D65, using 8° geometry, measurement range: 360-700 nm. Based on the measured spectral characteristics, the degree of whiteness according to CIE (WCIE), tint value (TV) and tint deviation (TD) of the cellulose substrates before and after the exhaustion procedure were calculated using the software package.

2.3.3. UV/Vis spectrophotometry

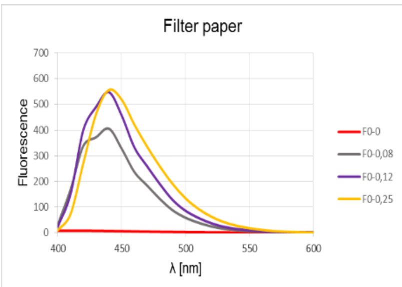
The UPF value was measured on a UV-Vis spectrophotometer, Cary 50 Solascreen from Varian, with an integrated sphere. These values were measured using in vitro method in accordance with AS/NZS 4399 [15]. The obtained results indicate the degree of protection provided by the material when worn in close proximity to the skin, which in this case is adapted for filter paper as well.

3. Results and discussion

The evaluation of the influence of metal ions, Fe and Cu, on stilbene FWA solutions was performed indirectly through the values of the optical and protective properties of cellulose substrates by monitoring the relative fluorescence intensity, whiteness degree, tint value, tint deviation and UPF value.

3.1. Relative fluorescence intensity

Figs.2-8 show the curves of relative fluorescence intensity of filter paper and cotton fabric treated with different concentrations of FWA (0, 0.08, 0.12 and 0.25%) with the addition of the previously mentioned concentrations of metal ions, iron and copper (0, 1, 5, 10 and 30 ppm). The selected conc. are numerically linked to each individual substrate in the results display.
As the concentration of FWA increases, the relative fluorescence intensity of the filter paper also increases, whereby the characteristic peaks of the curves (0.12 and 0.25%) almost overlap, Fig.2a. In the case of cotton fabric, smaller differences in the fluorescence intensity of the applied concentrations of FWA are observed, although there was a slight decrease in fluorescence at the highest concentration of FWA (0.25%), Fig.2b. The characteristic peaks of the fluorescence intensity curves of both substrates treated with 0.25% have the same value ((Φrel=550), while the remaining concentrations do not follow this ratio. A higher relative fluorescence intensity of cotton fabric treated with 0.08 and 0.12% is observed compared to filter paper treated with the same conc. of FWA. The differences found can be attributed to differences in the initial levels of whiteness of the substrate (fabric: W_{CIE}= 64.6; paper: W_{CIE}= 39.9).
In the following, the influence of metal ions added to FWA solutions on the fluorescence intensity of filter paper, Figs.3-5 and cotton fabric, Figs.6-8 is analysed.



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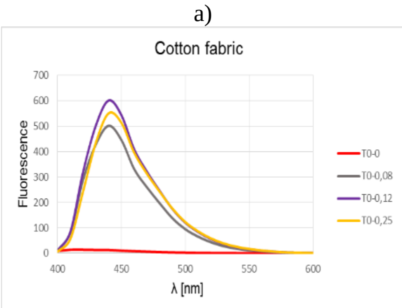
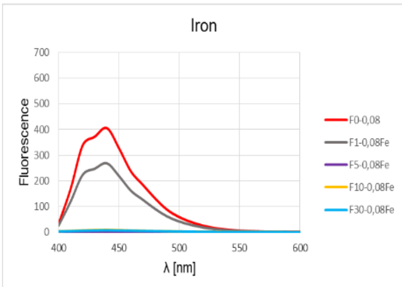


b)

Fig.2 Relative fluorescence intensity for a) filter paper (F) and b) cotton fabric (T) treated with different concentrations of FWA



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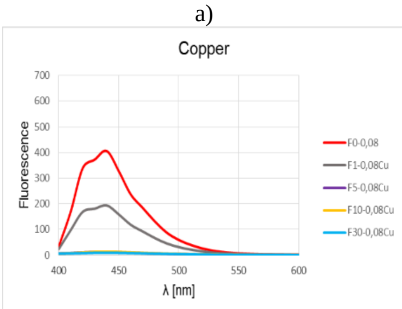
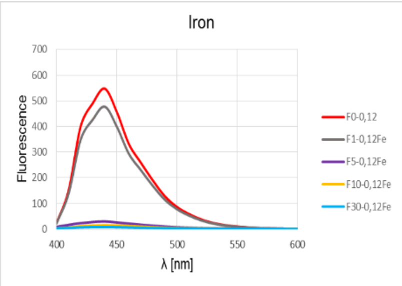


b)

Fig.3 Relative fluorescence intensity of filter paper treated with 0.08% FWA without and with the addition of a) iron (Fe) and b) copper (Cu) ions

Fig.3 shows the change in fluorescence intensity of filter paper treated with FWA (0.08%) with the addition of iron and copper ions to the treatment bath. The concentration of iron and copper ions (1 ppm) decreases the fluorescence intensity, and the observed decrease depends on the type of metal ion. From the results shown in Fig.3, it is evident that copper ions (1 ppm) reduce fluore-scence more strongly (Fig.3b) than iron ions (Fig.3a) at the same concentration. By further increasing the concentration of iron and copper ions, the fluorescence was completely quenching.



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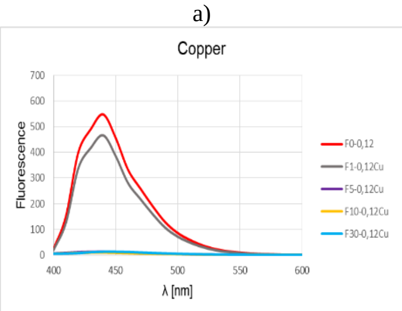
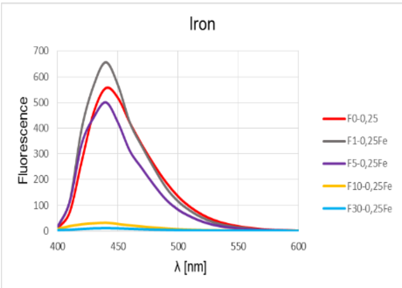


b)

Fig.4 Relative fluorescence intensity of filter paper treated with 0.12% FWA without and with the addition of a) iron (Fe) and b) copper (Cu) ions

Fig.4 shows that the fluorescence curves of the filter treated with 0.12% FWA with the addition of iron or copper ions are almost identical (Figs.4a and b). Copper and iron ions in a concentration of 1 ppm slightly reduce fluorescence, while other concentrations added to a 0.12% solution of FWA completely quenching fluorescence. A small difference is observed at a conc. of 5 ppm, where the quenching of fluorescence under the influence of iron ions (Fig.4a) is less than that of copper ions (Fig.4b).

The addition of both ions at a concentration of 1 ppm in a 0.25% solution of FWA increases the fluorescence intensity of the filter by almost 100 units compared to a solution of FWA (0.25%) without metal ions, Fig.5. The addition of iron ions at a concentration of 5 ppm reduces the fluorescence intensity by 56 units, Fig.5a, while the same concentration of copper quenching the fluorescence (32.4), Fig.5b. The fluorescence curves of the filter treated with 0.25% FWA with the addition of both metal ions at a concentration of 10 and 30 ppm are almost identical, fluorescence quenching occurred.



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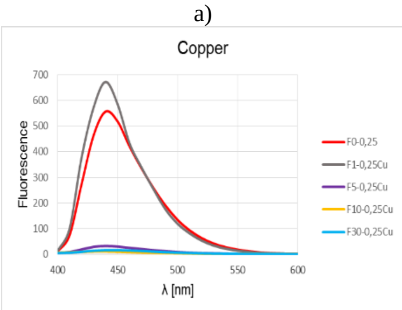
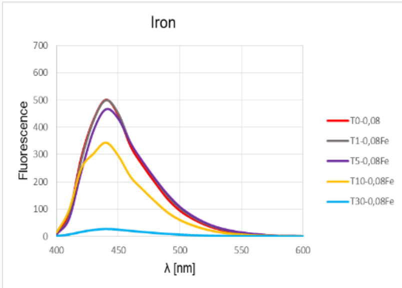


b)

Fig.5 Relative fluorescence intensity of filter paper treated with 0.25% FWA without and with the addition of a) iron (Fe) and b) copper (Cu) ions

Fig.6 shows the fluorescence intensity curves of cotton fabrics treated in solutions of 0.08% FWA without and with the addition of a concentration range of iron and copper ions depending on the wavelength. The influence of metal ions on the fluorescence intensity of cotton fabric is different compared to filter paper, and they also differ depending on the type of metal and the conc. (Figs.6a and b). Only the iron concentration (30 ppm) added to a 0.08% FWA solution drastically reduces the fluorescence of the cotton fabric, while the other concentrations cause no change (1 ppm) or gradually decrease (5 and 10 ppm). The influence of copper ions (Fig.6b) in a concentration of 1 ppm slightly reduces the intensity of fluorescence, while other concentrations of copper ions (5, 10 and 30 ppm) quenching the fluorescence.



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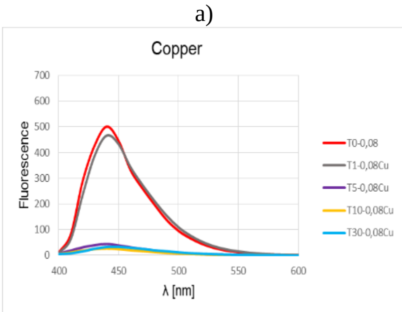


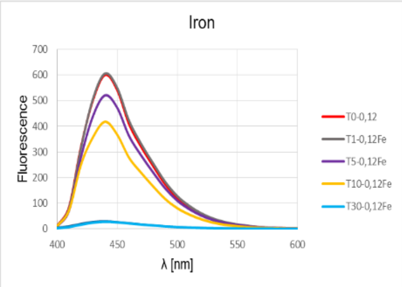
b)

Fig.6 Relative fluorescence intensity of cotton fabrics treated with 0.08% FWA without and with the addition of a) iron (Fe) and b) copper (Cu) ions

The fluorescence curve of filter paper treated with 0.08% FWA with the addition of 30 ppm of copper ions indicates that there is fluorescence quenching and a slight bathochromic shift, which is in accordance with previously conducted research [16].

Iron in a concentration of 30 ppm greatly reduces the intensity of fluorescence, i.e. it quenches the fluorescence of cotton fabric treated in a solution of 0.12% FWA. The remaining concentrations of iron ions (1, 5 and 10 ppm) have a similar effect on the fluorescence intensity of the fabric, Fig.7a, as the 0.08% solution,

Fig.6a. However, the influence of copper ions added to the 0.12% FWA solution is different compared to 0.08%.



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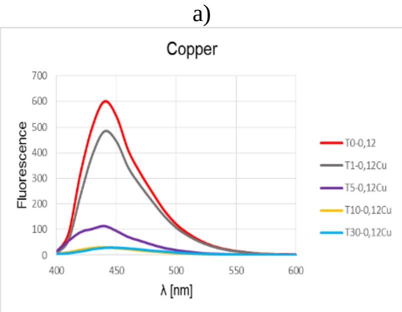

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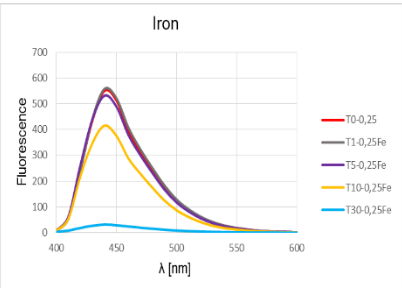
Fig.7 Relative fluorescence intensity of cotton fabrics treated with 0.12% FWA without and with the addition of a) iron (Fe) and b) copper (Cu) ions



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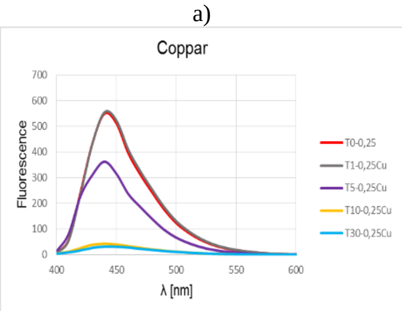


b)

Fig.8 Relative fluorescence intensity of cotton fabrics treated with 0.25% FWA without and with the addition of a) iron (Fe) and b) copper (Cu) ions

This influence is manifested through a gradual decrease in fluorescence intensity caused by copper ions (1 ppm), while these ions in concentrations (5, 10 and 30 ppm) quenches fluorescence, Fig.7b. Also in this case, 30 ppm of copper causes a slight bathochromic shift, as was also observed at 0.08%.The fluorescence intensity of the cotton fabric treated with 0.25% FWA is lower than the intensity obtained with 0.12% FWA (Fig.7), which means that the fluorescence intensity decreases with the increase of the concentration of FWA, (Fig.8).

The influence of the addition of iron ions to a solution of 0.25% FWA on the fluorescence intensity of the fabric, Fig.8a is almost equal to the concentration of 0.12%, Fig.7a, while the influence of copper ions is different, Fig.8b. A concentration of 1 ppm does not change the fluorescence intensity of the cotton fabric, a concentration of 5 ppm decreases it, and the remaining concentrations (10 and 30 ppm) quenches the fluorescence of the cotton fabric.

Similar effects were proven by the well-known scientist K. Weber in 1948, who graphically represented the decrease, that is, the quenches of fluorescence by increasing the concentration of the FWAs [17].

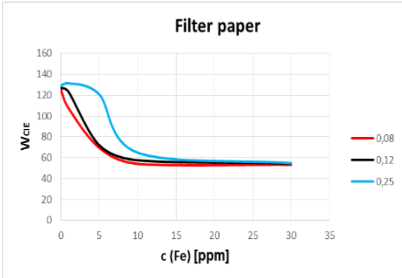
Tab.2 Bathochromic shift of fluorescence curves for filter paper and cotton fabric

Cu (30 ppm)		
Filter paper		
c [%]	**λ_{max} [nm]**	**Φ_{rel}**
0.12	450	13.17
Fabric		
c [%]	**λ_{max} [nm]**	**Φ_{rel}**
0.08	450	32.64
0.12	450	29.09

Table 2 shows selected samples where there was a bathochromic shift of the fluorescence curve, i.e. filter paper samples treated with 0.12% and fabric with 0.08% and 0.12% FWA and the addition of 30 ppm Cu show a shift of the characteristic peak from 440 nm to 450 nm.

3.2. Whiteness degree - W_{CIE}

The influence of the FWA concentration (0.08, 0.12 and 0.25%) as well as this concentration with the addition of iron and copper ions was monitored through the degree of whiteness of cotton fabric and filter paper, Figs. 9 and 10, and tint deviation, Tabs.3-5.



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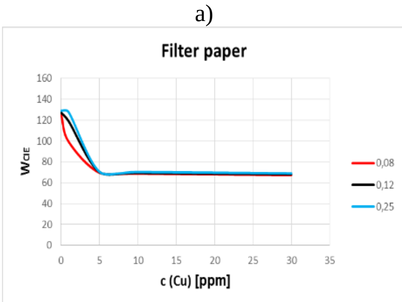
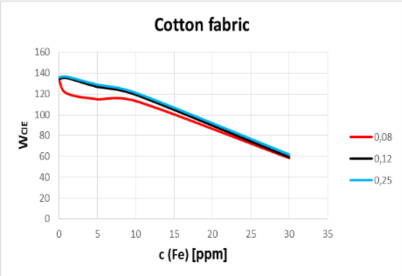


b)

Fig. 9 The whiteness degree of filter paper after treatment with different concentrations of FWA with the addition of different concentrations of a) iron and b) copper ions

The obtained results shown in Fig.9 show that an increase in the metal ion concentration affects the reduction in whiteness degree of the filter paper treated with all concentrations of the FWAs. However, the reduction index is different and depends on the concentration of the FWAs and the concentration of metal ions. The whiteness degree of the filter treated with 0.08 and 0.12% FWA gradually decreases with the addition of iron ions up to 10 ppm. In relation to the highlighted concentrations of 0.08 and 0.12%, the curve describing the decrease in whiteness degree of the filter treated with 0.25% FWA with the addition of iron ions is milder (less steep), while at concentrations above 15 ppm completely equalized, Fig.9a. From the results shown in Fig.9b, a uniform and almost equal slope of the curves can be observed, whereby it can be seen that the influence of copper ions after 5 ppm is unchanged.

It is important to emphasize that the whiteness degrees of filter paper treated with FWA with the addition of iron ions are lower than those of copper ions, W_{CIE} balance for iron is below 60 and approx. 70 for copper.



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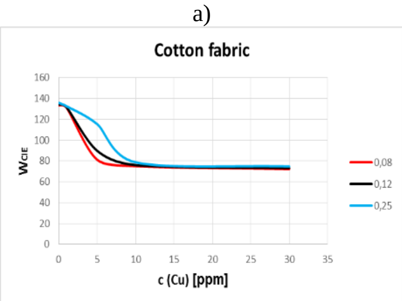

b)

Fig.10 The whiteness degree of cotton fabric after treatment with different concentrations of FWA and the addition of different concentrations of a) iron and b) copper ions

Fig.10 shows differences in the influence of iron ions added to the FWA solution on the decrease in fabrics whiteness degree, Fig.10a compared to the influence of copper ions under the same conditions, Fig.10b. By increasing the concentration of iron ions, the whiteness degree of fabric decreases linearly, while copper ions in concentrations up to 10 ppm gradually decrease the whiteness of the fabric, after which the equilibrium of the fabric whiteness is achieved. The curve that describes the decrease in the whiteness degree of the fabric treated with 0.25% FWA with the addition of copper ions is highlighted because it is milder than the curves of the decrease in the fabrics whiteness treated with 0.08% and 0.12% FWA.

Table 3 shows the changes in tint of filter paper and fabrics after treatment with different concentrations of FWA. Filter paper without FWA has an initial reddish tint (R1), which is intensified to (R2) by the addition of FWA in concentration of 0.08 and 0.12%, while a conc. of 0.25% changes the tint to green (G3).The fabric after treatment with 0.08 and 0.12% FWA has a green tint (G1), while after treatment with 0.25% FWA, the fabric has an even greener tint (G3). The concentration of 0.25% FWA had an almost equal effect on the change in the whiteness degree and equally on the tint of both substrates (G3). This can be attributed to the greenish tint of the selected FWA.

Tab.3 Promjena tona (TV, TD) filtar papira (F) i pamučnih tkanina (T) prije i nakon obrade otopinama optičkog bjelila

Filter	**TV**	**TD**
F0-0	-0.5	R1
F0-0.08	-1.7	R2
F0-0.12	-1.5	R2
F0-0.25	2.6	G3
Fabric	**TV**	**TD**
T0-0	-0.1	
T0-0.08	0.6	G1
T0-0.12	1.4	G1
T0-0.25	2.9	G3

Tab.4 Tint change (TV, TD) of filter paper (F) treated with FWA solutions and the addition of iron and copper ions

Filter - Fe	**TV**	**TD**
F1-0.08Fe	-1.3	R1
F1-0.12Fe	-1.2	R1
F1-0.25Fe	-0.1	
F5-0.08Fe	-0.2	
F5-0.12Fe	-0.2	
F5-0.25Fe	-0.7	R1
F10-0.08Fe	-0.6	R1
F10-0.12Fe	-0.5	R1
F10-0.25Fe	0.3	
F30-0.08Fe	-0.9	R1
F30-0.12Fe	-0.7	R1
F30-0.25Fe	-0.8	R1
Filter - Cu	**TV**	**TD**
F1-0.08Cu	-1.1	
F1-0.12Cu	-0.8	
F1-0.25Cu	0.4	G1
F5-0.08Cu	0.1	
F5-0.12Cu	0.1	
F5-0.25Cu	0.5	G1
F10-0.08Cu	0.2	
F10-0.12Cu	0.4	
F10-0.25Cu	0.8	G1
F30-0.08Cu	0.3	
F30-0.12Cu	0.8	G1
F30-0.25Cu	1.1	G1

The filter paper with the addition of iron ions to FWA solutions of all mentioned conc. (Tab.4) has a reddish tint, while the addition of copper ions to the same FWA solutions has a greenish tint. Both tints are of low intensity (label 1), indicating a slight deviation in green (G1) and red (R1) from the white standard. Fabric treated with copper ions added to FWA solutions also has a green tint, with its value varying from G1 to G4.

Tab.5 Tint change (TV, TD) of cotton fabrics (T) treated with FWA solutions and the addition of iron and copper ions

Fabric - Fe	**TV**	**TD**
T1-0.08Fe	2.9	G3
T1-0.12Fe	1.4	G1
T1-0.25Fe	3.2	G3
T5-0.08Fe	0.8	G1
T5-0.12Fe	1.2	G1
T5-0.25Fe	2.0	G2
T10-0.08Fe	-0.8	R1
T10-0.12Fe	0.2	
T10-0.25Fe	1.6	R1
T30-0.08Fe	-0.9	R1
T30-0.12Fe	-0.7	R1
T30-0.25Fe	-0.8	R1
Fabric - Cu	**TV**	**TD**
T1-0.08Cu	1.9	G2
T1-0.12Cu	2.1	G2
T1-0.25Cu	3.6	G4
T5-0.08Cu	1.0	G1
T5-0.12Cu	1.0	G1
T5-0.25Cu	1.6	G2
T10-0.08Cu	1.0	G1
T10-0.12Cu	1.1	G1
T10-0.25Cu	1.7	G2
T30-0.08Cu	1.7	G2
T30-0.12Cu	1.8	G2
T30-0.25Cu	2.9	G3

Based on these changes, it can be said that in fabric treated with FWA and the addition of copper ions, a high concentration of FWA (0.25%) is key to the enhancement of the green tint. The influence of the FWA concentration prevails over the influence of lower concentrations of iron ions (1 ppm and 5 ppm), so the tint is green (G).
However, the addition of iron ions at higher concentrations (10 and 30 ppm) has a dominant effect on the tint change, which changes to red (R).

3.3. UV Protection

Tabs.6-8 show the influence of different concentrations of FWA without and in combination with different concentrations of iron and copper ions on the UV protective properties of filter paper and cotton fabrics, which is monitored through the average UPF value and ratings. From the results of UV protection of the filter and fabric treated with different concentrations of FWA, excellent protection of both substrates can be seen.

Tab.6 Mean UPF values and UV protection rating for filter paper and cotton fabric treated or not with FWA solutions without the addition of metal ions

	Mean UPF	Rating
Filter		
F0-0	21.394	15
F0-0.08	1000.000	50+
F0/0.12	1000.000	50+
F0-0.25	1000.000	50+
Fabric		
T0-0	11.124	10
T0-0.08	891.712	50+
T0-0.12	1000.000	50+
T0-0.25	1000.000	50+

The influence of metal ions on the UV protection of filter paper can be seen from the results in Tab. 7. The high level of protection (rating 50+) is the result of the action of the FWA (high fluorescence intensity). Accordingly, the reduced degree of protection is the result of the basic whiteness, despite the fact that the fluorescence intensity is reduced or quenched.
Concentration of iron or copper ions of 1 ppm does not change the rating of the filter paper, although the mean value drops to 621.720 with the addition of iron and to 366.892 with the addition of copper and that only at the lowest concentration of FWA. The reason for this is the quenching of the fluorescence of the treated filter paper. At higher concentrations of FWA, the fluorescence is quenched, but the UV protection of the substrate is not significantly affected by metal ions. By increasing the concentration of metal ions to 5 ppm, the rating drops to 20 or 25, and continues to decrease with a further increase in the concentration of copper ions, while this phenomenon is not so pronounced with iron ions.
An excellent protection rating of 50+ is achieved not only by the addition of 1 ppm iron ions, but also by the addition of 10 ppm and 30 ppm in a 0.12% FWA solution, as well as with the addition of 5 ppm in a 0.25% FWA solution.

Tab.7 Mean UPF values and UV protection rating for the cellulose filter treated with FWA solutions with the addition of iron and copper ions

	Mean UPF	Rating
Filter - Fe		
F1-0.08Fe	621.720	50+
F5-0.08Fe	27.069	20
F10-0.08Fe	30.929	25
F30-0.08Fe	31.184	25
F1-0.12Fe	1000.000	50+
F5-0.12Fe	21.102	15
F10-0.12Fe	181.057	50+
F30-0.12Fe	65.127	50+
F1-0.25Fe	1000.000	50+
F5-0.25Fe	1000.000	50+
F10-0.25Fe	19.576	15
F30-0.25Fe	15.590	15
Filter - Cu		
F1-0.08Cu	366.892	50+
F5-0.08Cu	28.592	25
F10-0.08Cu	16.994	10
F30-0.08Cu	16.963	15
F1-0.12Cu	1000.000	50+
F5-0.12Cu	19.818	15
F10-0.12Cu	27.180	20
F30-0.12Cu	17.578	15
F1-0.25Cu	1000.000	50+
F5-0.25Cu	24.894	20
F10-0.25Cu	21.611	15
F30-0.25Cu	21.295	15

Tab.8 Mean UPF values and UV protection rating of cotton fabric treated with optical whitening solutions and the addition of iron and copper ions

	Mean UPF	Rating
Fabric - Fe		
T1-0.08Fe	1000.000	50+
T5-0.08Fe	1000.000	50+
T10-0.08Fe	1000.000	50+
T30-0.08Fe	493.338	50+
T1-0.12Fe	1000.000	50+
T5-0.12Fe	1000.000	50+
T10-0.12Fe	1000.000	50+
T30-0.12Fe	449.015	50+
T1-0.25Fe	1000.000	50+
T5-0.25Fe	1000.000	50+
T10-0.25Fe	1000.000	50+
T30-0.25Fe	591.837	50+
Fabric - Cu		
T1-0.08Cu	1000.000	50+
T5-0.08Cu	24.676	20
T10-0.08Cu	15.661	10
T30-0.08Cu	20.662	15
T1-0.12Cu	1000.000	50+
T5-0.12Cu	24.470	20
T10-0.12Cu	21.120	20
T30-0.12Cu	20.103	15
T1-0.25Cu	1000.000	50+
T5-0.25Cu	1000.000	50+
T10-0.25Cu	29.936	25
T30-0.25Cu	30.602	25

From the results presented in Tab.8, it can be seen that iron ions have no effect on reducing the protection level of the fabric (rating is 50+), regardless of the concentration of FWA and the concentration of iron ions. However, a drop in the mean UPF value is observed for the highest iron ion concentration of 30 ppm.
Copper ions affect the reduction of the protection degree for cotton fabric, when their concentration is higher than 1 ppm. The exception is fabric treated with 0.25% FWA

with the addition of 5 ppm copper ions, where the level of protection is still rated 50+. This can be attributed to the high degree of fluorescence of this sample, Fig.8b.

It should be noted that by increasing the concentration of the FWA, the fluorescence intensity, and thus the whiteness, decreases, while the UV protection remains maximal [18, 19]. In contrast to the prominent phenomenon of fluorescence quenching, the influence of metal ions causes fluorescence quenching, but also affects the absorption of UV radiation and reduces UV protection.

4. Conclusions

The influence of the concentration of metal ions on the effect of FWAs for cellulose substrates was investigated by comparing the optical and protective effects of cotton fabric and filter paper, which are chemically related and structurally different. The long chains of cotton cellulose macromolecules are twisted into a yarn of a dense structure, resulting in lower the availability and openness of cotton cellulose less compared to the shorter cellulose chains of filter paper.

The results of the research showed a decrease in the whiteness and fluorescence intensity of cellulose substrates, fabric and filter paper, after treatment with FWA, with an increase in the concentration of iron and copper ions.

The decrease in the whiteness of filter paper and cotton fabric when using lower concentrations of FWA with the addition of quencher is more pronounced. For this reason, at lower concentrations of FWA, the free molecules of FWAs are sooner exhausted than at higher concentrations. This can be interpreted by the fact that the quenching of fluorescence is caused by an external static mechanism, that is, by the association of quencher ions (iron and copper ions) with the FWA molecule. The highest concentrations of copper ions did not affect the decrease in whiteness degree of the cotton fabric, which can be explained by the fact that copper ions give the solutions a bluish tint. The blue absorbs a part of the yellow spectrum, and the remission in this part is reduced, which increases the whiteness.

Quenching is less pronounced on fabrics adsorbates, since molecules of FWA burdened by the addition of quenchers have a harder time penetrating the structure of the fabrics and binding to the cellulose chains. Therefore, there are fewer inactive FWA molecules in the fabric (in the cellulose chain), so the fluorescence quenching is also weaker.

Professor Weber established that in the case of quenching of fluorescence by an external static mechanism on paper adsorbates, the fluorescence is quenched almost as intensively as in solutions. If the fluorescence quenching in solutions is caused by an external kinetic mechanism, then there will be no fluorescence quenching on paper adsorbates, even though the quenching in solutions is very intense. As it was found that the fluorescence quenching of FWAs by the addition of metal ions is caused by an external static mechanism, then it will be caused both in solutions and on paper adsorbates.

FWAs increase the UV protection of cotton fabrics and filter paper. A decrease in UV protection was also recorded with an increase in the concentration of metal ions. The protective properties of fabrics decrease after the addition of 30 ppm iron ions and 5 ppm copper ions.

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