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Novel Bleaching of Linen Fabrics Using Ultraviolet Irradiation

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Abstract

The bleaching of greige linen woven fabric using ultraviolet irradiation on hydrogen peroxide impregnated samples was studied. The effect of a photoinitiator, sodium hydroxide, sodium peroxydisulphate for hydrogen peroxide, the irradiation time and distance between the fabric and ultraviolet light lamp on the samples' whiteness, lightness, weight loss, moisture sorption and wettability properties was investigated. The UV/H₂O₂ bleaching process was optimised with the aid of Box-Behnken experimental design and three optimum recipes were achieved. As a result of the study, a novel bleaching process using ultraviolet irradiation and hydrogen peroxide for greige linen woven fabric was developed which saves on energy and time

Key words: advanced oxidation process, bleaching, finishing, H₂O₂/UV, linen, ultraviolet radiation.

Introduction

Oxidative bleaching with hydrogen peroxide is generally used for the decomposition of flax fibre natural pigments [1]. Conventional bleaching of linen consumes high amounts of hazardous chemicals and needs lengthy operation times, thus it is a costly and non-environmentally friendly treatment [2 - 5]. Nowadays researchers are involved in developing innovative non-traditional techniques which are both environmentally friendly and economically viable.

Conventional oxidation treatments cannot usually oxidise a complex structure of organic compounds at low concentration [6]. Advanced oxidation processes (AOPs) have been developed to generate hydroxyl free radicals to overcome the problems generated during conventional oxidation treatments. **Table 1** shows the relative oxidation potentials of several chemical oxidisers [6].

AOP offers different possible ways for the generation of OH• radicals (**Table 2**). The generation of hydroxyl free radicals (OH•) is commonly accelerated by com-

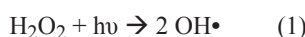
Table 1. Oxidizing potential for conventional oxidizing agents [6].

Oxidizing agent	Electrochemical oxidation potential (EOP), V
Fluorine	3.06
Hydroxyl radical	2.80
Oxygen (atomic)	2.42
Ozone	2.08
Hydrogen peroxide	1.78
Hypochlorite	1.49
Chlorine	1.36
Chlorine dioxide	1.27
Oxygen (molecular)	1.23

binning ozone (O₃), hydrogen peroxide (H₂O₂), titanium dioxide (TiO₂), ultraviolet (UV) irradiation, electron-beam irradiation and ultrasound. Of these, O₃/H₂O₂, O₃/UV and H₂O₂/UV hold the greatest promise to oxidize textile wastewater [6].

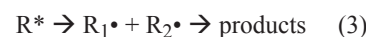
The development of AOPs based on ultraviolet photolysis, capable of mineralising a wide range of recalcitrant or hazardous organic compounds, has had a strong impact on the progress of technology associated with photochemistry and photochemical processes [7 - 9]. Ultraviolet light is electromagnetic radiation spread between the wavelengths 100 nm and 400 nm [10]. The process usually involves the use of low-pressure UV lamps with a principal wavelength of 254 nm. Since the maximum absorption of ozone molecules is at 253.7 nm, the light source commonly used is a medium-pressure mercury lamp wrapped in a quartz sleeve that can generate UV light at a wavelength of 200 - 280 [6, 11].

Because of its simple handling, oxidation is the most commonly used chemical discoloration process. In most cases the oxidising agent is hydrogen peroxide, which, due to its stability in pure form, needs to be activated. Peroxide is activated by UV light [12 - 14]. H₂O₂/UV treatment generates hydroxyl radicals which are highly powerful oxidising species with oxidation potential 1.78 V [15, 16]. The formation of highly reactive hydroxyl radicals in UV/ H₂O₂ systems can be chemically expressed as (**Equation 1**) [6]:



UV radiation has tremendous oxidation potential (a 253.7 nm photon provides

4.89 eV) which is normally enough to interact with the electronic structure of matter. The degradation of the organic pollutant is normally initiated from an electronic excited state (**Equation 2**) which can undergo homolytic bond scission to form radicals that will react towards final products in a chain reaction with the participation (or not) of molecular oxygen (**Equation 3**), or initiate a process of electron transfer to a ground state oxygen molecule (**Equation 4**) [7].



The resulting radical caption can undergo hydrolysis or mesolytic bond scission into low weight products. The superoxide radical ion (O₂•-) is known to be capable of degrading aromatic molecules. Although the emission of a low pressure Hg at 253.7 nm alone is not very effective for the removal of simple organics from water, more complex substituted aromatics with more favorable absorption spectra can undergo efficient degradation [7].

Some examples of UV radiation in textile finishing already realised on an industrial scale are as follows:

Table 2. Advanced oxidation processes [6].

H ₂ O ₂ /UV/Fe ²⁺ (photo assisted Fenton)
H ₂ O ₂ /Fe ²⁺ (Fenton)
Ozone/UV (also applicable in the gas phase)
Ozone/H ₂ O ₂
Ozone/UV/H ₂ O ₂
Ozone/TiO ₂ /Electron-beam irradiation
Ozone/TiO ₂ /H ₂ O ₂
Ozone + electron-beam irradiation
Ozone/ultrasonic
H ₂ O ₂ /UV

Table 3. Hydrogen peroxide bleaching recipes.

H ₂ O ₂ (50%), g/l	Complexing agent, g/l	Non-ionic wetting agent, g/l	WPV, %
20	5	2	100
40	10		
60	15		

Table 4. The levels of variables chosen for the trials

	-1	0	1
Hydrogen peroxide concentration 50% X ₁ , g/l	20	40	60
Sodium peroxydisulphate concentration X ₂ , g/l	1	2	3
Sodium hydroxide concentration X ₃ , g/l	5	20	35
Process time for ultraviolet treatment X ₄ , min.	0	3	6
Distance between ultraviolet light lamp and the fabric X ₅ , cm	10	17	24

Table 5. The Box-Behnken design for the three independent variables

Trial No:	X ₁	X ₂	X ₃	X ₄	X ₅	Trial No:	X ₁	X ₂	X ₃	X ₄	X ₅
1	0	0	0	0	0	24	-1	1	0	0	0
2	0	1	0	1	0	25	0	1	-1	0	0
3	0	0	1	-1	0	26	0	0	-1	0	1
4	0	0	0	0	0	27	0	0	1	0	1
5	0	0	0	-1	1	28	-1	0	1	0	0
6	0	0	0	0	0	29	-1	0	0	-1	0
7	1	0	0	0	-1	30	0	0	0	1	-1
8	0	1	0	-1	0	31	0	-1	0	1	0
9	-1	0	-1	0	0	32	0	1	0	0	-1
10	1	0	-1	0	0	33	1	1	0	0	0
11	-1	-1	0	0	0	34	0	-1	-1	0	0
12	0	0	0	1	1	35	1	0	0	1	0
13	0	1	1	0	0	36	0	-1	1	0	0
14	0	1	0	0	1	37	0	0	0	0	0
15	0	0	0	-1	-1	38	1	0	1	0	0
16	1	0	0	0	1	39	1	-1	0	0	0
17	0	0	1	0	-1	40	0	-1	0	-1	0
18	0	-1	0	0	1	41	1	0	0	-1	0
19	0	0	0	0	0	42	-1	0	0	0	1
20	0	0	0	0	0	43	-1	0	0	1	0
21	-1	0	0	0	-1	44	0	0	-1	-1	0
22	0	0	-1	0	-1	45	0	0	1	1	0
23	0	-1	0	0	-1	46	0	0	-1	1	0

- UV radiation used for the reduction of dyes in dyeing with leucoethers of vat dyes,
- Finishing called Siroflash, used in Australia on an industrial scale for wool and cotton treatment for improvement of pilling performance,
- UV radiation together with ozone or catalysts like hydrogen peroxide or chlorine compounds to destroy the majority of dyes and other organic compounds,
- Curing of ink jet prints and pigment printing,
- Curing of coatings on textiles,
- Intensification of wool and cotton dyeing properties,
- Cotton bleaching,
- Possibility to dye irradiated wool fabrics at lower temperatures with good dyeing properties [17].

Our current work aims at developing the H₂O₂/UV treatment system for bleaching greige linen woven fabric. Thus peroxide bleaching bath assisted by ultraviolet energy were studied under a variety of conditions. The effectiveness of bleaching is evaluated through the whiteness index, lightness index, weight loss, moisture sorption property, and contact angle measurement of the fabrics.

■ Experimental

Materials

The greige 100% linen woven fabric used had the following specifications: plain weave, mass per unit area = 210 g/m², warp = 10 yarn/cm and weft = 9 yarn/cm. Linen fabric samples (3.5 g each) were firstly immersed in a hydrogen peroxide bleaching bath and then subjected

to ultraviolet light in accordance with the Box-Behnken Experimental Design. The nonionic wetting agent, complexing agent, nonionic washing agent, sodium hydroxide, sodium peroxydisulphate, and buffer acid were of laboratory reagent grade. The ultraviolet light lamp produces UV-B and its power consumption is 2000 W.

Methods

In accordance with the Box-Behnken design, three different process times for ultraviolet treatment, hydrogen peroxide concentrations, sodium hydroxide concentrations, sodium peroxydisulphate concentrations, and distances between the ultraviolet light lamp and fabric were investigated. The hydrogen peroxide bleaching baths were prepared according to **Table 3** and **4**. The samples were padded in a bleaching bath at room temperature with an impregnation time of 60 seconds and wet pick up of 100%, and then irradiated for 1, 2 and 3 minutes. After the irradiation of both sides of the samples, they were rinsed at 90 °C for 10 minutes, washed with 0.06 g/l catalase enzyme at 40 °C for 20 minutes, then washed with 1 g/l nonionic washing agent at 95 °C for 10 minutes, rinsed at 95 °C for 10 minutes, and then cold rinsing for 10 minutes was performed. Finally the samples were air dried.

Experimental design

Significant variables like the process time for ultraviolet treatment, hydrogen peroxide concentration, sodium hydroxide concentration, sodium peroxydisulphate concentration, and the distance between the ultraviolet light lamp and the fabric were chosen as the critical variables and designated as X₁, X₂, X₃, X₄, and X₅, respectively. The low, middle and high levels of each variable were designated as -1, 0 and +1, respectively, and are given in **Table 4**. The actual design of experiments is shown in **Table 5**.

To evaluate the results of experiments, the whiteness (*W*) and lightness (*L**) degree of samples was examined according to the Stensby and CIELab formula under a D65 illumination source, with a medium aperture and 0% UV, using a Minolta 3600d Model Spectralphotometer. The samples were measured in a triple-folded state to make them opaque at 3 points, and an average value was determined.

Table 6. Regression analysis for the W , L^* , W_L and MS (quadratic response surface model fitting).

	Source	df	Seq. SS	Adj. SS	Adj. MS	F	P
W R ² = 92.4% R ² (adj)= 86.4%	Regression	20	2323.02	2323.02	116.51	15.24	0.000
	Linear	5	1240.32	1240.32	248.064	32.56	0.000
	Square	5	773.17	773.17	154.634	20.30	0.000
	Interaction	10	309.53	309.53	30.953	4.06	0.002
	Residual Error	25	190.48	190.48	7.619		
	Lack of fit	20	189.18	189.18	9.459	36.47	0.000
	Pure error	5	1.3	1.3	0.259		
Total	45	2513.49					
L* R ² = 92.8% R ² (adj)= 87.0%	Regression	20	95.881	95.881	4.7940	15.99	0.000
	Linear	5	50.344	50.344	10.0689	33.59	0.000
	Square	5	17.849	17.849	3.5699	11.91	0.000
	Interaction	10	27.687	27.687	2.7687	9.24	0.000
	Residual Error	25	7.494	7.494	0.2998		
	Lack of fit	20	5.920	5.920	0.2960	0.94	0.591
	Pure error	5	1.575	1.575	0.3149		
Total	45	103.375					
W_L, % R ² = 94.3% R ² (adj)= 89.7%	Regression	20	22.9899	22.9899	1.14950	20.62	0.000
	Linear	5	12.9188	12.9188	2.58377	46.36	0.000
	Square	5	3.7136	3.7136	0.74272	13.33	0.000
	Interaction	10	6.3575	6.3575	0.63575	11.41	0.000
	Residual Error	25	1.3934	1.3934	0.05574		
	Lack of fit	20	1.2363	1.2363	0.06182	1.97	0.233
	Pure error	5	0.1571	0.1571	0.03142		
Total	45	24.3833					
MS, % R ² = 94.5% R ² (adj)= 90.1%	Regression	20	1.47604	1.47604	0.073802	21.45	0.000
	Linear	5	0.80719	0.80719	0.161437	46.92	0.000
	Square	5	0.59612	0.596125	0.119225	34.66	0.000
	Interaction	10	0.07273	0.072725	0.007273	2.11	0.063
	Residual Error	25	0.08601	0.086008	0.00344		
	Lack of fit	20	0.07887	0.078875	0.003944	2.76	0.131
	Pure error	5	0.00713	0.007133	0.001427		
Total	45	1.56205					

The weight loss (W_L) was determined on atmospherically conditioned linen fabrics after different treatments. The weight loss percentage was calculated from the differences in weight using *Equation 5*:

$$W_L = \frac{W_{pre} - W_{after}}{W_{pre}} \times 100(\%) \quad (5)$$

where, W_{pre} is the weight of the conditioned fabrics prior to treatment, and W_{after} is the weight after the treatment performed.

The moisture sorption (MS) of the linen samples was determined at 20 ± 2 °C and $65 \pm 2\%$ relative humidity according to Standards DIN 54 351 and DIN 53 802. The samples were exposed to such a condition for 24 hours. The amount of moisture absorbed was calculated as a weight percentage of absolute dry material.

Wettability was examined by contact angle measurements using distilled water. For this aim, equipment consisting of a camera (PULNIX TM-765), computer,

and monitor was used. The contact angles of water were measured with the sessile drop method. Images of each drop were captured by a camera connected to a computer-based image capture system. The images captured were viewed on the monitor.

Also the results of all assays were compared using ANOVA, followed by a post hoc test (Duncan's test).

Results and discussion

By applying multiple regression analysis methods, the response predicted for whiteness (W), lightness (L^*), weight loss (W_L in %) and moisture sorption (MS in %) can be obtained and given as

$$\begin{aligned} W = & -139 + 1.24 X_1 + 5.67 X_2 + \\ & + 1.24 X_3 + 30.4 X_4 + 3.95 X_5 + \\ & - 0.0124 X_1^2 + 0.0116 X_3^2 + \\ & - 5.44 X_4^2 - 0.0778 X_5^2 + \\ & - 0.0747 X_1 \times X_2 + \\ & - 0.138 X_2 \times X_5 - 0.39 X_3 \times X_4 \end{aligned} \quad (6)$$

$$\begin{aligned} L^* = & 65.1 + 0.344 X_1 + 0.225 X_3 + \\ & - 0.0018 X_1^2 + 0.00328 X_3^2 + \\ & + 0.714 X_4^2 - 0.0181 X_1 \times X_2 + \\ & - 0.00635 X_1 \times X_3 + 0.0182 X_2 \times X_3 + \\ & - 0.0632 X_3 \times X_4 \end{aligned}$$

$$\begin{aligned} W_L = & -6.55 + 0.136 X_1 + 0.547 X_2 + \\ & + 0.359 X_3 + 2.14 X_4 - 0.00128 X_1^2 + \\ & - 0.0378 X_2^2 - 0.00225 X_3^2 + \\ & - 0.25 X_4^2 - 0.00431 X_5^2 + \\ & - 0.00345 X_1 \times X_3 + 0.00556 X_2 \times X_3 - \\ & 0.033 X_3 \times X_4 \end{aligned} \quad (8)$$

$$\begin{aligned} MS = & 9.30 - 0.0227 X_3 - 0.502 X_4 + \\ & - 0.178 X_5 + 0.000194 X_3^2 + \\ & + 0.0552 X_4^2 + 0.00506 X_5^2 \end{aligned} \quad (9)$$

The statistical significance of *Equations 6 - 9* was checked by the F -test, and the analysis of variance (ANOVA) for the response surface quadratic model is summarised in *Table 6*. The ANOVA of the regression model demonstrates that the model is highly significant. The value of R^2 indicates (92.4% for W , 92.8% for L^* , 94.3% for W_L and 94.5% for MS) a good correlation between the experimental and predicted values of the response (*Table 6* and *7*). The lack-of-fit measures the failure of the model to represent data in the experimental domain at points which are not included in the regression. The non-significant value of lack of fit (>0.05) for L^* , W_L and MS revealed that the quadratic model is statistically significant for the response and, therefore, can be used for further analysis. The high lack of fit value (0.000) for W means that the model can sometimes make mistakes during the prediction of W of samples (*Table 6*).

After ANOVA for the quadratic model, all the model terms having P -values greater than 0.05 are eliminated since they are not statistically significant at the 95% confidence level. Further ANOVA for variables fitted in the model indicates that all of the parameters examined (hydrogen peroxide concentration ($P = 0.000$), sodium peroxydisulphate concentration ($P = 0.007$), sodium hydroxide concentration ($P = 0.004$), ultraviolet treatment time ($P = 0.000$) and distance between the ultraviolet light lamp and fabric ($P = 0.000$) for W ; hydrogen peroxide concentration ($P = 0.000$) and sodium hydroxide concentration ($P = 0.008$) for L^* ; hydrogen peroxide concentration ($P = 0.000$), sodium peroxydisulphate concentration ($P = 0.003$), sodium hydroxide concentration ($P = 0.000$) and ultraviolet treatment time ($P = 0.000$) for W_L ; sodium hydroxide concentration

Table 7. Experimental and theoretical predicted values for W, L*, W_L and MS.

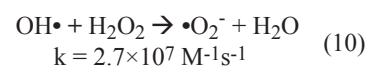
W			W			W		
No:	Actual Value	Predicted Value	No:	Actual Value	Predicted Value	No:	Actual Value	Predicted Value
1	-23.25	-23.74	17	-16.77	-15.14	33	-27.87	-28.67
2	-23.40	-21.44	18	-32.92	-29.20	34	-26.34	-29.82
3	-17.09	-15.70	19	-23.50	-23.74	35	-33.95	-33.30
4	-23.48	-23.74	20	-24.25	-23.74	36	-18.84	-19.69
5	-36.66	-34.80	21	-31.44	-30.86	37	-23.46	-23.74
6	-24.51	-23.74	22	-34.07	-32.91	38	-22.40	-23.22
7	-29.69	-32.32	23	-35.32	-33.15	39	-31.24	-29.97
8	-24.75	-23.65	24	-13.33	-15.45	40	-33.01	-34.83
9	-35.89	-32.13	25	-23.94	-22.61	41	-39.03	-39.23
10	-36.35	-33.21	26	-25.75	-30.15	42	-32.49	-29.90
11	-34.63	-34.67	27	-17.63	-21.57	43	-29.97	-31.84
12	-35.73	-33.01	28	-15.58	-15.78	44	-41.09	-40.57
13	-10.34	-6.39	29	-29.45	-32.17	45	-23.09	-24.26
14	-22.79	-24.73	30	-30.55	-29.83	46	-23.69	-25.74
15	-34.17	-34.31	31	-29.81	-30.77			
16	-36.33	-36.95	32	-13.62	-17.11			
L*			L*			L*		
No	Actual Value	Predicted Value	No	Actual Value	Predicted Value	No	Actual Value	Predicted Value
1	73.65	73.74	17	75.56	75.83	33	72.89	72.93
2	75.77	75.62	18	72.76	73.05	34	73.98	72.93
3	77.52	77.62	19	73.86	73.74	35	73.52	73.43
4	73.09	73.74	20	74.52	73.74	36	75.55	74.35
5	74.22	74.27	21	73.84	73.44	37	74.17	73.74
6	73.16	73.74	22	73.38	73.66	38	73.62	73.47
7	73.22	73.13	23	72.45	72.92	39	72.45	73.34
8	75.20	75.11	24	75.29	74.94	40	73.69	73.77
9	70.22	70.25	25	72.37	73.04	41	74.44	74.205
10	74.63	74.22	26	72.3	72.42	42	72.86	72.62
11	70.51	71.01	27	76.25	76.37	43	73.98	74.14
12	74.47	74.48	28	76.83	77.12	44	72.46	72.67
13	77.22	77.74	29	73.15	73.17	45	75.76	75.83
14	74.73	74.33	30	74.88	74.71	46	74.49	74.66
15	74.86	74.73	31	73.44	73.46			
16	73.19	73.25	32	75.37	75.15			
W _L , %			W _L , %			W _L , %		
No	Actual Value	Predicted Value	No	Actual Value	Predicted Value	No	Actual Value	Predicted Value
1	4.69	4.67	17	4.74	4.89	33	3.05	3.32
2	4.46	4.24	18	4.38	4.34	34	3.47	3.23
3	4.66	4.92	19	4.63	4.66	35	3.94	3.90
4	4.73	4.66	20	4.94	4.66	36	4.73	4.33
5	3.89	4.00	21	4.79	4.44	37	4.54	4.66
6	4.42	4.66	22	2.73	2.94	38	3.36	3.11
7	3.51	3.37	23	3.55	3.82	39	3.40	3.70
8	4.18	3.96	24	4.22	4.35	40	3.65	3.63
9	1.98	2.10	25	2.67	2.79	41	3.29	3.30
10	3.74	3.58	26	3.26	3.35	42	4.22	4.02
11	3.70	3.85	27	4.57	4.60	43	4.41	4.45
12	4.26	4.46	28	5.74	5.77	44	2.37	2.33
13	4.93	4.89	29	3.85	3.94	45	4.27	4.49
14	4.11	3.94	30	4.58	4.49	46	3.96	3.87
15	4.02	3.84	31	4.47	4.45			
16	3.91	3.91	32	4.20	4.34			
MS, %			MS, %			MS, %		
No	Actual Value	Predicted Value	No	Actual Value	Predicted Value	No	Actual Value	Predicted Value
1	7.00	7.03	17	7.23	7.21	33	7.26	7.12
2	6.82	6.89	18	7.24	7.24	34	7.02	7.01
3	7.27	7.27	19	7.08	7.03	35	6.82	6.84
4	7.07	7.03	20	7.00	7.03	36	7.09	7.07
5	7.57	7.55	21	7.18	7.17	37	7.01	7.03
6	7.00	7.03	22	7.34	7.32	38	7.13	7.11
7	7.23	7.29	23	7.28	7.24	39	6.98	6.99
8	7.32	7.36	24	7.09	7.03	40	7.28	7.25
9	7.11	7.12	25	7.16	7.18	41	7.35	7.36
10	7.06	7.07	26	7.35	7.36	42	7.38	7.37
11	6.92	7.02	27	7.36	7.38	43	6.91	6.91
12	7.33	7.22	28	7.02	7.00	44	7.45	7.41
13	7.03	7.04	29	7.25	7.24	45	6.89	6.94
14	7.37	7.42	30	7.05	7.02	46	6.87	6.88
15	7.48	7.54	31	6.86	6.86			
16	7.24	7.30	32	7.20	7.21			

($P = 0.012$), ultraviolet treatment time ($P = 0.001$) and distance between the ultraviolet light lamp and fabric for MS, have the greatest effect on the model (Table 8).

The effects of ultraviolet treatment on the whiteness of linen fabrics impregnated with various peroxide bleaching baths

The results of the whiteness measurements for untreated samples and those impregnated with various peroxide bleaching baths and then subjected to ultraviolet light for various treatment times are given in Figure 1. The results indicate that during irradiation, the whiteness of samples treated with distilled water remained almost unchanged. The lack of a photoinitiator could be the main reason for this effect, which clarifies that UV irradiation cannot act as a bleaching agent. On the other hand, an increase in sodium peroxydisulphate concentration increases the degree of whiteness obtained. The concentration of hydrogen peroxide attained importance when the sodium peroxydisulphate concentration used was higher than 1 g/l.

It is clearly seen from the results that whiteness of the samples increased as the doses of effective hydrogen peroxide increased up to a "critical" value. A high concentration of the H₂O₂ acts as a radical scavenger, while low concentration of H₂O₂ generates insufficient hydroxyl radicals (OH•), which are consumed by organic compounds, leading to a slow rate of oxidation. This is not unusual for the fact that hydrogen peroxide itself is a scavenger of hydroxyl radicals in accordance with the reaction below (Equation 10) [6, 18 - 20];



With increasing H₂O₂ concentration, more hydroxyl radicals are available to attack the aromatic rings and the rate of reaction increases (Equations 11 - 13). Moreover above the limiting point, hydroxyl radicals efficiently react with H₂O₂ and produce HO₂• (Equation 14). Because HO₂• radicals are less reactive than OH•, increasing HO₂• results in a negligible contribution [8, 21];

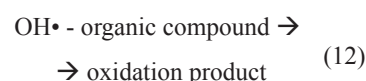
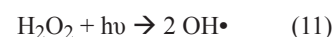
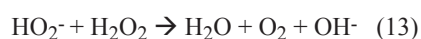


Table 8. ANOVA for the variables in the model fitted for W , L^* , W_L and MS .

Predictor	W				L*			
	Coef	StDev	T	P	Coef	StDev	T	P
Constant	-138.79	17.22	-8.06	0.000	65.100	3.416	19.06	0.000
X ₁	1.2439	0.3106	4.00	0.000	0.34416	0.06161	5.59	0.000
X ₂	5.667	1.939	2.92	0.007	0.6847	0.3846	1.78	0.087
X ₃	1.2367	0.3948	3.13	0.004	0.22476	0.07830	2.87	0.008
X ₄	30.408	6.212	4.90	0.000	-1.015	1.232	-0.82	0.418
X ₅	3.9549	0.9214	4.29	0.000	-0.2208	0.1828	-1.21	0.238
X ₁ ²	-0.012383	0.002336	-5.30	0.000	-0.0018	0.0004633	-3.88	0.001
X ₂ ²	0.1672	0.1038	1.61	0.120	0.00361	0.02059	0.18	0.862
X ₃ ²	0.011608	0.004153	2.80	0.010	0.0032815	0.0008237	3.98	0.001
X ₄ ²	-5.4365	0.9344	-5.82	0.000	0.7142	0.1853	3.85	0.001
X ₅ ²	-0.07777	0.01907	-4.08	0.000	0.001803	0.003782	0.48	0.638
X ₁ ×X ₂	-0.07471	0.02300	-3.25	0.003	-0.018083	0.004563	-3.96	0.001
X ₁ ×X ₃	-0.005300	0.004600	-1.15	0.260	-0.00635	0.0009125	-6.96	0.000
X ₁ ×X ₄	0.07000	0.06901	1.01	0.320	-0.02187	0.01369	-1.60	0.123
X ₁ ×X ₅	-0.009982	0.009858	-1.01	0.321	0.001696	0.001955	0.87	0.394
X ₂ ×X ₃	0.03389	0.03067	1.1	0.280	0.018222	0.006084	3.00	0.006
X ₂ ×X ₄	-0.1542	0.4600	-0.34	0.740	0.06833	0.09125	0.75	0.461
X ₂ ×X ₅	-0.13774	0.06572	-2.10	0.046	-0.01131	0.01304	-0.87	0.394
X ₃ ×X ₄	-0.39000	0.09201	-4.24	0.000	-0.06317	0.01825	-3.46	0.002
X ₃ ×X ₅	-0.02186	0.01314	-1.66	0.109	0.004214	0.002607	1.62	0.119
X ₄ ×X ₅	-0.0961	0.1972	-0.49	0.630	0.00821	0.03911	0.21	0.835
	W _L , %				MS, %			
Constant	-6.551	1.473	-4.45	0.000	9.3025	0.3659	25.42	0.000
X ₁	0.13588	0.02657	5.11	0.000	0.005924	0.0066	0.90	0.378
X ₂	0.5468	0.1658	3.30	0.003	-0.01667	0.0412	-0.40	0.689
X ₃	0.35908	0.03376	10.64	0.000	-0.022681	0.008388	-2.70	0.012
X ₄	2.1412	0.5313	4.03	0.000	-0.5016	0.132	-3.80	0.001
X ₅	0.16134	0.07881	2.05	0.051	-0.1775	0.01958	-9.07	0.000
X ₁ ²	-0.0012802	0.0001998	-6.41	0.000	0.0000151	0.0000496	0.30	0.763
X ₂ ²	-0.037824	0.008879	-4.26	0.000	0.000579	0.002206	0.26	0.795
X ₃ ²	-0.00225	0.0003552	-6.33	0.000	0.0001935	0.0000882	2.19	0.038
X ₄ ²	-0.24958	0.07992	-3.12	0.004	0.05521	0.01985	2.78	0.010
X ₅ ²	-0.004311	0.001631	-2.64	0.014	0.0050553	0.0004052	12.48	0.000
X ₁ ×X ₂	-0.003625	0.001967	-1.84	0.077	0.0004583	0.0004888	0.94	0.357
X ₁ ×X ₃	-0.00345	0.0003935	-8.77	0.000	0.0001333	0.0000978	1.36	0.185
X ₁ ×X ₄	0.001125	0.005902	0.19	0.850	-0.002375	0.001466	-1.62	0.118
X ₁ ×X ₅	0.0017321	0.0008432	2.05	0.051	-0.0003393	0.0002095	-1.62	0.118
X ₂ ×X ₃	0.005556	0.002623	2.12	0.044	-0.0011111	0.0006517	-1.70	0.101
X ₂ ×X ₄	-0.045	0.03935	-1.14	0.264	-0.006667	0.009776	-0.68	0.502
X ₂ ×X ₅	-0.010952	0.005621	-1.95	0.063	0.002500	0.001397	1.79	0.086
X ₃ ×X ₄	-0.033	0.007870	-4.19	0.000	0.003333	0.001955	1.70	0.101
X ₃ ×X ₅	-0.001667	0.001124	-1.48	0.151	0.0002857	0.0002793	1.02	0.316
X ₄ ×X ₅	-0.00679	0.01686	-0.40	0.691	0.006786	0.004190	1.62	0.118



Thus a trade-off between them will result in an optimum H_2O_2 dose, which still needs to be verified experimentally. The usage of 30 - 35 g/l hydrogen peroxide and 5.5 - 6 g/l sodium peroxydisulphate in the impregnation bath could be enough to achieve the highest whiteness value under the experimental conditions (*Figure 1.a*).

As seen from *Figure 1.b*, there is no linear relation between the hydrogen peroxide concentration used in the impregnation bath and the ultraviolet treatment

time. Ultraviolet treatment of a sample impregnated with a bath consisting of 30 or 40 g/L of hydrogen peroxide for 2 minutes provides the highest whiteness level.

It is well known that the photochemical degradation rate of H_2O_2 is variable under certain pH conditions, and this can affect the $\text{H}_2\text{O}_2/\text{UV}$ reaction to degrading different contaminants [8, 22, 23]. By creating alkaline pH, sodium hydroxide acted with the whiteness enhancement as an activator. The increase in sodium hydroxide concentration increases the degree of whiteness obtained irrespective

of the hydrogen peroxide concentration. The impregnation bath should consist of a minimum of 20 - 30 g/l of hydrogen peroxide and 30 g/l sodium hydroxide to achieve the maximum whiteness level (*Figure 1.c*).

The distance between the lamp and fabric should be between 14 and 20 cm during the ultraviolet treatment to reach the maximum whiteness level. However, no further increase in the whiteness of the samples was seen lower than 14 cm and higher than 20 cm (*Figure 1.d*). *Figure 1.e* shows that an ultraviolet treatment time of 2 min under the experimental conditions result in the highest whiteness level of linen samples. It is obvious that the concentration of sodium hydroxide used in the impregnation bath is more important than the concentration of sodium peroxydisulphate in terms of whiteness value of samples; minimum 4 g/l sodium peroxydisulphate and 30 g/l sodium hydroxide should be used in the impregnation bath to achieve maximum whiteness level of samples (*Figure 1.f*).

These results mentioned above were demonstrated with the photographs of the samples (*Figure 2*). The appearance of linen samples impregnated with the peroxide bleaching bath, which contains high amount of sodium peroxydisulphate (6 g/l) and sodium hydroxide (35 g/l), were whiter. The increase in hydrogen peroxide concentration, used in an impregnation bath, caused no change on the appearance and whiteness values of linen samples.

The effects of ultraviolet treatment on to the lightness of linen fabrics impregnated with various peroxide bleaching baths

Figure 3 shows that an increase in hydrogen peroxide and sodium hydroxide concentration increases the degree of lightness obtained. When the hydrogen peroxide concentration was set to 20 g/l and the sodium hydroxide concentration was increased from 5 g/l to 20 g/l and 35 g/l, the lightness value of linen samples increased from 72 to 74 and higher than 76 respectively. On the other hand, the increase in hydrogen peroxide concentration affected the lightness values of samples differently related with the sodium hydroxide concentration used in the bath.

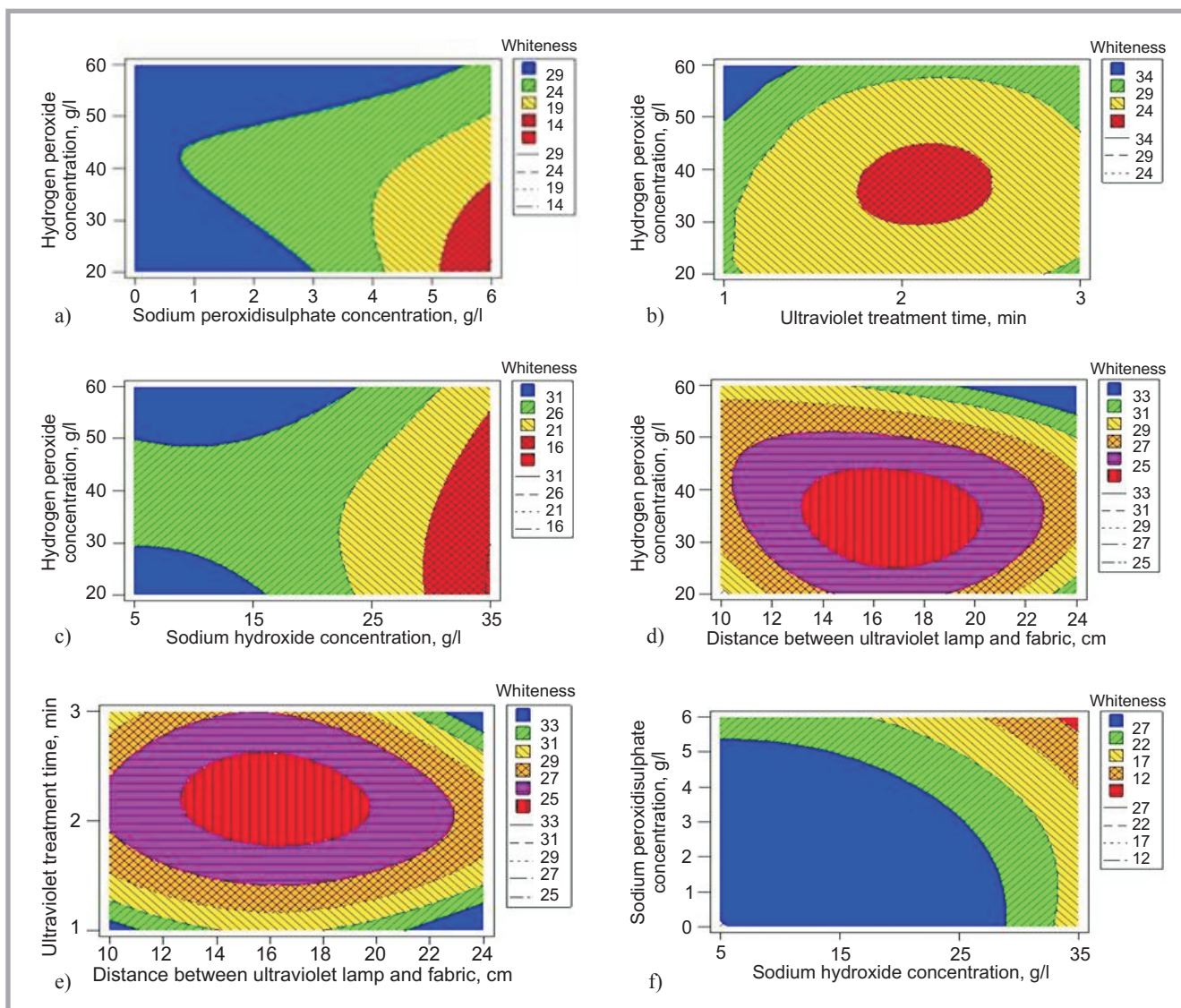


Figure 1. Effect of hydrogen peroxide concentration & sodium peroxydisulphate concentration (a); ultraviolet treatment time & hydrogen peroxide concentration (b); sodium hydroxide concentration & hydrogen peroxide concentration (c); distance between ultraviolet lamp-fabric & hydrogen peroxide concentration (d); distance between ultraviolet lamp-fabric & ultraviolet treatment (e); sodium hydroxide concentration & sodium peroxydisulphate concentration (f) on the whiteness of the greige linen fabric

The effects of ultraviolet treatment on to the weight loss of linen fabrics impregnated with various peroxide bleaching baths

The results of the weight loss measurements for treated samples are given in **Figure 4**. The increase in sodium peroxydisulphate concentration and hydrogen peroxide concentration up to 40 g/l increases the weight loss obtained (**Figure 4.a**). The other important parameter in terms of achieved weight loss was sodium hydroxide concentration. When the sodium hydroxide concentration was increased from 5 g/l to 20 and 35 g/l, the percent weight loss increased from 3 to 4 and 5 respectively (**Figure 4.b - 4.c**). It is enough to work with 20 g/l hydrogen peroxide, 3 g/l sodium peroxydisulphate and 20 g/l sodium hydroxide to achieve

weight loss higher than 4%. Under these circumstances, the ultraviolet treatment time can be adjusted to 2 minutes (**Figure 4.d**).

The effects of ultraviolet treatment on to the moisture sorption of linen fabrics impregnated with various peroxide bleaching baths

It is seen from **Figure 5** that the amount of moisture sorption of linen samples decreased with the increase in ultraviolet treatment time independent from the used sodium hydroxide concentration. For example; when 30 g/l sodium hydroxide concentration used in the impregnation bath was accepted as constant, the MS value of linen sample decreased from 7.4% to lower than 7% with the increase in ultraviolet treatment time.

During all treatment times except 1 minute, the change in the amount of sodium hydroxide used in the impregnation bath caused no difference in the MS values of samples. During the ultraviolet treatment for 1 minute, the increase in sodium hydroxide concentration caused decrease in MS values of linen samples.

The effects of ultraviolet treatment on to the hydrophilicity of linen fabrics impregnated with various peroxide bleaching baths

To investigate the effect of developed process on to the wettability properties of greige linen fabrics, contact angle measurement was performed. It is clearly seen from **Figure 6** that the wettability properties of linen fabrics significantly improved after ultraviolet treatment. Bet-









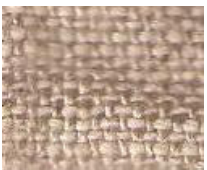


	
Greige linen fabric ($W = -55.56$; $L = 61.17$)	
Effect of sodium peroxydisulphate concentration on to the greige linen fabric ($X_1 = 40$ g/l; $X_3 = 20$ g/l; $X_4 = 1$ min.; $X_5 = 17$ cm)	
	
0 g/l ($W = -41.09$; $L = 72.46$)	6 g/l ($W = -17.09$; $L = 77.52$)
Effect of distance between ultraviolet lamp and fabric on to the greige linen fabric ($X_1 = 40$ g/l; $X_2 = 6$ g/l; $X_3 = 20$ g/l; $X_4 = 2$ min.)	
	
10 cm ($W = -13.62$; $L = 75.37$)	24 cm ($W = -22.79$; $L = 74.73$)
Effect of sodium hydroxide concentration on to the greige linen fabric ($X_1 = 40$ g/l; $X_2 = 3$ g/l; $X_4 = 2$ min.; $X_5 = 24$ cm)	
	
5 g/l ($W = -25.75$; $L = 72.30$)	35 g/l ($W = -17.63$; $L = 76.25$)
Effect of hydrogen peroxide concentration on to the greige linen fabric ($X_2 = 3$ g/l; $X_3 = 5$ g/l; $X_4 = 2$ min.; $X_5 = 17$ cm)	
	
20 g/l ($W = -35.89$; $L = 70.22$)	60 g/l ($W = -36.35$; $L = 74.63$)
Effect of ultraviolet treatment time on to the greige linen fabric ($X_1 = 40$ g/l; $X_2 = 6$ g/l; $X_3 = 20$ g/l; $X_5 = 17$ cm)	
	
1 min. ($W = -24.75$; $L = 75.20$)	3 min. ($W = -23.40$; $L = 75.77$)

Figure 2. The photographs of untreated and treated linen samples.

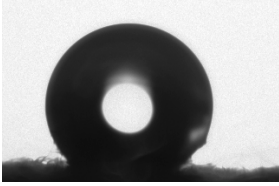
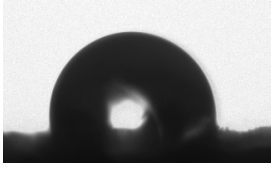
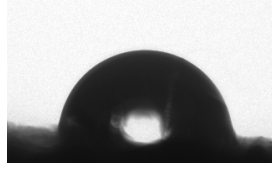
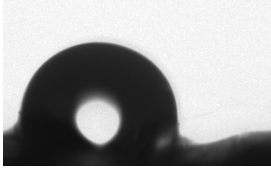
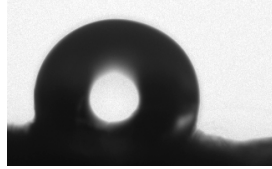
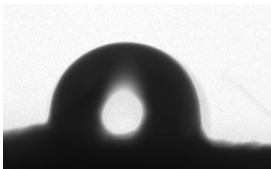
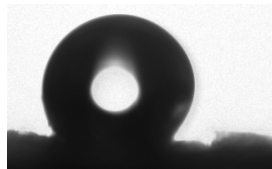
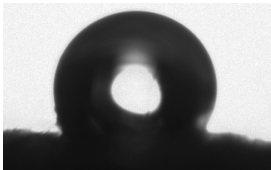
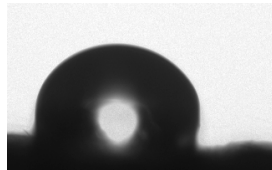
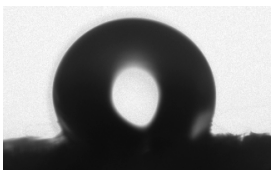
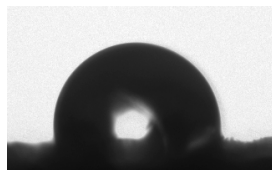
	
Greige linen fabric ($t \geq 2$ min.)	
Effect of ultraviolet treatment time on to the greige linen fabric ($X_1 = 40$ g/l; $X_2 = 6$ g/l; $X_3 = 20$ g/l; $X_5 = 17$ cm)	
	
1 min. ($t = 1.728$ sec.)	3 min. ($t = 1.216$ sec.)
Effect of distance between ultraviolet lamp and fabric on to the greige linen fabric ($X_1 = 40$ g/l; $X_2 = 6$ g/l; $X_3 = 20$ g/l; $X_4 = 2$ min.)	
	
10 cm ($t = 0.960$ sec.)	24 cm ($t = 1.088$ sec.)
Effect of hydrogen peroxide concentration on to the greige linen fabric ($X_2 = 3$ g/l; $X_3 = 5$ g/l; $X_4 = 2$ min.; $X_5 = 17$ cm)	
	
20 g/l ($t = 1.472$ sec.)	60 g/l ($t = 1.472$ sec.)
Effect of sodium hydroxide concentration on to the greige linen fabric ($X_1 = 40$ g/l; $X_2 = 3$ g/l; $X_4 = 2$ min.; $X_5 = 24$ cm)	
	
5 g/l ($t = 0.832$ sec.)	35 g/l ($t = 0.192$ sec.)
Effect of sodium peroxydisulphate concentration on to the greige linen fabric ($X_1 = 40$ g/l; $X_3 = 20$ g/l; $X_4 = 1$ min.; $X_5 = 17$ cm)	
	
0 g/l ($t = 1.728$ sec.)	6 g/l ($t = 0.960$ sec.)

Figure 3. The effect of ultraviolet and hydrogen peroxide bleaching on to the linen fabric's wettability properties. Images belong to samples subjected to the contact angle measurement (t = drop penetration time).

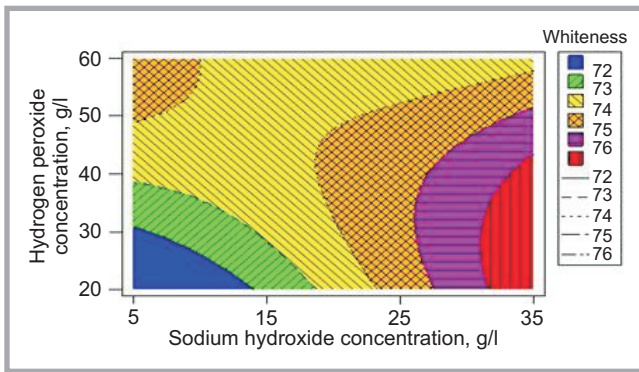


Figure 3. Effect of sodium hydroxide concentration & hydrogen peroxide concentration on the lightness of the greige linen fabric

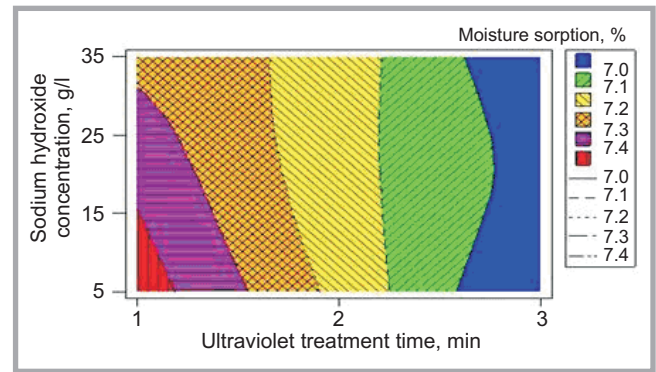


Figure 5. Effect of sodium hydroxide concentration & ultraviolet treatment time on to the moisture sorption values of linen fabrics

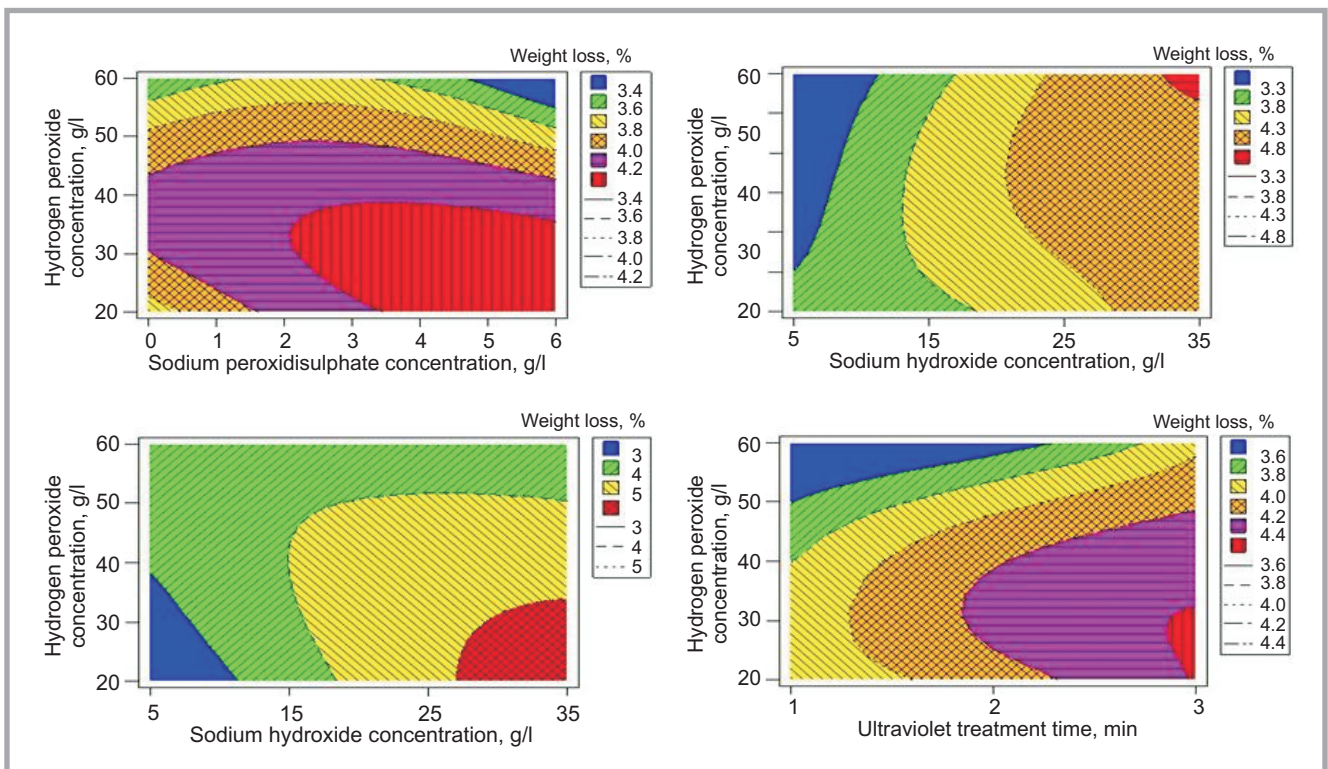


Figure 4. The effect of hydrogen peroxide concentration & sodium peroxydisulphate concentration (a); sodium hydroxide concentration & sodium peroxydisulphate concentration (b); sodium hydroxide concentration & hydrogen peroxide concentration (c); ultraviolet treatment time & hydrogen peroxide concentration (d) on to the weight loss values of linen fabrics

ter wettability properties and lower drop penetration time were obtained with the increase in ultraviolet treatment time and the decrease in the distance between the fabric and ultraviolet lamp. Meanwhile, the increase in sodium hydroxide and sodium peroxydisulphate concentration supplied the decrease in drop penetration time. For example; when the sodium hydroxide concentration was increased from 5 g/l to 35 g/l, the drop penetration time decreased from 0.832 to 0.192 s. When the contact angle measurements were evaluated in terms of the effect of hydrogen peroxide concentration, it can be told that the photographs of the drops on to the samples treated with 20 and

60 g/l hydrogen peroxide seems differently but, the drop penetration time of the both samples was the same (1.472 s).

Conclusions

Consequently, the application of UV irradiation on hydrogen peroxide impregnated woven linen fabric created a new possibility of having a single process for bleaching. On the other hand, three optimum recipes can be obtained as a result of Box-Behnken Experimental Design;

- If the aim is to achieve maximum $W (> -14$ Stensby), $L^* (> 76$ CIELab), $MS (> 7.4\%)$ and $W_L (> 4.2\%)$, the greige

linen samples should be impregnated with 35 g/l hydrogen peroxide, 35 g/l sodium hydroxide, 5.5 g/l sodium peroxydisulphate and then placed at 14 - 20 cm far away from ultraviolet light lamp and irradiated for 2 minutes with UV.

- If the aim is to achieve mean increase in $W (-19/-24$ Stensby), $L^* (74 - 75$ CIELab), $MS (7.2\%)$ and $W_L (3.8 - 4\%)$, the greige linen samples should be impregnated with 30 g/l hydrogen peroxide, 25 g/l sodium hydroxide, 4 g/l sodium peroxydisulphate and then placed at 14 - 20 cm far away from ultraviolet light lamp and irradiated for 2 minutes with UV.

■ If the aim is to achieve minimum increase in W (< -29 Stensby), L^* (< 72 CIELab), MS (7%) and W_L ($< 3.4\%$), the greige linen samples should be impregnated with 20 g/l hydrogen peroxide, 5 g/l sodium hydroxide, 1 g/l sodium peroxydisulphate and then placed at 22 - 24 cm far away from ultraviolet light lamp and irradiated for 1 minutes with UV.



Acknowledgment

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