(REFEREED RESEARCH)

THE EFFECTS OF ACTIVATOR ON WHITENESS AND HYDROHILITY DURING THE HYDROGEN PEROXIDE BLEACHING

HİDROJEN PEROKSİT AĞARTMASINDA AKTİVATÖRÜN BEYAZLIK DERECESİ VE HİDROFİLLİĞE ETKİSİ

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ABSTRACT

Hydrogen peroxide bleaching is a common bleaching process in the textile finishing. Rate of hydrogen peroxide decreasing is very important for effective, economical and problem-free bleaching process. Optimal temperature, pH, concentrations of hydrogen peroxide and stabilizers are used in the bleaching bath to bleach the cotton fabric effectively. In the study, it is tried to optimize the bleaching recipes in terms of hydrophility and whiteness degree.

Key Words: Bleaching, Hydrogen peroxide, Pretreatment, Activator.

ÖZET

Hidrojen peroksit ağartması günümüzde pamuklu mamullerin ağartılmasında en çok kullanılan yöntemdir. Yeterli, sorunsuz ve verimli bir ağartma için hidrojen peroksitin parçalanma hızı önemlidir. Ağartma sırasında sıcaklık ve pH ayarlayarak ve stabilizatörün ve aktivatörün ilavesiyle en uygun şekilde pamuklu kumaşlar ağartılmaktadır. Bu çalışmada pamuklu kumaşların en iyi beyazlık ve hidrofillik değerlerinin sağlanması amacıyla optimizasyon işlemi yapılmıştır.

Anahtar Kelimeler: Ağartma, Hidrojen peroksit, Ön terbiye, Aktivatör.

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1. INTRODUCTION

Hydrogen peroxide is used in a large number of applications such as bleaching, disinfecting and oxidation processes. It is such an attractive oxidising chemical because its reaction products are oxygen and water. Hydrogen peroxide is the most frequently applied textile bleaching agent because of the environmentally friendly and toxicologically acceptable reaction products – oxygen and water. Hydrogen peroxide bleaching, particularly of cotton, has gained in importance in view of the effluent problems (AOX) caused by hypochlorite bleaching (1-9).

There are a lot of studies about decomposition of hydrogen peroxide. The mechanism of this reaction is still not completely understood. The decomposition of hydrogen peroxide may proceed by both a chain and a non-chain process (7,10). The predominant opinion is that ionic decomposition products of the hydrogen peroxide have a bleaching effect and radical decomposition products cause damage. Dannacher and Schlenker postulate, on the other hand, a direct involvement of the perhydroxyl radical ion as a bleaching agent. Several mechanisms are considered possible with regard to the bleaching effect of hydrogen peroxide:

a) Because bimolecular oxygen has no bleaching effect, oxygen “in statu nascendi” (in the nascent state) is assumed to be an intermediate stage of decomposition from H_2O_2 to O_2, and atomic oxygen (O) is actually produced. Since normal atmospheric oxygen has no corresponding bleaching effect, it is conceived that a reactive progenito is formed in decomposition and then converted into harmless oxygen. It is called as active oxygen in older literature (8).

b) Though hydrogen peroxide is stable in acidic medium, but bleaching occurs by the addition of alkali or by increased temperature. If alkali is added to an aqueous hydrogen peroxide solution, perhydroxyl anions are formed. The perhydroxyl is highly unstable and in the presence of oxidisable substance (coloured impurities in cotton), it is decomposed and thus bleaching action takes place. Sodium hydroxide activates hydrogen peroxide because H^+ ion is neutralised by alkali which is favourable for liberation of HO_2^-.

The activation energy of the characteristic decomposition is reduced in alkaline liquors. Cellulose is broken down via radical mechanisms, preferably forming keto groups in the process. The chain scission will then occur via a nucleophile substitution by the perhydroxyl anion. However, a reaction chain is conceivable which commences with a hydrogen peroxide adduct; Fe^{3+} will increase the speed of this process, but produce the same end products. The bleaching reaction can be initiated by nucleophile substitution by means of the perhydroxyl anion. Conversely, chromophores also act as free-radical scavengers, with the result that, besides the bleaching effect of the radicals, the breakdown of the cellulose by dyes is generally prevented. Perhydroxyl anion HO_2^- functions as a nucleophile and can therefore be added to an electrophile carbonyl group. The peroxidation mechanism may correspond to a Dakin rearrangement (Figure 1). The decomposition of the hydrogen peroxide develops according to the equations (8,11).

c) Hydroxyl radical is formed with radical decomposition of H_2O_2. The pH dependency of the bleaching effect recalls the speed at which the decomposition of hydrogen peroxide develops. It is assumed that this decomposition occurs in a radical chain reaction. This reaction is started by the transfer of an electron by an electron donator to hydrogen peroxide. The closed loop of hydrogen peroxide decomposition is interrupted by the recombination of two radicals.

The intermediate radicals here (the hydroxyl radical and the perhydroxyl radical) have likewise been postulated to be the species of hydrogen peroxide bleach active in the bleaching (8).

d) Perhydroxyl radicals are very acidic, comparable with acetic acid: they are therefore almost totally dissociated in the pH range of the bleaching maximum. Dannacher and Schlenker rejected the role of the perhydroxyl anion in bleaching because of a belief that there is an optimum pH beyond which bleaching decreases. But these authors also point out that this has not been substantiated experimentally. This pH dependence of H_2O_2 bleaching suggests that the perhydroxyl anion is not the active bleaching agent. They purposed instead that the active oxygen is the superoxide radical $^{\bullet}O_2^-$, formed in an alkaline medium from the perhydroxyl radical. The relationship they use to estimate the concentration of this radical is not clearly defined but has a lot of similarity to that used by Duke and Haas to measure the decomposition of H_2O_2 (8,10).

Peroxide bleaching systems contain regulators to reduce fibre damage and oxygen release. The process of regulation or control of perhydroxyl ion prevents rapid decomposition. Stabilisers must be added to the liquor in order to prevent H_2O_2 decomposition in the liquor under textile bleaching conditions (particularly with increased temperature and alkaline activation). The use of organic activators to enhance the bleaching performance of hydrogen peroxide for cellulosic materials is well known. They are urea, some kinds of amide and cationic activator. Such activators work by generating more kinetically active bleaching species in situ using a reaction between the activator and hydrogen peroxide under the bleaching conditions. The advantage of using an activated peroxide system is that bleaching can be achieved under milder conditions (for instance, at lower temperature, lower pH, shorter treatment time and lower peroxide concentration), thereby minimising the degradation of the desirable qualities of the fibre material (8, 10, 11, 12).

$$H_2O_2 + HOO^{\ominus} \longrightarrow H_2O + HO^{\ominus} + O_2$$

or

$$H_2O_2 + HOO^{\ominus} \longrightarrow {}^{\bullet}OH + H_2O + {}^{\bullet}O_2^{\ominus}$$

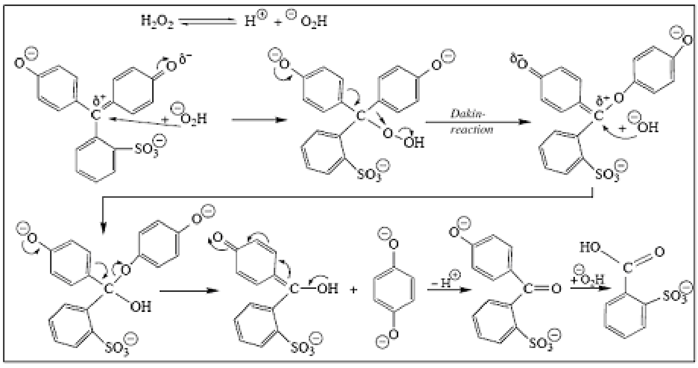

Figure 1. Oxidation mechanism involving the perhydroxyl anion

start: $H_2O_2 + \text{donator} \rightleftharpoons HO^{\ominus} + HO^{\bullet} + D^{\oplus}$

chain: $H_2O_2 + HO^{\bullet} \longrightarrow HO_2^{\bullet} + H_2O$

$H_2O_2 + HO_2^{\bullet} \longrightarrow H_2O + HO^{\bullet} + O_2$

termination: $2\,HO^{\bullet} \longrightarrow H_2O_2$

Table 1. The levels of factors for central composite design

Factors	Levels				
	-2	-1	0	1	2
X_1- Concentation of activator (ml/l)	0	0,5	1,0	1,5	2,0
X_2-Concentation of hydrogen peroxide (ml/l)	0,5	2,0	3,5	5,0	6,5
X_3- Temperature (˚C)	64	72	80	88	96
X_4- Duration (min)	30	40	50	60	70

Table 2. Central Composite Experimental Design for bleaching of cotton fabrics

	X_1	X_2	X_3	X_4
1	-1	-1	-1	-1
2	1	-1	-1	-1
3	-1	1	-1	-1
4	1	1	-1	-1
5	-1	-1	1	-1
6	1	-1	1	-1
7	-1	1	1	-1
8	1	1	1	-1
9	-1	-1	-1	1
10	1	-1	-1	1
11	-1	1	-1	1
12	1	1	-1	1
13	-1	-1	1	1
14	1	-1	1	1
15	-1	1	1	1
16	1	1	1	1

	X_1	X_2	X_3	X_4
17	-2	0	0	0
18	2	0	0	0
19	0	-2	0	0
20	0	2	0	0
21	0	0	-2	0
22	0	0	2	0
23	0	0	0	-2
24	0	0	0	2
25	0	0	0	0
26	0	0	0	0
27	0	0	0	0
28	0	0	0	0
29	0	0	0	0
30	0	0	0	0

Table 3. Analysis of variance for whiteness degree

Source	DF	SS	MS	F	P
Regression	5	188,390	37,678	116,85	0,000
Residual Error	24	7,738	0,322		
Total	29	196,129			
Source	DF	Seq SS			
Hydrogen peroxide	1	66,817			
$Activator^2$	1	7,800			
Activator *duration	1	105,751			
Activator *temperature	1	2,316			
Temperature *duration	1	5,706			

The aim of the study is optimization and modeling of activator usage in terms of hydrophility and whiteness degree statistically.

2. MATERIAL AND METHOD

Single jersey 100% cotton knitted fabric (30/1) weighing 138 g/m2 was used for these experiments. Bleaching processes were performed on a jet type sample dyeing machine with a capacity of 30 g and liquor ratio was 1/20. Then a central composite experimental design was used to determine an estimated optimized bleaching recipe (Table 1 and Table 2). The bleaching recipe contains 0,5 g/l of caustic soda and 0,2 ml/l of organic stabilizer in addition to variables in table 1. After bleaching, the fabrics was rinsed at 95 ˚C for 10 min. and washed in detergency solution at 55 ˚C. Finally cold rinsing was performed.

In order to evaluate the results obtained, the wettability of the fabrics was determined according to DIN 53924 and whiteness of fabrics was examined with a Minolta 3600d spectrophotometer according to the Stensby formula.

3. RESULTS AND DISCUSSION

3.1 Effects of Factors on Whiteness Degree

The regression equation is

Whiteness = 57,2 + 1,11 hydrogen peroxide - 4,23 $activator^2$ + 0,116 activator *duration+ 0,0263 activator *temperature + 0,000767 temperature *duration

All the factors and coefficients of regression equation is analysed and regression coefficient is 95,2% for the 95% confidence interval of the difference. According to variance analysis, F value is very high and P value is zero. So regression equation and all the factors are significant.

3.1.1 Effects of activator and hydrogen peroxide on whiteness degree

Whiteness degree is the highest on the red area and the lowest values are on the blue one.The best whiteness values were obtained with 6,5 ml/l hydrogen peroxide and 1-1,5 ml/l activator. After this critical value, an increase in concentration of activator caused the whiteness to decrease gradually. It is thought that increasing in concentration of activator increased decomposition of hydrogen peroxide.

3.1.2 Effects of activator and duration on whiteness degree

The highest whiteness degree was obtained with 1-1,5 ml/l activator and 70 min of processing. Whiteness of fabrics decreased with less than 1 ml/l and more than 1,5 ml/l activator.

3.1.3 Effects of duration and hydrogen peroxide on whiteness degree

The highest whiteness degree was obtained with 6,5 ml/l hydrogen peroxide and 70 min of bleaching. Increasing of duration and amount of hydrogen peroxide improved the whiteness of the samples. Colour substances decomposed increasingly because of long duration of process and high concentration of hydrogen peroxide.

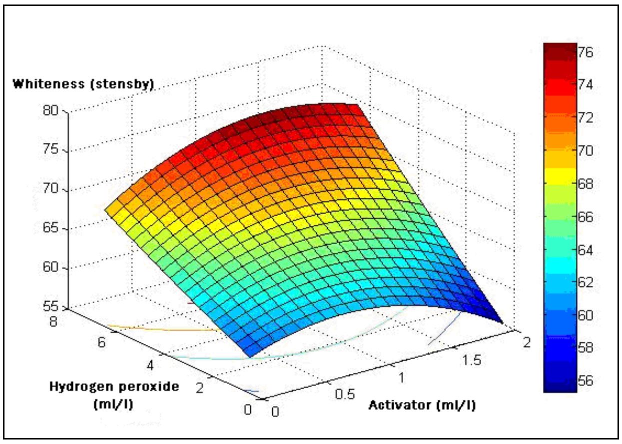

Figure 2. Effects of activator and hydrogen peroxide on whiteness degree

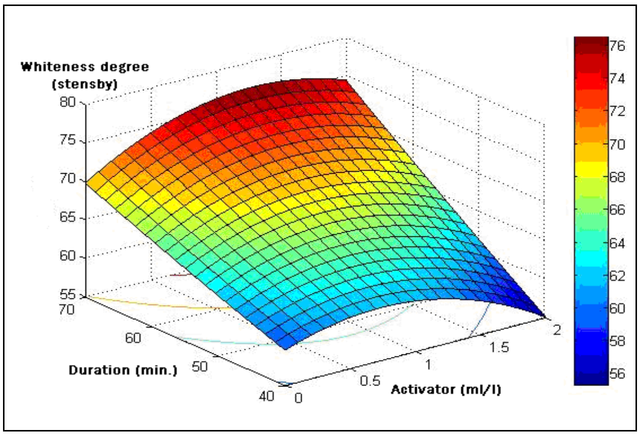

Figure 3. Effects of activator and duration on whiteness degree

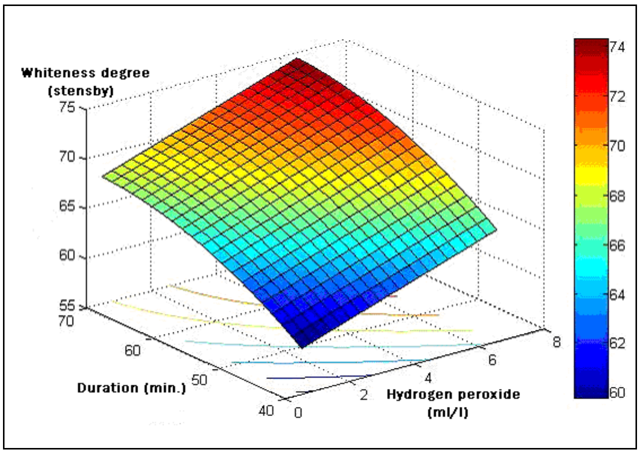

Figure 4. Effects of hydrogen peroxide and duration on whiteness degree

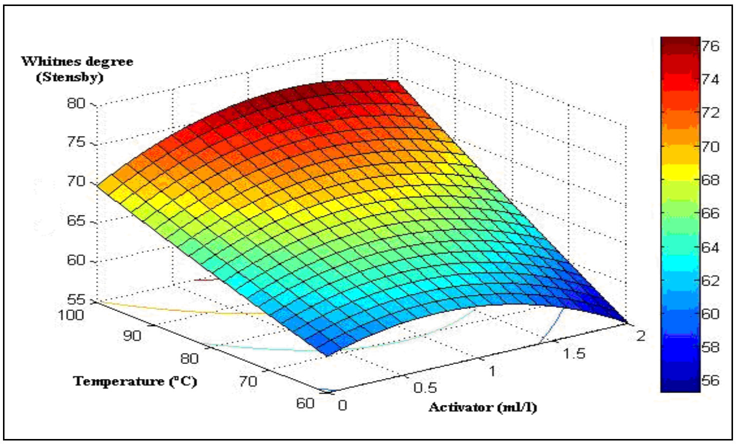

Figure 5. Effects of activator and temperature on whiteness degree

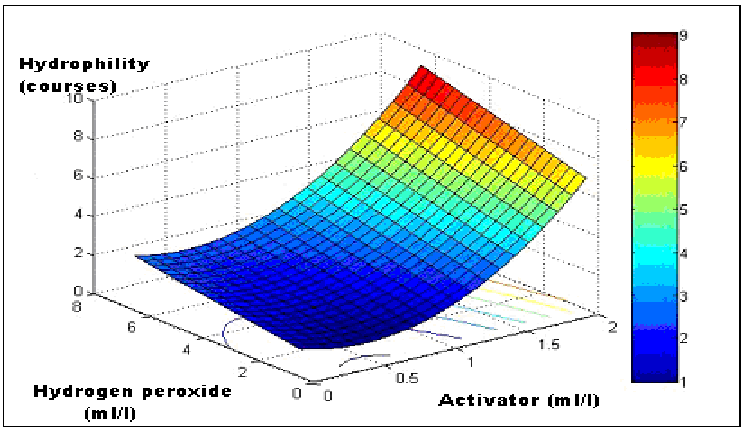

Figure 6. Effects of activator and hydrogen peroxide on hydrophility of knitted fabrics in the direction of courses

Table 4. Analysis of variance for Hydrophility of knitted fabrics in the direction of courses

Source	DF	SS	MS	F	P
Regression	5	39,5165	7,9033	72,45	0,000
Residual Error	24	2,6181	0,1091		
Total	29	42,1347			
Source	DF	Seq SS			
Temperature	1	0,3541			
Activator^2	1	2,0863			
Temperature ^{2}	1	6,6471			
Activator *duration	1	25,6505			
Hydrogen peroxide*duration	1	4,7786			

3.1.4 Effects of temperatur and activator on whiteness degree

According to Figure 5, the highst whiteness was carried out at 96 ^{0}C and the concentration of activator were between 1 and 1,5 ml/l. Whiteness degree decreased with less than 1 ml/l of activator because of inadequate decreasing of hydrogen peroxide. On the other hand more than 1,5 ml/l of activator effected whiteness of samples negatively. Because decreasing of hydrogen peroxide was excessive.

3.2. Effects of Factors on Hydrophility of Knitted Fabrics in the Direction of Courses

The regression equation is

Hydrophility of knitted fabrics in the direction of courses (cm) = 41,0 - 1,07 temperature (°C) - 1,32 activator^2 + 0,00681 temperature^2 + 0,0694 Activator*duration + 0,00565 Peroxide* duration

All the factors and coefficients of regression equation is analysed and regression coefficient is 92,5% for the 95% confidence interval of the difference. According to variance analysis, F value is very high and P value is zero. So regression equation and the factors are significant.

3.2.1 Effects of activator and hydrogen peroxide on hydrophility of knitted fabrics in the direction of courses

The highest hydrophility value was obtained with 5 ml/l activator and 6,5 ml/l hdydrogen peroxide. Increasing of hydrogen peroxide concentration caused the hydrophility to improve because hydrogen peroxide extracted wax and oil from the cotton fabric. Although an increase in activator concentration decreased whiteness degree of the fabric, content of detergency in the activator improved the hydrophility.

3.2.2 Effects of activator and duration on hydrophility of knitted fabrics in the direction of courses

As seen in Figure 7, the highest hydrophility values were obtained from 1,5-2 ml/l activator in 70 minutes.

3.2.3 Effects of duration and hydrogen peroxide on hydrophility of knitted fabrics in the direction of courses

According to Figure 5, the best hydrophility values were carried out the concentration of hydrogen peroxide were between 4,5 and 6,5 ml/l for 70 minutes processing time.

3.2.4 Effects of activator and temperature on hydrophility of knitted fabrics in the direction of courses

The highest temperature (96 °C) and 1,5-2 ml/l activator maximized the hydrophility.

3.2.5 Effects of peroxide and temperature on hydrophility of knitted fabrics in the direction of courses

The highest hydrophility values were carried out at 96 ^{0}C and the concentration of hydrogen peroxide were between 4 and 6,5 ml/l. Because high temperature and hydrogen peroxide concentration extracted natural impurities like wax and oil.

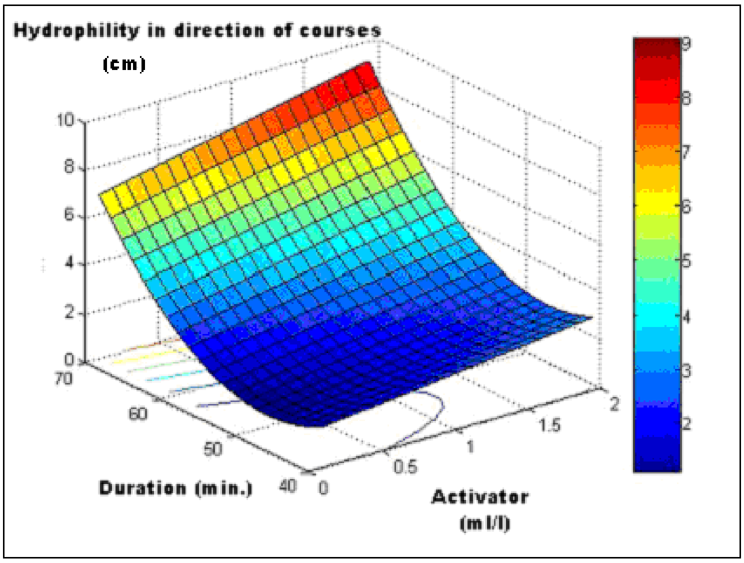

Figure 7. Effects of activator and duration on hydrophility of knitted fabrics in the direction of courses

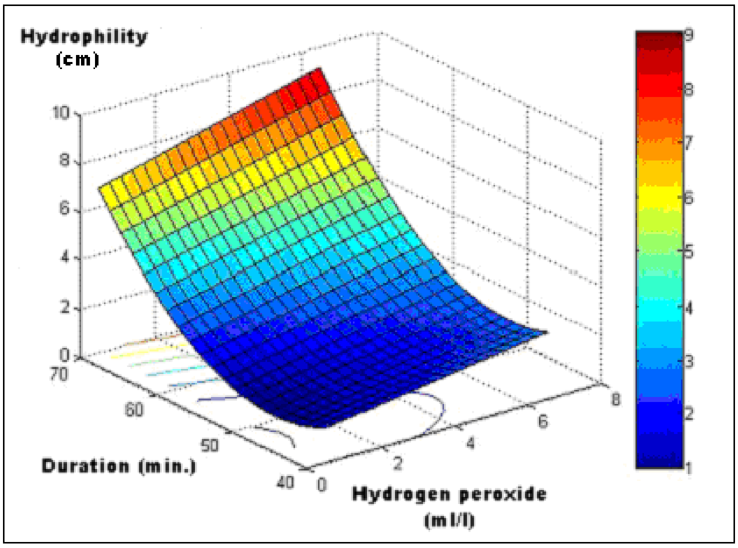

Figure 8. Effects of hydrogen peroxide and duration on hydrophility of knitted fabrics in the direction of courses

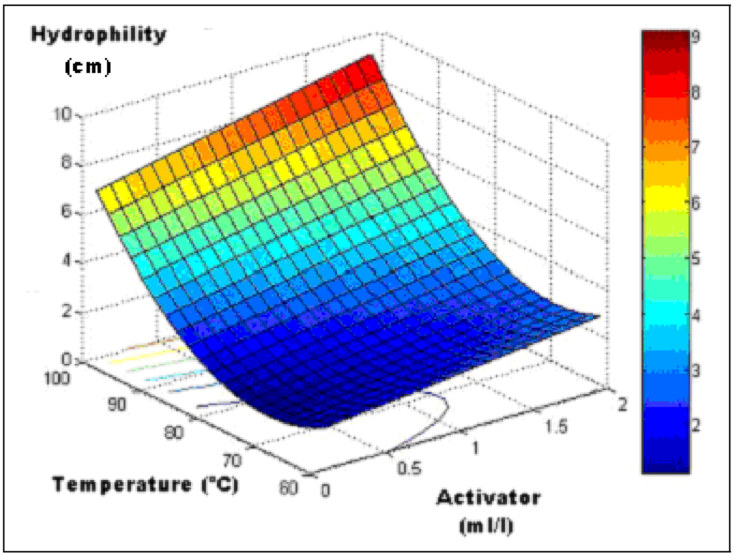

Figure 9: Effects of temperature and activator on hydrophility of knitted fabrics in the direction of courses

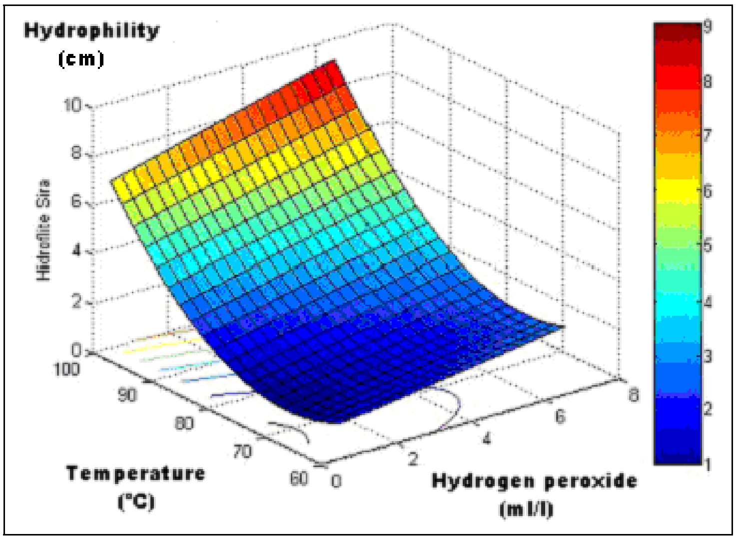

Figure 10: Effects of temperature and hydrogen peroxide on hydrophility of knitted fabrics in the direction of courses

Table 5. Analysis of variance for Hydrophility of knitted fabrics in the direction of wales

Source	DF	SS	MS	F	P
Regression	4	38,0885	9,5221	20,13	0,000
Residual Error	25	11,8273	0,4731		
Total	29	49,9157			
Source	DF Seq SS				
Peroxide^2	1 8,3545				
Temperature^2	1 2,2625				
Activator *duration	1 14,7387				
Activator*temperature	1 12,7328				

3.3 Effects of Factors on Hydrophility of Knitted Fabrics in the Direction of Wales

The regression equation is Hydrophility of knitted fabrics in the direction of wales (cm) = - 3,10 + 0,0548 Peroxide^2 + 0,000520 temperature^2 + 0,0894 Activator*duration - 0,0450 Activator* temperature

All the factors and coefficients of regression equation is analysed and regression coefficient is 72,5% for the 95% confidence interval of the difference. According to variance analysis, F value is P value is zero. So regression equation and the factors are fairly significant.

Regression coefficient of hydrophility in the direction of course was higher than that of wale, because of the structure of knitted fabric. The solution used for the hydrophility test ran off the same yarn in the direction course. But wales made of individual yarn. So the solution ran off different yarns during the test.

All the results weren't informed in the paper because of lower regression coefficient than the other.

4. CONCLUSION

All the regression equations and the factors were important. They were

Whiteness = 57,2 + 1,11 hydrogen peroxide - 4,23 activator^2 + 0,116 activator *duration+ 0,0263 activator *temperature + 0,000767 temperature *duration

Hydrophility of knitted fabrics in the direction of courses (cm) = 41,0 - 1,07 temperature (°C) - 1,32 activator^2 + 0,00681 temperature^2 + 0,0694 Activator*duration + 0,00565 Peroxide*duration

Hydrophility of knitted fabrics in the direction of wales (cm) = - 3,10 + 0,0548 Peroxide^2 + 0,000520 temperature^2 + 0,0894 Activator* duration - 0,0450 Activator*temperature

The equations were checked by control tests in the table 6. Actual values were too close to predicted values for control trials. So the regression equations and experimental design were very significant and effective.

Increasing of hydrogen peroxide and activator concentrations, temperature and duration improved the hydrophility and whiteness degree generally. But the highest whiteness degrees were obtained by 1 and 1,5 ml/l of activator. Bleaching bath contained more concentrated activator decreased the whiteness degree of the fabric.

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Table 6: Control tests

	Recipes	Actual value			Predicted value		
		Whiteness degree	Hydrophility (course)	Hydrophility (wale)	Whiteness degree	Hydrophility (course)	Hydrophility (wale)
Control 1	1 ml/l Activator 4 ml/l H_2O_2 70˚C and 45 min	66,981	2,183 cm	1,209 cm	66,887	2,109 cm	1,197 cm
Control 2	0,5 ml/l Activator 5 ml/l H_2O_2 80˚C and 50 min	68,801	1,721 cm	2,007 cm	68,712	1,702 cm	2,023 cm

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