ARTICLE

COMPARATIVE STUDY OF THE CHELATING AGENTS INFLUENCE ON THE WEIGHT LOSS OF COTTON FABRICS DURING ENZYMATIC SCOURING

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Abstract: *The proposed study offers an alternative to classical cotton fabrics scouring treatment. It is based on reagents and process utilization with low environmental impact. The experimental design studies the weight loss of cotton fabric during enzymatic scouring in ultrasound media due to the variation of two independent factors at five levels: enzyme concentration weight over fiber (1, 1.3, 2, 2.7, and 3 %) and treatment time (15, 21, 35, 49 and 55 min.), using two complexing agents individually (EDTA or sodium citrate at 2g/L). The weight loss of cotton fabric (dependent variable) was expressed in the percentage from the initial weight. The polynomial equations obtained by multiple regression analysis indicate that the influence of the two factors on the studied intervals decreases in order: time>enzyme concentration when EDTA is used, and vice versa in the case of sodium citrate. In the studied intervals of the variables, the weight loss varies between 0.43-2.40 % in the EDTA version and 0.77-1.79 % in the sodium citrate version. Response surface graphics for the two variants of complexants show how much enzyme concentration and time can be reduced in the process to obtain a suitable scouring treatment. Analyzing the obtained results, we consider sodium citrate a viable alternative for bioscouring from technological and environmental aspects.*

Keywords: bioscouring, chelating agents, pectinases, multiple regression analysis, optimization.

INTRODUCTION

There were considered the aspects regarding the environment, costs, and fiber structural damages. Green approaches to classical industrial processes and technologies are continually developed in the last decade. This trend is well represented also in the textile industry, known as environment and human health harmful due to the high quantity of chemicals present in the wastewaters. (Dey et al. 2015, Sarayu et al. 2012, Djehaf et al. 2017). Thus, in the finishing of the cotton, the simple step of samples washing in boiling water facilitates the pectinases access to the substrate, thus contributing to the increase of the hydrolysis reaction yield (Wang et al. 2007). The same principle is also based on the influence of ultrasound (US) on the bioscouring treatment (Erdem et al. 2018). Due to the cavitation effect, the diffusion of enzyme molecules in the textile substrate is improved by using ultrasound energy, shortening the reaction time and the amount of enzyme used (Yachmenev et al. 2002).

An eco-friendly vision should involve all industrial processes. This perspective is found in the fabrics manufacturing units. The concern for cleaner treatments is present from the first steps, meaning scouring.

It is an important preparative phase step in the technological flow. It assumes removing different noncellulosic attendants (wax, dust, pigments, pectin, lignin) on the natural fibers. Many studies underline the possibility of successfully replacing the alkaline scouring treatment with the enzymatic one.

For cotton, single or combined enzymes were used to hydrolyze the pectin (Rajulapati et al. 2020, Shanmugavel et al. 2018, Hebeish et al. 2009) or polymerized esters of different fatty acids and pectin (Hong et al. 2019). After such treatment, the fabrics' technical parameters were comparable (Rajulapati et al. 2020) or improved compared with the classical treatment (Shanmugavel et al. 2018).

For bioscouring treatment, pectinases were found to be the most effective. So far, many studies have been done with different pectinases to optimize cotton scouring. In the beginning, one disadvantage was the prolonged treatment time, but the development of new pectinases and auxiliaries made the process more feasible for industrial-scale application (Madhu and Chakraborty 2017).

In the pretreatments of cellulosic fabrics, besides enzymes, the complexing and sequestering agents like EDTA are used to bind Ca^{2+} ions and enhance the efficiency of enzymes, to accelerate the removal of non-cellulosic impurities from the textile support (Csiszár et al. 2001, Hebeish et al. 2012). EDTA has a high affinity for most of the metal ions but is a non-biodegradable compound, and the activity of some enzymes like pectate lyases depends on the amount of calcium ions; thus, the effectiveness of the bioscouring could be affected by the total removal of Ca^{2+} ions (Chiliveri and Linga 2014).

Various approaches with promising results on the use of sodium citrate as a complexing agent in the bioscouring treatment of cellulosic and lignocellulosic fabrics have been developed by Dochia et al. Sodium citrate is an eco-friendly biodegradable complexing agent that could successfully replace EDTA in the bioscouring process (Dochia et al. 2016, Dochia et al. 2018a, Dochia et al. 2018b).

The fabric weight loss was one of the parameters evaluated to establish the bioscouring efficiency, as a difference before and after the treatment.

It is a significant factor because it indicates the overall degradation impact of the applied treatments and is relevant for subsequent finishing operations influencing the fabric's quality, comfortability, and other properties (Bahrum Prang Rocky 2012).

The purpose of our study was to compare the effects of the two chelating agents (EDTA and sodium citrate) on the weight loss of cotton fabrics and to establish the best experimental conditions for bioscouring treatments using mathematical models and response surface methodology (RSM).

MATERIALS AND METHODS

Materials

For the bioscouring treatment, 100% cotton fabric was used. The technical specifications were the follows 150±3 cm width and 200±10 g/m^2 weight, 25/2 Ne (Number English) on warp yarns, and 25/1 Ne on weft yarns.

The enzymatic treatment bath contained: Beisol PRO, a commercial pectinases mixture, and the Denimcol Wash RGN surfactant purchased from CHT Benzema. Sodium citrate (monosodium citrate, CAS: 18996-35-5) and EDTA (ethylenedinitrilotetraacetic acid-disodium salt, CAS: 6381-92-6) were provided by Sigma-Aldrich.

Methods

Cotton fabrics pretreatment

Naturally, cotton fabrics have physically bind impurities that need to be removed before the specific technological treatments. In this regard, the samples were subjected to water washing in an AATCC standardized Lander-Ömeter, model M228-AA from SDL Atlas Company-USA at 100°C, followed by room temperature drying. For the conditioning of the samples, the drying method (water evaporation) of the samples was used until a constant mass was obtained. For this, the Sartorius MA 100 balance was utilized.

Bioscouring treatment

The reaction was developed in an ultrasound media at 45 kHz. A 1:20 fabric to liquid ratio was used. The enzymatic product content in the treatment bath varied between 1-3% (1, 1.3, 2, 2.7, and 3 % o.w.f.), and the hydrolysis time was between 15-55 min (15, 21, 35, 49, and 55 min.), at 55°C (see Table 1).

There were also used 2g/L of complexing agents: monosodium citrate (~10 mmol·L^{-1}) or EDTA(~ 5 mmol·L^{-1}) and 0.5% surfactant (Denimcol Wash RGN). The reason for using two different molar concentrations of complexing agents was explained in a previous paper (Dochia et al. 2018).

The pectinases were inhibited after the time expired, keeping the samples for 15 min. in hot water at 80°C. Then, they were washed several times with cold distilled water, dried at room temperature, and afterward weighed after drying at 105 ^{o}C until constant mass in a Sartorius MA100 balance.

The weight loss determination

The weight loss evaluation was done using the modified IS:1383-1977 standard. To avoid the influence of water absorbed from the atmosphere, the samples were dried at 105 ^{0}C until constant mass in a Sartorius MA100 balance. The results were obtained based on gravimetric determinations and the percentage of weight loss was calculated according to equation (1):

%weight loss=(W1-W2) x 100/W1 **(1)**

where: W1, W2 - dried samples fabric weights before and after bioscouring.

The calculated values represent the amount of non-cellulosic attendants (pectin) removed from the fabrics after bioscouring treatment.

Design of experiments (DOE)

A fractional factorial experiment, with two independent variables, X_1 (enzyme concentration) and X_2 (treatment time), using a variable-centered approach at five variation levels, was used to study their effect on the weight loss of cotton (dependent variable) during enzymatic scouring in ultrasound media. Two variants of the process were used, one with EDTA and another with sodium citrate (SC) as chelating agents. The variable values, X_1 and X_2, and corresponding encodings, x_1 and x_2, are presented in Table 1.

Table 1. Independent variable values of the process, the corresponding levels, and their codification

	Independent variables		
	Cod	Enzyme conc. (% o.w.f)	Time (min.)
	x_i	X_1	X_2
Level	-1	1	15
	-0.7	1.3	21
	0	2	35
	0.7	2.7	49
	1	3	55

Data analysis

The multiple regression procedure and analysis of variance (ANOVA) from MS Excel 2019 software was used (Home Page of Excel 2019). The codified and experimental data (Table 2) were fitted to a polynomial model and

regression coefficients were obtained. The generalized polynomial model used for establishing the importance and interaction of the studied factors was as follows:

$$Yi = \beta_0+\beta_1x_1+\beta_2x_2+\beta_{12}x_1x_2+\beta_{11}x_1^2+\beta_{22}x_2^2 \quad \textbf{(2)}$$

Where: Yi is predicted response, β_0 is intercept, β_1, β_2, β_{11}, *and* β_{22} are linear and quadratic effect terms, and β_{12} is interaction effects.

RESULTS AND DISCUSSIONS

Yi data analysis

ANOVA of *Yi* series of experimental values, corresponding to the variants with EDTA and SC (Tabs. 2 and 4), show that they differ significantly (hypothesis H_1). Both the *Fischer* test and the *P-value* confirm this hypothesis:

$$F = 3.63 > 2.60 = F_{crit}$$

$$P\text{-}value = 0.014 < 0.05$$

Consequently, enzyme concentration and treatment time are significant factors for cotton's ultrasonic enzymatic scouring process using EDTA and SC complexing agents.

Fitting the model

The multiple regression equation obtained with MS Excel 2019 is an empirical relationship between the weight loss of cotton (% from the initial weight) and the two factors in coded units. The significance of each coefficient was appreciated using the *Student t-test* and *P-value*. The corresponding variables will be more significant if the absolute *t-Stat* value is larger or the *P-value* is smaller (Home Page of NIST/SEMATECH, 2013). The fractional factorial experiment and the results for the two variants of complexing agents are mentioned in Tables 2 and 4.

Table 2. Fractional DOE for EDTA variant, the observed responses, and predicted values for weight loss of cotton fabric

EDTA	Variable levels		Experimental	Predicted
	x_1	x_2	Yi (%)	Yi (%)
1	-0.7	-0.7	0.48	0.60
2	0.7	-0.7	0.59	0.70
3	-0.7	0.7	0.64	0.92

4	0.7	0.7	1.63	1.90
5	-1	0	0.51	0.65
6	1	0	1.27	1.42
7	0	-1	0.44	0.49
8	0	1	1.75	1.57
9	0	0	1.04	1.03
10	0	0	1.01	1.03
11	0	0	1.01	1.03
12	0	0	1.02	1.03
13	0	0	1.08	1.03

Table 3. Significance of regression coefficients for weight loss of cotton fabric (% from the initial weight) for EDTA variant

Coefficients		*t Stat*	*P-value*
β_0	1.032	18.73	3.06983E-07
β_1	0.384	6.21	0.000440618
β_2	0.540	8.72	5.21848E-05
β_{12}	0.445	3.54	0.009425801
β_{11}	-0.220	-2.35	0.051318147
β_{22}	-0.015	-0.16	0.874465109

The coefficients β_{11}, β_{22} , , and their *t-Stat* are small, and their *P-value* is big (Table 3), so the corresponding terms can be neglected. The equation for the EDTA variant becomes:

$$Yi = 1.032+0.384x_1+0.54x_2+0.445x_1x_2 \quad \textbf{(3)}$$

The plus sign of the coefficients indicates a direct action of factors on the weight loss. The action of the factor is stronger if the absolute value of its coefficient is greater. Consequently, the significance of the factors decreases in the order x2>x1 in studied intervals, and there is an interaction between them, x1x2>0 (Table 3).

Table 4. Fractional DOE for SC variant, the observed responses, and predicted values for weight loss of cotton fabric

SC	Variable levels		Experimental	Predicted
	x_1	x_2	*Yi* (%)	*Yi* (%)
1	-0.7	-0.7	0.87	1.05
2	0.7	-0.7	0.56	0.97
3	-0.7	0.7	0.87	0.95
4	0.7	0.7	1.21	1.52
5	-1	0	0.85	0.95
6	1	0	1.52	1.30
7	0	-1	0.99	0.97
8	0	1	1.16	1.28
9	0	0	1.01	1.13
10	0	0	1.18	1.13
11	0	0	1.27	1.13
12	0	0	1.16	1.13
13	0	0	1.02	1.13

Table 5. Significance of regression coefficients for weight loss of cotton (% from the initial weight) for SC variant

Coefficients		*t Stat*	*P-value*
β_0	1.125	12.02	6.28437E-06
β_1	0.177	1.68	0.136442878
β_2	0.158	1.50	0.176812475
β_{12}	0.334	1.56	0.161691597
β_{11}	-0.063	-0.40	0.704594935
β_{22}	-0.180	-1.13	0.296410667

The coefficients β_{11}, β_{22}, and their *t-Stat* are small, and their *P-value* is big (Table 5), so the corresponding terms can be neglected. The equation for the SC variant becomes:

$$Yi = 1.125+0.177x_1+0.158x_2+0.334x_1x_2 \quad \textbf{(4)}$$

The significance of the factors decreases in the order $x_1>x_2$ in studied intervals, and there is an interaction between them, $x_1x_2>0$ (Table 5).
These relations were verified by comparing the experimental values with the calculated values. The correlation coefficients illustrate the agreement of these values: 0.95 for equation **(3)** and 0.69 for equation **(4)**. The accuracy offered by experiments and measurements is better in the case of the EDTA variant than the one with SC. ANOVA also confirms that the series of experimental and predicted values (Tabs. 2 and 4) are similar for both variants (Tab. 6).

Table 6. *P-value*>0.05 and $F<F_{crit}$ for the experimental and calculated value series shows the validity of the H_0 hypothesis, that the compared series are not different

Variant	*P-value*	*F*	*F crit*
EDTA	0.659	0.199	4.260
SC	0.370	0.835	4.260

Analysis of response surfaces

The relationship between independent and dependent variables is illustrated in a three-dimensional representation of the response surfaces generated by the models for the weight loss of cotton (Myers & Montgomery, 2002). The coordinates of the highest points on the surfaces correspond to the values of the factors that ensure the maximum weight loss of cotton fibers. For the variant with EDTA, the surface in Fig.1 indicates that the maximum ($Y_{\max}$=2.40 %)

is reached at a marginal point: enzyme concentration (X_1, 3% o.w.f) and temperature (X_2, 55°C). This maximum point can be calculated with equation **(3)** for x_1=1 and x_2=1. For the variant with SC as a complexing agent, the surface from Fig.2 indicates the maximum at Y_{max}=1.79% for the same values of independent factors, enzyme concentration (X_1, 3% o.w.f) and temperature (X_2, 55°C).

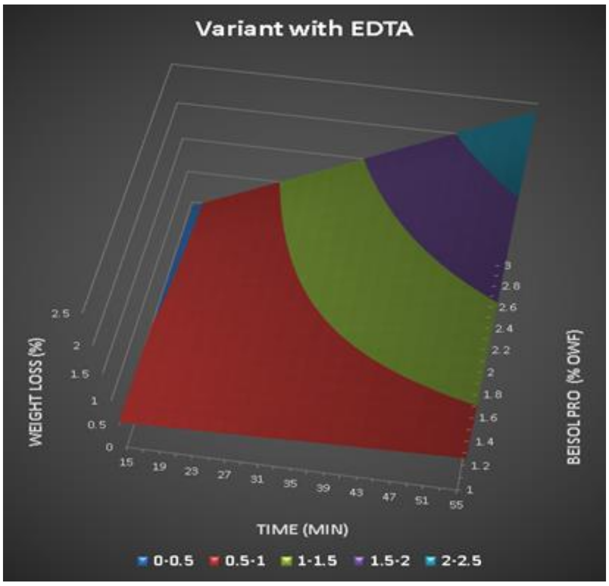

Fig. 1 Response surface plot (Eq.3) showing the effect of Beisol PRO concentration and treatment time at a constant EDTA concentration (2g/L), on the weight loss of cotton fabrics during enzymatic scouring in ultrasound.

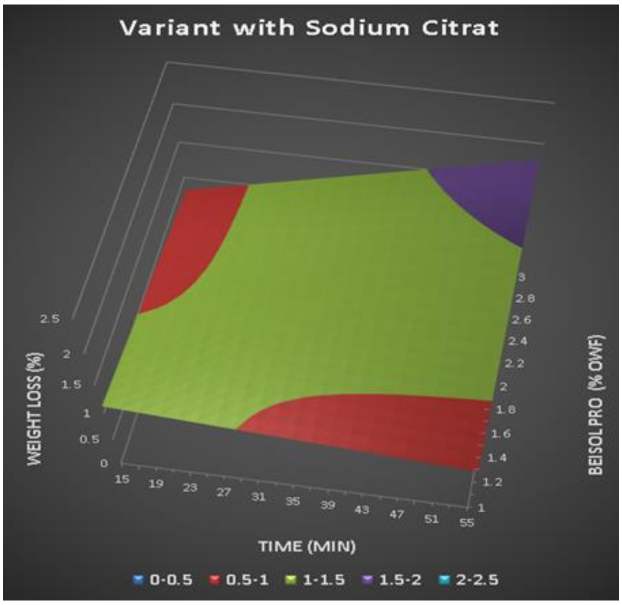

Fig. 2 Response surface plot (Eq.4) showing the effect of Beisol PRO concentration and treatment time at a constant sodium citrate (SC) concentration (2g/L), on the weight loss of cotton fabrics during enzymatic scouring in ultrasound.

For the minimum weight loss values, the EDTA variant also offers the extreme value, Y_{min}=0.43% (for x_1=1 and x_2=-1) compared to that of the SC variant, Y_{min}=0.77 % (for x_1=-1 and x_2=1).

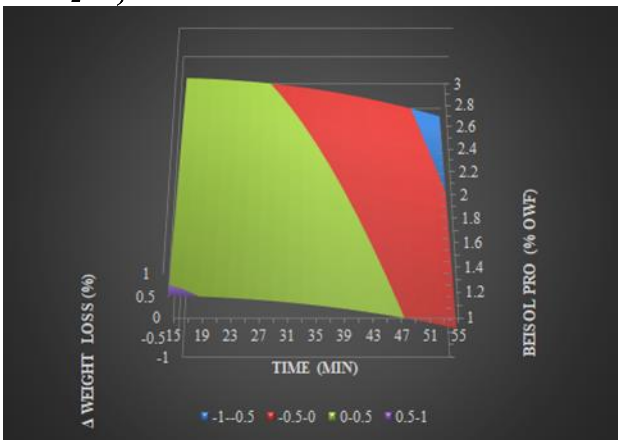

Fig. 3 Response surface plot (Eq.5) showing the effect of Beisol PRO concentration and bioscouring time on the weight loss difference of cotton fabrics using SC and EDTA complexing agents.

The response surface plot could be used to establish how much Beisol PRO concentration and work time can be reduced to get the desired treatment degree. To optimize the process so that enzymes' Beisol PRO consumption and treatment time is minimal was calculated and represented the response area (Fig. 3) corresponding to the difference regarding weight loss between the variant with SC and the one with EDTA. For this purpose, was used equation **(5)**, that results from multiple regression and ANOVA:

$$\Delta Yi = 0.0931-0.2076x_1-0.3822x_2-0.1647x_1x_2 \quad \textbf{(5)}$$

The green and purple area of the surface indicates positive values of this difference (Fig.3), they are being placed at low values of enzyme concentration and treatment time. This indicates a faster complexation performed by SC than EDTA, thus facilitating easier access of the pectinases to the substrate. The sodium citrate molecules have a lower molecular volume than EDTA and can more easily diffuse into the "egg-box" structure. Also, the diffusion process of complexing agent molecules was favoured by the presence of ultrasound. On the other hand, the enzymatic activity decreases more pronounced with increasing time when using SC compared to EDTA.

CONCLUSIONS

The multiple regressions and the response surface methodology were successfully used to control the weight loss of cotton fabrics during ultrasound bioscouring. The use of sodium citrate as a complexing agent is a promising alternative to the classical one because it ensures an acceptable degree of complexation in a shorter time with low consumption of the enzyme. In addition, there are natural circuits in which this substance can be integrated for sodium citrate. Considering those the proposed treatment represents a viable eco-friendly option. The experimental design and data processing described herein may constitute an optimal industrial enzymatic scouring treatment management model.

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