

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

SYNTHESIS OF BLEACH ACTIVATORS FOR TEXTILE INDUSTRY



Ph.D. THESIS

PELİN ALTAY

Department of Textile Engineering

Textile Engineering Programme

JUNE 2021

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

SYNTHESIS OF BLEACH ACTIVATORS FOR TEXTILE INDUSTRY



Ph.D. THESIS

PELİN ALTAY

(503132801)

Department of Textile Engineering

Textile Engineering Programme

Thesis Advisor: Prof. Dr. Nevin Çiğdem GÜRSOY

Thesis Co-Advisor: Prof. Dr. Peter J. HAUSER

JUNE 2021

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

TEKSTİL SEKTÖRÜ İÇİN AĞARTMA AKTİVATÖRLERİNİN SENTEZİ

DOKTORA TEZİ

PELİN ALTAY

(503132801)

Tekstil Mühendisliği Anabilim Dalı

Tekstil Mühendisliği Programı

Tez Danışmanı: Prof. Dr. Nevin Çiğdem GÜRSOY

Eş Danışman: Prof.Dr. Peter J. HAUSER

HAZİRAN 2021

Pelin ALTAY, a Ph.D. student of ITU Graduate School student ID 503132801, successfully defended the thesis/dissertation entitled “SYNTHESIS OF BLEACH ACTIVATORS FOR TEXTILE INDUSTRY”, which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor : **Prof. Dr. Nevin Çiğdem GÜRSOY**
Istanbul Technical University

Co-advisor : **Prof.Dr. Peter J. HAUSER**
North Carolina State University

Jury Members : **Prof. Dr. İsmail KOYUNCU**
Istanbul Technical University

Prof. Dr. Abdülkadir Sezai SARAÇ
Istanbul Technical University

Assoc. Prof. Dr. Fevzi Çakmak CEBECİ
Sabancı University

Prof. Dr. Gülay ÖZCAN
Istanbul Technical University

Prof. Dr. Emine Dilara KOÇAK
Marmara University

Date of Submission : 3 June 2021

Date of Defense : 29 June 2021





To my advisors and family,



FOREWORD

First and foremost, I would like to express my deepest gratitude to my supervisor Prof. Dr. Nevin Ç. GÜRSOY and my co-advisor Prof. Dr. Peter J. HAUSER (North Carolina State University/USA), for their endless and tremendous knowledge, guidance, support, patience, and encouragement throughout all my study and for giving me chance to study under their supervision.

I would like to extend my sincere gratitude to my thesis committee members, Prof. Dr. İsmail KOYUNCU (Rector of ITU), Prof. Dr. A. Sezai SARAÇ, and Assoc. Prof. Dr. Fevzi Çakmak CEBECİ, whose knowledge and expertise greatly contributed to my Ph.D. education, for their precious time, contribution, discussions and recommendations throughout the thesis progress meetings that shed light to my way.

I'm deeply indebted to Prof. Dr. Ahmed EL-SHAFEI (North Carolina State University/USA), who has profound expertise on organic chemistry, molecular modelling, synthesis and characterization of bleach activators and mentored me throughout all my study in North Carolina State University/USA. I would like to express my special thanks to Dr. Erol YILDIRIM, who has great knowledge on computational chemistry, for his guidance and support on geometry optimization and molecular modelling part of my thesis.

I gratefully acknowledge the funding sources that made my Ph.D. work possible. This study is supported by TUBITAK (The Scientific and Technological Research Council of Turkey) for 2214/A – International Research Scholarship Program for Doctorate Student. I wish to offer my appreciation to Setaş Kimya Ltd.Co., who took place as an industrial part of this study and supports the industrial scale production and commercialization of the developed product.

Last but not the least, my greatest thanks to my family, who motivated me throughout my life, for all their continuous love and encouragement.

29 June 2021

Pelin ALTAY
(M.Sc. Textile Engineer)



TABLE OF CONTENTS

	<u>Page</u>
FOREWORD	vii
TABLE OF CONTENTS	ix
ABBREVIATIONS	xi
SYMBOLS	xiii
LIST OF TABLES	xv
LIST OF FIGURES	xvii
SUMMARY	xix
ÖZET	xxiii
1. INTRODUCTION	1
1.1 Conventional Bleaching	3
1.1.1 Chlorine-based bleaching	3
1.1.2 Peroxide-based bleaching	4
1.1.2.1 Peroxide-based bleaching mechanism	6
1.2 Activated Bleach Systems	8
1.2.1 Bleaching with peracetic acid.....	9
1.2.2 Bleach activators.....	10
1.2.2.1 Cationic bleach activators (CBAs).....	13
1.3 Problem Statement and Purpose of Thesis	15
1.4 Literature Review	17
2. EXPERIMENTAL STUDY	25
2.1 Materials	25
2.2 Instrumentation.....	25
2.3 Methods	25
2.3.1 Designing of novel bleach activator	25
2.3.2 Synthesis of bleach activator	28
2.3.2.1 Synthesis of N-[4-(N,N,N)-triethylammoniumchloride-butyl] caprolactam, TBUC	29
2.3.2.2 Synthesis of N-[4-(N,N,N)-triethylammoniumchloride- butanoyl] butyrolactam (TBUCB).....	30
2.3.3 Bleaching method: <i>Hot peroxide bleaching</i>	31
2.3.3.1 Activated bleaching.....	31
2.3.3.2 Conventional bleaching.....	32
2.3.4 Evaluation of bleaching performance	32
2.3.4.1 Whiteness measurement	32
2.3.4.2 Water absorbency measurement.....	32
2.3.4.3 Determination of fiber damage	32
2.3.5 Central composite design and statistical evaluation	33
2.3.6 Determination of the limitations of TBUCB at molecular level for cotton: Computational methods.....	34

3. RESULTS AND DISCUSSIONS	37
3.1 Characterization.....	37
3.1.1 Fourier transform infrared spectroscopy (FTIR)	37
3.1.2 Mass spectra results	40
3.1.3 ¹ H-NMR analysis.....	42
3.2 Bleaching Performance.....	43
3.2.1 Whiteness measurement	43
3.2.1.1 TBUCC-activated peroxide bleaching system	43
3.2.1.2 TBUCB-activated peroxide bleaching system	45
3.2.2 Water absorbency	51
3.2.3 Determination of fiber damage	51
3.3 Computational Results.....	53
4. CONCLUSIONS.....	61
APPENDICES	65
REFERENCES	75
CURRICULUM VITAE	83



ABBREVIATIONS

ADCH	: Atomic dipole moment corrected Hirshfeld population analysis
CBA	: Cationic bleach activator
CCD	: Central composite design
DFT	: Density functional theory
ESP	: Electrostatic potential surface
FTIR	: Fourier transform Infrared spectroscopy
¹H-NMR	: Proton nuclear magnetic resonance
HOMO	: Highest occupied molecular orbitals
IEFPCM	: Integral equation formalism polarizable continuum model
LUMO	: Lowest unoccupied molecular orbitals
MK	: Merz-Singh-Kollman (Electrostatic potential fitting method)
NOBS	: Sodium salt of nonanoylbenzenesulphonic acid
PAA	: Peracetic acid or peracid
RSM	: Response Surface Methodology
TAED	: Tetraacetylenediamine
TBLC	: N-[4-(triethylammoniomethyl) benzoyl]lactam chloride
TBUCB	: N-[4-(N,N,N) triethylammoniumchloride-butanoyl] butyrolactam
TBUCC	: N-[4-(N,N,N)- triethylammoniumchloride-butyryl] caprolactam
THF	: Tetrahydrofuran
WI	: Whiteness index



SYMBOLS

H₂O₂	: Hydrogen peroxide
HOO⁻	: Perhydroxyl anion
DP	: Degree of polymerization
Et₃N, HCl	: Triethylammonium hydrochloride salt
Å	: Angström, a unit of length used to measure very small distances 1 Å = 10 ⁻¹⁰ meters



LIST OF TABLES

Table 2.1: Different lactam-based leaving groups and their hydrolytic stabilities ...	27
Table 2.2: Recipe of conventional hot peroxide bleaching.	32
Table 3.1: Bleaching performances of TBUCC-activated bleached samples under different concentrations of activator, H ₂ O ₂ and NaOH.	44
Table 3.2: Bleaching performances of TBUCC-activated bleached samples using 36.7 mmol/L activator at a large excessive amount of hydrogen peroxide at 60 °C and 70 °C.....	45
Table 3.3: Process parameters and levels of each parameters.....	46
Table 3.4: Design matrix and CCD response data for TBUCB.	47
Table 3.5: Analysis of variance for WI.	48
Table 3.6: DP of bleached cotton fabric for activated and conventional peroxide bleaching.....	52



LIST OF FIGURES

Figure 1.1: Oxidation of cellulose.....	8
Figure 1.2: Epoxidation of double bonds via peracid	9
Figure 1.3: Reaction of bleach activator with H_2O_2 to form peracid	11
Figure 1.4: Perhydrolysis of TAED.	12
Figure 1.5: Reaction of NOBS with H_2O_2 to produce pernonanoic acid and NOBS side reaction to produce DAP.	12
Figure 1.6: Aromatic-based cationic bleach activator (where $n=1-5$)	13
Figure 1.7: Perhydrolysis of TBLC ($n=1-5$)	14
Figure 1.8: Hydrolysis reaction of cationic bleach activators to form N-[4- (triethylammoniomethyl)benzoic acid (TBA)	14
Figure 2.1: Synthesis of bleach activator.	28
Figure 2.2: Synthesis of 4-chlorobutyryl caprolactam ($n=3$) ($M_w=217.5$).	30
Figure 2.3: Synthesis of N-[4-(N,N,N)-triethylammoniumchloride- butyryl]caprolactam (TBUCC) ($n=3$) ($M_w=318.74$).	30
Figure 2.4: Synthesis of N-[4-(N,N,N)-triethylammoniumchloride- butanoyl] butyrolactam (TBUCB), ($n=1$) ($M_w=290.83$).	31
Figure 2.5: Experimental set up for viscosity measurement (Ostwald cannon–fenske routine viscometer).	33
Figure 3.1: FTIR spectrum of synthesized bleach activator (TBUCC).	38
Figure 3.2: FTIR spectrum of the bleach activator (TBUCC) after removal of hydrochloride salt.....	39
Figure 3.3: FTIR spectrum of the bleached and unbleached fabric.	40
Figure 3.4: Mass spectrum of intermediate product-zoom in.	41
Figure 3.5: Mass spectra of intermediate product after removal of $\text{Et}_3\text{N}+\text{HCl}$	41
Figure 3.6: Mass spectrum of final product (after quaternization).	42
Figure 3.7: ^1H NMR spectrum of TBUCC.	42
Figure 3.8: a) LUMO and b) HOMO frontier molecular orbital isosurfaces, c) electrostatic potential (ESP) surface mapped on the optimized geometries. Atomic charges based on the d) electrostatic potential fitting method (MK) and e) atomic dipole moment corrected Hirshfeld (ADHC) population analysis f) Fukui reactivity indices showing the most susceptible sites for nucleophilic attack.....	54
Figure 3.9: Vibration with imaginary frequency for the transition state of perhydroxyl anion attack for the TBUCB.....	54
Figure 3.10: Vibration with imaginary frequency for the transition state of peracid dissociation for the TBUCB.....	55
Figure 3.11: Vibration with imaginary frequency for the transition state of perhydroxyl anion attack for the TAED.....	55
Figure 3.12: Vibration with imaginary frequency for the transition state of peracid dissociation for the TAED.....	55

Figure 3.13: Free energy diagrams of the perhydroxyl anion attack and peracid formation for the a) TBUCB and b) TAED. The relative energies are in kcal/mol and distances are in Å.	57
Figure 3.14: a-c) Non coplanar low energy structures for TBUCB in the gauche1 (a-c) and gauche2 (b-d) conformations, e) phenyl modified TBUCB f) alkene modified TBUCB.	59
Figure A.1: Cartesian coordinates for the transition state of perhydroxyl anion attack for the TBUCB.	66
Figure B.1: Cartesian coordinates for the transition state of peracid dissociation for the TBUCB.	68
Figure C.1: Cartesian coordinates for the transition state of perhydroxyl anion attack for the TAED.	70
Figure D.1: Cartesian coordinates for the transition state of peracid dissociation for the TAED.	72



SYNTHESIS OF BLEACH ACTIVATORS FOR TEXTILE INDUSTRY

SUMMARY

Cotton fiber, is the most widely used natural fiber worldwide, contains undesired natural yellowish-brown coloring matters that hinder absorbency (wetting), reduce the natural whiteness of the fibers. These coloring impurities, which may cause poor dyeing quality, poor finishing performance and end product defects, must be removed by bleaching process to prepare the textile materials for dyeing and finishing. Hydrogen peroxide (H_2O_2), a universal and environment-friendly bleaching agent, is widely used for cotton and cotton blends.

Conventional hot hydrogen peroxide bleaching is conducted under alkaline medium (pH 10.5–12) at high temperatures near boiling (at around 98 °C), leading extensive use of energy and severe chemical damage to textiles. Increasing demands for textile bleaching include reduction in processing costs (energy and water consumption), reduction in environmental impact and improvement in quality. Since energy is one of the main cost factors in textile industry, there has been considerable interest in recent years in “low temperature” bleaching. Activated peroxide systems have been investigated as an alternative approach to cotton bleaching at lower temperatures. Although there have been many reports on the use of cationic bleach activators for cotton bleaching, yet it has never reached the commercial success due to either production cost on a large scale, environmental concerns and/ or activity. This study focuses on the development and synthesis of novel, sustainable based on aliphatic acid chloride and more cost-effective cationic bleach activators, with the aim of reduced production cost, improved affinity and bleaching performance, reduced fiber damage for low temperature cotton bleaching to overcome the drawbacks of conventional hot hydrogen peroxide bleaching and other cationic bleach activators based on aromatic acid chloride.

Compared to conventional peroxide bleaching, using a bleach activator in a peroxide bleaching bath is an effective and kinetically more potent oxidation generating highly reactive peracid in situ, providing low-temperature bleaching. Activated bleach systems have the potential to produce more efficient kinetically potent bleaching systems through increased oxidation rates with reducing energy cost, saving time and, hence, causing less cellulose polymer chains damage or degradation than conventional hot peroxide bleaching. Cationic bleach activators have been investigated as the next generation bleach activators with inherent substantivity towards cellulosic fibers.

In this study, facile synthesis of more sustainable and cost-effective bleach activators (N-[4-(N,N,N)-triethylammoniumchloride- butyryl] caprolactam, TBUCC, and N-[4-(N,N,N)-triethylammoniumchloride- butanoyl] butyrolactam, TBUCB, based on an aliphatic acyl chloride (4- chlorobutyryl chloride), was reported. Fourier transform

infrared and high resolution mass spectrometry and ^1H NMR confirmed the molecular structure of the synthesized bleach activator. Bleaching performance of newly-synthesized bleached activators was evaluated in terms of whiteness index, water absorbency and fiber damage (degree of polymerization) and compared with conventional peroxide system. Central composite design (CCD) (orthogonal blocks) was used to establish an optimized TBUCB-activated hot peroxide-cotton bleaching system at lower temperature for providing reduced energy cost and maintaining the integrity of cellulose polymer chains. The significance of the process parameters (independent variables) and their interactions were statistically evaluated using Minitab. First principles density functional theory (DFT) calculations were performed to elucidate the reaction mechanism via identifying plausible transition state(s) of the nucleophilic attack of perhydroxyl anion (HOO^-) with different carbonyl carbons and identifying the advantages and limitations of TBUCB activator for hydrogen peroxide bleaching for cotton.

The synthesis of bleach activators was conducted using a two-step reaction procedure. In the first step, intermediate product was synthesized by condensation reaction of 4- chlorobutyl chloride with lactam leaving groups (caprolactam and butyrolactam). In the second step, quaternization step was performed to obtain the cationic bleach activators. Experimental results show that, in TBUCB- H_2O_2 system, the whiteness index (WI) of bleached samples improved when 1:8 and 1:10 molar ratio of TBUCB: H_2O_2 was used at 60 °C for 30 min. Using 1:8 molar ratio of TBUCB: H_2O_2 at 36.7 mmol/L activator provided a WI of 70. As the temperature increased from 60 to 70 °C, WI increased to 75.72 and 78.97 at 1:10 and 1:12 molar ratio of TBUCB to H_2O_2 , respectively. The optimum pH was found to be 11.5 for effective bleaching performance. It was concluded that the effective concentration of generated PAA depends on the concentration of H_2O_2 up to a certain level. Based on the results of the experimental design and statistical analysis, a WI higher than 70 was achieved for TBUCB-activated bleach system at 9.47 g /L (29.7 mmol/L) and higher activator concentrations and at a molar ratio of 1:6-1:10 activator: H_2O_2 . WI higher than 80 can be achieved between 11.7 g/L (36.7 mmol/L) and 13.93 g/L (43.7 mmol/L) of activator concentrations at a temperature of 80 °C. Considering the significance of the process parameters (independent variables) and their interactions, temperature (D) followed by molar ratio of activator: H_2O_2 (B) and concentration of activator (A), respectively, have the highest statistical relevance on whiteness index. On the other hand, it was revealed that the two-way interaction between the concentration of activator (A) and the molar ratio of activator: H_2O_2 (B) is greater than the other two-way interactions.

When the bleached samples with similar whiteness values were compared (WI= ~ 75) in terms of fiber damage for conventional and activated peroxide bleaching systems, a 19.5% decrease in the average degree of polymerization (DP) was observed in conventional peroxide bleaching, while a decrease of 11.4% and 9.8% was observed in the TBUCB and TBUCB activated peroxide bleach systems, respectively. All these results show that whiteness index greater than 80 for cotton can be achieved by using TBUCB and TBUCB activated peroxide bleaching systems at lower temperature, providing reduced energy cost while maintaining the integrity of cellulose polymer chains.

Density functional theory calculations were performed to elucidate the reaction mechanism of the bleach activator with cellulose and rationalize the superior efficiency of the bleach activator while maintaining the integrity of cellulose polymer

chains compared to conventional hydrogen peroxide bleaching. DFT calculations elucidated the reaction mechanism, reactivity and peroxide bleaching reaction pathway of the perhydroxyl anion attack at carbonyl group of the butanoyl segment not at the carbonyl carbon of the butyrolactam, which is consistent with the experimental results. Reactions were found to follow two step mechanisms, which are perhydroxyl anion attack at the carbonyl carbon and the peracid formation. Reaction barrier for the perhydroxyl anion attack at the carbonyl carbon was calculated by using sum of electronic and thermal free energies at 70°C under water solvation effect and determined as 12.55 kcal/mol. For perhydroxyl anion attack, TBUCB was found to have a lower reaction barrier and higher solubility than TAED, which was determined as 13.72 kcal/mol.

These newly developed and synthesized aliphatic acid chloride-based cationic bleach activators, which are more cost-effective, sustainable and highly reactive compared to other aromatic based cationic bleach activators, enable peroxide bleaching possible at lower temperature (70 °C) compared to conventional hot peroxide bleaching (98 °C). With a sustainable production approach, using these novel cationic bleach activators in hot peroxide bleaching bath provides many advantages such as energy savings, reduced production cost, improved affinity and bleaching efficiency (whiteness index), and less fiber damage. This study provides key fundamental science principles and suggestions at the molecular level of novel and sustainable bleach activators for cotton using a combined experimental and first principles DFT calculations. This study is expected to provide a great contribution to the commercialization of these novel, more sustainable and effective cationic bleach activators for cellulose and cellulosic materials and to the future development of cost-effective industrial bleach activators and sustainable bleaching systems.



TEKSTİL SEKTÖRÜ İÇİN AĞARTMA AKTİVATÖRLERİNİN SENTEZİ

ÖZET

Dünyada en yaygın kullanılan doğal elyaf olan pamuk elyafı, emiciliği (ıslanma) engelleyen, elyafların doğal beyazlığını azaltan istenmeyen doğal sarımsı-kahverengi renklendirici maddeler içerir. Kötü boyama kalitesine, kötü terbiye performansına ve son ürün kusurlarına neden olabilen bu renklendirme safsızlıkları, tekstil malzemelerini boyama ve terbiyeye hazırlamak için ağartma işlemi ile giderilmelidir. Evrensel ve çevre dostu bir ağartma maddesi olan hidrojen peroksit (H_2O_2), pamuk ve pamuk karışımlarında yaygın olarak kullanılmaktadır.

Konvansiyonel sıcak hidrojen peroksit ağartma, alkali ortam (pH 10.5–12) altında, kaynamaya yakın yüksek sıcaklıklarda (yaklaşık 98 °C'de) gerçekleştirilerek, yoğun enerji kullanımına ve tekstil ürünlerinde ciddi kimyasal hasara yol açar. Tekstil ağartma için artan talepler arasında, işleme maliyetlerinde azalma (enerji ve su tüketimi), çevresel etkide azalma ve kalitenin iyileştirilmesi bulunmaktadır. Enerji, tekstil endüstrisindeki ana maliyet faktörlerinden biri olduğundan, son yıllarda "düşük sıcaklıkta" ağartmaya önemli bir ilgi olmuştur. Daha düşük sıcaklıklarda pamuk ağartılmasına alternatif bir yaklaşım olarak aktifleştirilmiş peroksit sistemleri araştırılmaktadır. Pamuklu ağartma için katyonik ağartma aktivatörlerinin kullanımına ilişkin birçok çalışma olmasına rağmen, büyük ölçekli üretim maliyeti, çevresel kaygılar ve/veya oksidasyon aktivitesi nedeniyle ticari başarıya hiçbir zaman ulaşamamıştır. Bu çalışma, konvansiyonel sıcak hidrojen peroksit ağartmanın ve aromatik asit klorüre dayalı diğer katyonik ağartma aktivatörlerinin dezavantajlarının üstesinden gelmek amacıyla; düşük sıcaklıkta pamuklu ağartma için daha düşük üretim maliyeti, geliştirilmiş afinite ve ağartma performansı, azaltılmış elyaf hasarı sağlayarak, alifatik asit klorür ve daha uygun maliyetli katyonik ağartma aktivatörüne dayalı yeni, sürdürülebilir bir ürünün geliştirilmesi ve sentezine odaklanmaktadır.

Konvansiyonel peroksit ağartma ile karşılaştırıldığında, peroksit ağartma banyosunda ağartma aktivatörü kullanmak, düşük sıcaklıkta ağartma sağlayan, yerinde yüksek reaktif perasit üreten etkili ve kinetik olarak daha güçlü bir oksidasyondur. Aktifleştirilmiş ağartma sistemleri, enerji maliyetini düşürerek, zamandan tasarruf ederek ve dolayısıyla, konvansiyonel sıcak peroksit ağartmaya göre daha az selüloz polimer zincir hasarına veya bozunmasına neden olan yükseltilmiş oksidasyon oranları yoluyla daha verimli kinetik olarak güçlü ağartma sistemleri üretme potansiyeline sahiptir. Katyonik ağartma aktivatörleri, selülozik liflere karşı doğal substantivite (afinite) sergileyen yeni nesil ağartma aktivatörleri olarak araştırılmaktadır.

Bu çalışmada, alifatik asil klorür (4-klorobütiril klorür) bazlı, daha sürdürülebilir ve uygun maliyetli ağartma aktivatörlerinin, N- [4- (N, N, N) -triethylamonyumklorür-butiril] kaprolaktam, TBUCC, ve N- [4- (N, N, N) -triethylamonyumklorür-bütanoil] bütrolaktam, TBUCB, kolay sentezi rapor edilmiştir. Fourier dönüşümü kızılötesi spektroskopisi (FTIR) ve yüksek çözünürlüklü kütle spektrometresi ve ¹HNMR karakterizasyon testleri sentezlenen ağartma aktivatörünün moleküler yapısını doğrulamıştır. Sentezlenmiş ağartma aktivatörleri beyazlık indeksi, su emiciliği (hidrofillik) ve lif hasarı (polimerizasyon derecesi) açısından değerlendirilmiş ve konvansiyonel peroksit sistemi ile karşılaştırılmıştır. Enerji tasarrufu sağlamak ve selüloz polimer zincirlerinin bütünlüğünü korumak amacıyla, daha düşük sıcaklıkta TBUCB-sıcak peroksit-pamuk ağartma sistemi Merkezi kompozit tasarımı (CCD) (ortogonal bloklar) kullanılarak optimize edilmiştir. İşlem parametrelerinin önemi (bağımsız değişkenler) ve etkileşimleri, Minitab program kullanılarak istatistiksel olarak değerlendirilmiştir. Farklı karbonil karbonlar ile perhidroksil anyonun (HOO⁻) nükleofilik saldırısının makul geçiş durumlarını tanımlayarak ve hidrojen peroksit ile pamuk ağartma için TBUCB aktivatörünün avantajlarını ve sınırlamalarını belirleyerek reaksiyon mekanizmasını aydınlatmak için yoğunluk fonksiyonel teorisi (DFT) hesaplamaları yapılmıştır.

Ağartma aktivatörlerinin sentezi, iki aşamalı bir reaksiyon prosedürü kullanılarak gerçekleştirilmiştir. İlk aşamada, 4-klorobütiril klorürün laktam ayrılan gruplarla (kaprolaktam ve bütrolaktam) kondenzasyon reaksiyonu ile ara ürün sentezlenmiştir. İkinci aşamada, katyonik ağartma aktivatörlerini elde etmek için kuaternizasyon aşaması gerçekleştirilmiştir. Deneysel sonuçlar, TBUCC-H₂O₂ aktive edilmiş ağartma sisteminde, 1:8 ve 1:10 TBUCC:H₂O₂ molar oranı kullanıldığında 60 °C'de 30 dakika işlem süresinde, ağartılmış numunelerin beyazlık indeksinin (WI) arttığını göstermektedir. 1:8 TBUCC: H₂O₂ molar oranında ve 36.7 mmol/L aktivatör konsantrasyonunda, WI değeri 70 olarak elde edilmiştir. Sıcaklık 60 °C'den 70 °C'ye arttığında, WI değeri, 1:10 ve 1:12 TBUCC: H₂O₂ molar oranlarında sırasıyla 75.72 ve 78.97'ye yükselmiştir. Etkili ağartma performansı için optimum pH değerinin 11.5 olduğu bulunmuştur. Üretilen perasetik asidin (PAA) etkin konsantrasyonunun belirli bir seviyeye kadar H₂O₂ konsantrasyonuna bağlı olduğu sonucuna varılmıştır. Deneysel tasarım ve istatistiksel analiz sonuçlarına göre, TBUCB ile aktive edilen peroksit ağartma sistemi için 9.47 g/L (29.7 mmol/L) ve daha yüksek aktivatör konsantrasyonlarında ve 1:6-1:10 molar oranında 70'den yüksek WI değeri elde edilmiştir. 80 °C sıcaklıkta 11.7 g/L (36.7 mmol/L) ile 13.93 g/L (43.7 mmol/L) aktivatör konsantrasyonları arasında 80'den yüksek WI elde edilebileceği sonucuna varılmıştır. Proses parametrelerinin (bağımsız değişkenler) ve etkileşimlerinin önemi göz önüne alındığında, sıcaklık (D), ardından aktivatör: H₂O₂ molar oranı (B) ve aktivatör konsantrasyonu (A), beyazlık indeksi üzerinde en yüksek istatistiksel öneme sahiptir. Diğer taraftan, aktivatör konsantrasyonu (A) ile aktivatör:H₂O₂ molar oranı (B) arasındaki iki yönlü etkileşimin diğer iki yönlü etkileşimlerden daha büyük olduğu ortaya konmuştur.

Konvansiyonel ve aktive edilmiş peroksit ağartılmış sistemler için benzer beyazlık değerlerine sahip ağartılmış numuneler (WI= ~ 75) lif hasarı açısından karşılaştırıldığında, konvansiyonel peroksit ağartmada ortalama polimerizasyon derecesinde (DP) % 19.5'lik bir düşüş gözlenirken, TBUCC ve TBUCB ile aktive edilmiş peroksit ağartma sistemlerinde sırasıyla % 11.4 ve % 9.8 azalma gözlenmiştir. Tüm bu sonuçlar, TBUCC-H₂O₂ ve TBUCB-H₂O₂ aktive edilmiş ağartma sistemleri ile pamuk esaslı tekstil ürünleri için 80'den büyük beyazlık

indeksinin, konvansiyonel peroksit ağartma sistemi karşılaştırıldığında daha düşük sıcaklıkta elde edilebileceğini ve selüloz polimer zincirlerinin bütünlüğü korunurken enerji maliyetinin azaltılabileceğini göstermektedir.

Yoğunluk fonksiyonel teorisi (DFT) yöntemi kullanılarak, ağartma aktivatörünün selüloz ile reaksiyon mekanizması aydınlatılmış ve ağartma aktivatörünün konvansiyonel hidrojen peroksit ağartmaya kıyasla, selüloz polimer zincirlerinin bütünlüğünü korurken üstün ağartma etkinliği rasyonelleştirilmiştir. DFT hesaplamaları, deneysel sonuçlarla tutarlı olan butanoil segmentinin karbonil grubuna ait perhidroksil anyon saldırısının reaksiyon mekanizmasını, reaktivitesini ve peroksit ağartma reaksiyon yolunu aydınlatmıştır. Reaksiyonların, karbonil karbonuna perhidroksil anyon saldırısı ve perasit oluşumu olan iki aşamalı mekanizmayı takip ettiği bulunmuştur. Karbonil karbonunda perhidroksil anyon saldırısı için reaksiyon bariyeri, 70°C'de su çözme etkisi altında elektron ve termal serbest enerjilerin toplamı kullanılarak hesaplanmış ve 12.55 kcal/mol olarak belirlenmiştir. Perhidroksil anyon saldırısı için TBUCB'nin, 13.72 kcal/mol olarak belirlenen TAED'e göre daha düşük reaksiyon bariyerine ve daha yüksek çözünürlüğe sahip olduğu bulunmuştur.

Diğer aromatik bazlı katyonik ağartma aktivatörlerine göre daha uygun maliyetli, sürdürülebilir ve yüksek reaktiviteye sahip bu yeni geliştirilen ve sentezlenen alifatik asit klorür bazlı katyonik ağartma aktivatörleri, konvansiyonel sıcak peroksit ağartmasına göre daha düşük sıcaklıkta (70 °C) peroksit ağartmayı mümkün kılmaktadır. Sürdürülebilir bir üretim yaklaşımıyla, bu yeni katyonik ağartma aktivatörlerinin sıcak peroksit ağartma banyosunda kullanılması, enerji tasarrufu, düşük üretim maliyeti, iyileştirilmiş afinite ve ağartma verimliliği (beyazlık indeksi) ve daha az elyaf hasarı gibi birçok avantaj sağlamaktadır. Bu çalışma, kombine bir deneysel ve ilk prensip DFT hesaplamaları kullanılarak pamuk için yeni ve sürdürülebilir bir ağartma aktivatörünün moleküler düzeyde temel bilim ilkelerini ve önerilerini sunmaktadır. Bu çalışmanın, selüloz ve selülozik malzemeler için bu yeni, daha sürdürülebilir ve etkili katyonik ağartma aktivatörünün ticarileştirilmesine ve uygun maliyetli endüstriyel ağartma aktivatörlerinin ve sürdürülebilir ağartma sistemlerinin gelecekteki gelişimine büyük katkı sağlaması beklenmektedir.



1. INTRODUCTION

Textile wet processing, which includes pretreatment (or preparation), coloration (dyeing or printing) and finishing, is the most energy intensive subsector in the textile industry. A reduction in processing costs, a reduction in environmental impact and improvement in textile quality are highly desired factors for textile wet processes. Bleaching is a critical and essential textile wet process for the preparation of cotton-based textiles prior to dyeing and finishing in order to remove undesired inherent coloring matter, water-borne stains, oil-borne soils and to provide the complete removal of seed husks and trash. Most of fiber-forming polymers are white in their natural state. However, impurities and coloring matters in fibers hinder wetting and mask the natural whiteness of fibers by absorbing light, causing a yellowish brown or dull appearance. Synthetic fibers that are usually sufficiently white do not require bleaching unless they are dyed in very vivid light colors or super white finish textiles are required. If it is desired, whiteness of synthetic textiles is improved by the bleaching process [1-8].

Cotton fiber, a plant derived natural seed fiber, is the most widely used natural fiber worldwide and one of the most important raw materials in the textile industry. Cotton fiber is an ideal material for apparel, bedding and linens due to its high water absorbency, comfort and relative ease of dyeing and finishing. It consists largely of cellulose and has up to 6-14% non-cellulosic materials such as fat, waxes, pectins and mineral matters [9-12]. It also contains natural coloring matters that give a yellowish-brown color and significantly reduce the inherent white appearance of cotton cellulose. This yellowish and brown discoloration which may be due to the flavone pigments of the cotton flower, varies depending on the area of cultivation, climate, soil, drought and frost and other extraneous materials. The natural color of cotton may affect the tone and brightness of the shade obtained by dyeing, especially for light to medium shades. These coloring matters must be removed in bleaching to achieve full white or extra bright shades in further dyeing and finishing. However, bleaching step is generally skipped in case of material to be dyed in dark and dull

shades. In bleaching, these colored substances on cotton are chemically converted into water-soluble molecules to be removed or their conjugated chromophores are destroyed by oxidation [4-7,13].

This process is generally applied to grey goods to produce white fabrics or to fabrics to prepare them for dyeing in pastel shades, by destroying the coloring matter with the help of bleaching agents with minimum degradation of the fiber. In addition to purpose of achieving sufficiently high and uniform whiteness degree with minimum fiber damage, bleaching improves water absorbency (wetting) and uniformity of appearance, which help to obtain high quality and level dyeing. The process must also be ecologically and economically sensible, providing good user and technological properties of textile material [4-8, 14-15].

Hydrogen peroxide (H_2O_2), which is the most common and universally used bleaching agent, has been used for industrial cotton bleaching for decade. Generally, cotton substrates can be bleached in the presence of H_2O_2 under alkali pH at high temperature ($>95\text{ }^\circ\text{C}$) by rapid exhaustion process (Hot peroxide bleaching). The high temperatures, as well as the addition of alkali, are necessary to activate the required hydrogen peroxide. Hot peroxide bleaching method consists of three main steps. First step includes the saturation of the fabric with bleaching agent and other required chemicals. The second step involves increasing the temperature to the recommended level for the particular textile material and maintaining this temperature for required process time. These steps are followed by the third step, the washing and drying of the fabric. Hot peroxide bleaching provides acceptable whiteness and high yield due to its short processing time. However, high temperature bleaching causes high energy consumption with increased fiber damage [1, 3-5, 8, 13, 15].

Cotton substrates can alternatively be bleached at room temperature for a long dwell time up to 24 h by cold pad-batch process [16-17]. While the cold pad-batch process eliminates the fiber damage and high energy cost problems observed in the hot bleaching process, two factors, which are storage space and whiteness level, often limit its widespread application. After the fabric is impregnated with a peroxide-based bleach solution, a significant amount of storage space is required to keep the fabric at room temperature. Secondly, conventional cold pad-batch bleaching may not achieve the sufficient whiteness required for white and light colored products.

Considering these limitations, the studies in the literature have focused on reducing the dwell time of cotton fabric to shorten the processing time in the cold pad-batch process, and lowering the bleaching temperature to save energy in the rapid exhaustion process [16-35].

1.1 Conventional Bleaching

Bleaching agents convert colored impurities into colorless particles. A chromophore, which is the part of a molecule responsible for its color, contains conjugated double bonds. These double bonds are attacked by the oxidizing species during bleaching and destroyed by cleaving the conjugated chain, or by oxidation of one of the other moieties in the conjugated chain. As a result, electromagnetic radiation is not absorbed and reflected in the visible region of the spectrum, causing discoloration [7, 36].

Oxidizing agents are more commonly used in bleaching than reducing agents. The most commonly used oxidizing agents for cotton bleaching are hydrogen peroxide, sodium chlorite (NaClO_2) and sodium hypochlorite (NaClO).

1.1.1 Chlorine-based bleaching

Hypochlorite is one of the oldest industrial bleaching agents. The main advantage of hypochlorite is that it is an inexpensive bleaching agent and used to bleach socks and other inexpensive textile products. Hypochlorous acid (HOCl), which is unstable and dissociates to give active oxygen and hydrochloride acid (HCl), is generated as a result of dissolving sodium hypochlorite in water. The optimum condition for sodium hypochlorite bleaching is pH 9-11 at 20 °C. A fall in pH (below 9) may cause severe damage to the cellulose due to the formation of oxy-cellulose. Before the hypochlorite bleaching of cellulosic fibers, it is necessary to remove all impurities such as fats, oils, waxes and pectin, which would reduce available hypochlorite and, accordingly, bleaching efficiency. There is a risk of yellowing of the bleached fabric during storage. Antichlor treatment is applied to remove the residual chlorine from the bleached fabric after the hypochlorite bleaching.

Sodium chlorite (NaClO_2) is relatively expensive compared to H_2O_2 and NaClO . In NaClO_2 bleaching, chlorous (HClO_2) acid is generated as a result of the hydrolysis of sodium chlorite with water. The pH of the medium should be 3.5-4 in order to

achieve an adequate concentration of chlorous acid. The two most important issues to be considered in sodium chlorite bleaching are the release of toxic chlorine dioxide gas and corrosion of the devices. Sodium chlorite causes the least chemical damage to cotton as compared to other bleaching agents, and its decomposition is not catalyzed in the presence of metal ions. Due to the partial removal of waxes, chlorite bleached fabric has a softer touch than NaClO and H₂O₂ bleaching, but it has poor absorbency for subsequent dyeing and printing.

However, commercial use of chlorine based bleaching agents have considerably limited due to the environmental impact resulting from the release of highly toxic chlorinated organic by products (AOX). Nowadays, hydrogen peroxide has almost entirely replaced the chlorine oxidizing agents [1-5, 7-8, 14].

1.1.2 Peroxide-based bleaching

The current most common industrial and universal bleaching agent is hydrogen peroxide due to its simplicity of use, low cost and eco-friendly nature (decomposes to O₂ and H₂O). H₂O₂ is the most commonly used in diluted form (e.g. 35% w/w), owing to its very low cost, abundance, and ease of application from a solution. Rapid hydrogen peroxide bleaching (hot peroxide bleaching), one of the most common bleach methods, is conducted under alkaline medium (pH 10.5-12) at high temperatures near boiling to produce active oxygen which decomposes coloring substances. The conventional bleaching results in a higher WI of 73-75, which is accompanied by extensive use of energy, water and chemical consumption, and a high level of fiber damage (decrease in the degree of polymerization of cellulose) [4-6, 37-38]. In addition, the excessive amount of bleaching agent leads to increased contamination load of wastewater effluents discharge after bleaching step [5, 7-8, 17-20, 36]. Moreover, conventional bleaching requires extensive rinsing process to remove any hydrogen peroxide residues, which may interfere with the subsequent dyeing process resulting in color loss [39].

The advantages of hydrogen peroxide bleaching as compared to others can be summarized as follow: [1-8].

- Hydrogen peroxide, which is a universal and widely used bleaching agent, can be applied to jute, linen, wool, silk, etc. as well as cotton.

- It is highly environment-friendly since it decomposes into water and oxygen, which are nontoxic and innocuous wastewater products. One of the most important issues to be considered in sodium chlorite bleaching is the release of toxic chlorine dioxide (ClO_2) gas. Therefore, special equipment construction is required for the safety of the employees.
- It is non-corrosive and does not have any unpleasant odours. Especially in sodium chloride bleaching, which is performed under acidic conditions and at high temperatures, the devices used in the bleaching corrode over time, even if they are made of stainless steel.
- It causes less fiber damage (less chemical degradation, and less weight loss) as compared to other bleaching systems.
- Its bleaching effect is good and permanent, causing no yellowing at later stages.
- It allows combined scouring and bleaching process since peroxide bleaching is carried out under alkaline conditions at or near boiling.
- It shows compatibility with optical brighteners and most dyes.
- It can be applied by hot or cold, and batch or continuous methods.
- Residuals in cotton (fats, oils, waxes and pectines) do not diminish the bleaching effectiveness since they have a significant stabilizing effect on hydrogen peroxide by preventing excessive loss of oxygen before bleaching. However, before hypochlorite bleaching, it is necessary to remove all these impurities from natural cellulosic fibers by boiling with NaOH for a long time since they deplete the available hypochlorite resulting in reduced bleaching effectiveness.
- No antichlor treatment is required after peroxide bleaching.

The limitations of hydrogen peroxide bleaching can be summarized as follow: [1-8].

- Cotton bleaching with H_2O_2 requires harsh processing conditions (extremely alkaline conditions at or near the boiling temperature) leading to intensive energy consumption and severe fiber damage.

- Hydrogen peroxide is a highly unstable molecule under alkaline medium, decomposing readily to water and oxygen with release of heat. This reaction is catalyzed in the presence of metal ions (Fe, Cu, Co, Mn, etc.). Catalytic degradation of cellulose may occur with catalytic decomposition of peroxide due to the presence of the metal ions in the fabric or in the bleach solution.
- Stabilizers must be added to the bleach solution to control the decomposition of H_2O_2 .
- After bleaching, a large amount of water is required to remove the residual H_2O_2 from the bleached substrate. In addition, neutralization process is applied to remove the residual alkali remaining on the substrate.

1.1.2.1 Peroxide-based bleaching mechanism

The most common conventional bleaching process uses a perhydroxyl anion (HO^{2-}) as the primary oxidation species. Hydrogen peroxide behaves like a very weak acid in aqueous medium and is relatively stable under acidic medium. It ionizes in water to form perhydroxyl ion (HO^{2-}), which is an active bleaching agent, and hydrogen ion ($K_{\text{diss}}=1.78 \times 10^{-12}$). The perhydroxyl is highly unstable and decomposes in the presence of organic substances/ oxidisable substance (coloured impurities in cotton) resulting in bleaching action as below: [4, 8, 10, 40-43].



Since H_2O_2 is a very weak acid, strong alkaline such as sodium hydroxide is often used in bleach bath to promote the formation of HOO^- anions in combination with other textile auxiliaries including stabilizers and wetting agents. Sodium hydroxide activates hydrogen peroxide by neutralizing the H^+ ion and shifting the reaction to the right, which is favourable for liberation of HO^{2-} [4-5, 8, 14, 40-42].



Hydrogen peroxide can also decompose to water and molecular oxygen under high temperature, high alkaline charge and in the presence of metal impurities, which can severely damage cotton. At pH 10 to 11 (pH 10.2 to 10.7), there is a moderate concentration of perhydroxyl ions, providing a safe and optimum pH for controlled bleaching, where the evolution rate of perhydroxyl ion is equal to the consumption rate for bleaching. The presence of more alkali (at higher pH above 10.8) will result in instability and rapid generation of perhydroxyl anion (rapid liberation of HO^{2-} ion), but more alkali will also promote the hydrogen peroxide decomposition. The peroxide rapidly breaks down and results in formation of oxygen gas which has no bleaching property. This reaction is catalyzed by the presence of transition metal ions (e.g. Fe, Mn, Cu, Co, Ag, etc.) in bleach bath, which reduces the possibility of bleaching. If the rate of decomposition is too high, the unused HO^{2-} may damage the fiber [1-4, 6, 14-15].



During oxidation, the polymerization degree of cellulose can be reduced due to the formation of oxycellulose (oxidized cellulose) (Figure 1.1). As the oxygen consumption increases, the carboxyl, aldehyde and ketone groups gradually increase. However, it is seen that ketone groups are the predominant functional groups formed on cellulose by hydrogen peroxide oxidation. Oxidised cellulose containing the electronegative aldehyde and ketone groups, which are in position to the glucosidic linkage, is sensitive to chain cleavage causing a significant decrease in the polymerization degree. To control the decomposition of peroxide and cellulose damage, stabilizers including sodium silicate, organic compounds and phosphates are often added to the bleach bath. They act as a pH buffer to maintain the pH at the optimum level and to form a complex with metals traces, which catalyze the degradation of the fibers [1, 6-8, 42-46].

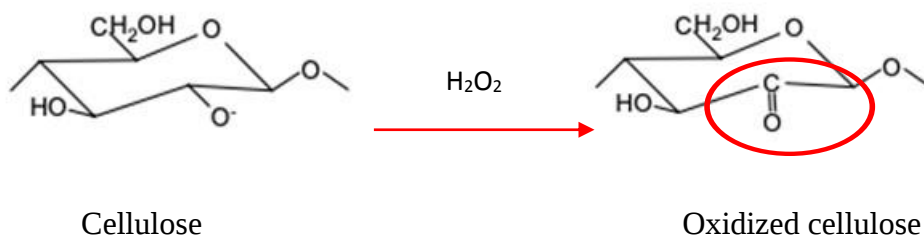


Figure 1.1: Oxidation of cellulose [47].

1.2 Activated Bleach Systems

In general, textile wet processes consist of a sequence of various processes involving the consumption of huge amounts of water and energy and the use of toxic and hazardous chemicals, which are the main source of environmental pollution. Furthermore, aggressive process conditions are also accompanied by deteriorating the product quality. Therefore; the main concerns in textile wet processes are reduction in production costs (energy and water consumption), reduction in environmental impact and improvement in product quality in order to make a contribution toward sustainability.

There has been an increasing demand for developing new and more sustainable bleaching systems for cotton under mild conditions (lower temperature, shorter process time, and lower chemical concentration, etc.) since bleaching is an essential process required for the pretreatment of cotton fibers. The industry and academic communities have conducted extensive research to reduce the temperature for industrial cotton bleaching. Compared to conventional hot peroxide bleaching at or near boiling temperature, the low temperature bleaching significantly reduces energy cost, saves time and causes less fiber damage. In addition, by shortening the bleaching time, energy consumption is reduced and the capacity to treat more fabric is increased [36, 48-51].

Since the beginning of the twenty-first century, researchers have focused on activated peroxide systems in the textile industry as an alternative approach to low temperature-cotton bleaching to minimize the problems caused by the conventional peroxide bleaching [16-19, 38, 42, 49-50]. Activated bleaching systems enable more efficient bleaching by increasing the oxidation rates [6, 38, 40, 52-54].

1.2.1 Bleaching with peracetic acid

In recent years, there has been considerable interest in low temperature-cotton bleaching. Peracetic acid (PAA), also known as peroxyacetic acid, peracid, peroxy-carboxylic acid, is most often used in the textile industry and has been also investigated for energy-saving and environmentally friendly bleaching systems. Peracids have superior low temperature bleaching capabilities as they are stronger oxidizing agent than hydrogen peroxide. The peracids are safe and efficient bleaching agent at mild condition. Based on the literature, the preferable process conditions for the use of peracids as a bleaching agent of cotton are the pH range of 6-7, the bleaching temperature of 50-80 °C and the bleaching time of 20-60 min.

PAA is environmentally safe as it decomposes to oxygen and acetic acid. PAA, an industrial chemical agent, is easily available and can be safely incorporated into an existing process. This acid can be produced directly in the bleaching bath. The bleaching action of PAA occurs as a result of epoxidation of double bonds present in undesirable-colored compounds as shown in Figure 1.2. Higher whiteness values can be achieved with less fiber damage at lower temperatures with this process [48-58].

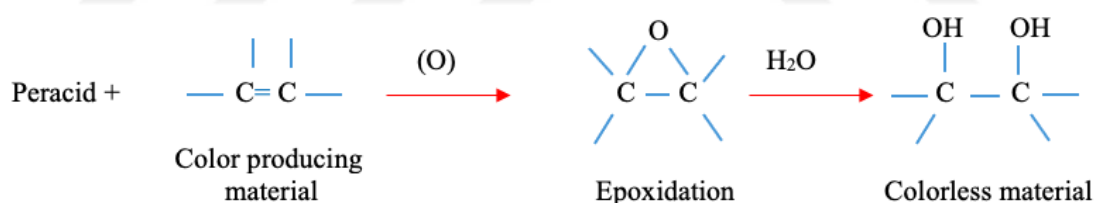


Figure 1.2: Epoxidation of double bonds via peracid [59].

PAA is commercially available for textile bleaching in 5%, 15% and 40% solutions known as "equilibrium peracid". Although PAA is not toxic compared to chlorine dioxide, highly concentrated solutions (35-40%) are dangerously explosive and difficult to use because the acid is volatile and has a sharp, irritating odor. All PAA solutions decompose to some extent during storage, hence stabilizers can be added to the solution to minimize decomposition. Tracking and control of inventory, including the amount of product, type of storage container and transportation method, plays a crucial role during storage.

Commercial PAA can be produced from hydrogen peroxide and glacial acetic acid with the use of strong mineral acid such as sulphuric acid in an equilibrium reaction, yielding a commercial product containing a mixture of PAA and peroxide. Alternatively, it can be produced from hydrogen peroxide and acetic anhydride at room temperature using suitable catalyst such as caustic soda or EDTA. However, surplus acetic anhydride should be avoided during this synthesis because the excess acetic anhydride may give rise to an undesirable side reaction yielding highly explosive diacetyl peroxide [4-5, 18, 56, 60]. In earlier work, Rucker and Cates found that excellent bleaching of cotton fibers can be achieved at 30 °C for 60 minutes by using acetic anhydride in peroxide bleaching bath [16, 61].

To reduce the danger in the on-site production of PAA from acetic anhydride/hydrogen peroxide and overcome transportation and storage problems, activators can be used to generate PAA in situ, resulting in increased oxidation activity of hydrogen peroxide, accordingly improved bleaching performance, decreased energy cost and process time and reduced fiber damage [1, 49, 56, 62-63]. A promising method to decrease energy consumption and lessen fiber damage is to add bleach activators into the peroxide bleaching solution to produce kinetically reactive peracid, which can make low-temperature bleaching possible [24, 62].

Bleach activators like anionic nonanoyloxybenzene sulphonate (NOBS), nonionic tetraacetylenediamine (TAED) and cationic N-[4 (triethylammoniomethyl)-benzoyl] caprolactam chloride (TBLC) generate peracids allowing bleaching at lower temperature and at reduced time, resulting in energy savings and reduced fiber damage [16-31, 47-48, 51, 63-66].

1.2.2 Bleach activators

Bleach activators, which are organic peracid precursors with O- or N-bounded acetyl groups, generate peracids in situ in hydrogen peroxide solution to increase the oxidation rates and consequently to reduce the bleaching temperature.

Under alkaline conditions, hydrogen peroxide first dissociates to form perhydroxyl anion. Bleach activators would be nucleophilically attacked by the perhydroxyl anions dissociated from hydrogen peroxide to form more kinetically active peracid species in situ as shown in Figure 1.3. This reaction is also called perhydrolysis. The formed peracids would be a more kinetically active bleaching agent than hydrogen

peroxide and play a key role in low-temperature bleaching. Generated peracid increases the oxidation rates and consequently lower the bleaching temperature [16, 18, 20-21, 28, 32, 38, 40, 56, 67-69].

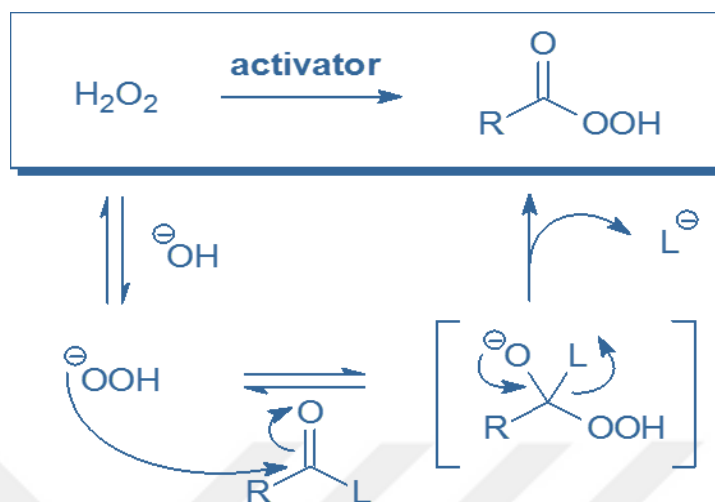


Figure 1.3: Reaction of bleach activator with H_2O_2 to form peracid [70].

A variety of bleaching activators have been investigated for use in activated peroxide systems such as tetraacetythylenediamine (TAED) [63, 65, 71], nonanoyloxybenzenesulfonate (NOBS) [45-46, 63], guanidine derivatives [66] and N-[4 (triethylammoniomethyl)benzoyl]lactam chlorides (TBLCs) [28-30], thiourea [72], and aminonitrile [34] and etc. [72-75].

Tetraacetythylenediamine (TAED), and the sodium salt of nonanoylbenzenesulphonic acid (NOBS) are two activators in widespread commercial use and are widely used in laundry detergent formulations for removal of coloring contaminants from textiles. In TAED-activated hydrogen peroxide bleaching system, TAED react with perhydroxyl ions derived from H_2O_2 to form triacetythylenediamine (TriAED) and diacetythylenediamine (DAED) with the release of two molecules of peracids in situ (Figure 1.4). However, TAED has poor solubility in water and its bleaching effectiveness has been found to be insufficient at temperatures below 50°C [8, 48, 50, 73].


$$\begin{array}{ccc} \text{C}_8\text{H}_{17}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{C}_6\text{H}_4-\text{SO}_3\text{Na} + \text{HOO}^- & \longrightarrow & \text{C}_8\text{H}_{17}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OOH} + ^-\text{O}-\text{C}_6\text{H}_4-\text{SO}_3\text{Na} \\ \text{NOBS} & & \text{Pernonanoic acid} \end{array}$$

$$\text{C}_8\text{H}_{17}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{C}_6\text{H}_4-\text{SO}_3\text{Na} + \text{C}_8\text{H}_{17}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OO}^- \longrightarrow \text{C}_8\text{H}_{17}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_8\text{H}_{17}$$

DAP

Figure 1.5: Reaction of NOBS with H_2O_2 to produce pernonanoic acid and NOBS side reaction to produce DAP [66].

With the aim of avoiding these limitations, an activated bleaching system using lactam-based cationic bleach activators **[N-[4-(triethylammoniomethyl)benzoyl]lactam chloride (TBLC)]** consisting of aromatic benzoyl chloride was developed and designed by the Procter and Gamble Company. It contains one

cationic group (quaternary ammonium cations), which can provide high water solubility and inherent great affinity toward negatively charged cellulosic fibers in aqueous solutions, leading to improved bleach effectiveness [24, 28, 35, 48, 77-78].

1.2.2.1 Cationic bleach activators (CBAs)

Cationic bleach activators (CBAs), a class of quaternary ammonium peracid precursors, were first developed by the Procter and Gamble Company in the mid 1990s to be incorporated into laundry and automatic dishwashing detergents. N-[4-(triethylammoniomethyl)benzoyl]lactam chlorides (TBLCs) are a promising class of cationic bleach activators for industrial cotton bleaching, consisting of aromatic benzoyl chloride (aromatic acid chloride). TBLCs have the same mechanism of activating peroxide with other bleach activators. However, differently from anionic bleach activators, TBLCs have at least one cationic group, providing high water solubility and inherent affinity toward negatively charged materials in aqueous solutions such as cellulosic fibers (Figure 1.6) [77-83]. Previous studies show that TBLCs can be applied by both cold pad-batch and hot peroxide bleaching processes for cotton [16-17, 20, 23, 29-30, 84].

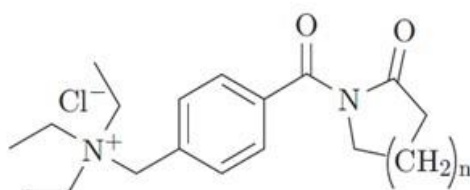


Figure 1.6: Aromatic-based cationic bleach activator (where n=1-5) [35].

N-[4-(triethylammoniomethyl)benzoyl] butyrolactam chloride (TBBC) and N-[4-(triethylammoniomethyl)benzoyl] caprolactam chloride (TBCC), the most promising cationic bleach activators to date, have similar structures except for the leaving group. In TBCC, caprolactam is the leaving group while in TBBC, the butyrolactam is the leaving group. During their synthesis, the chlorine substituent in the benzoyl chloride moiety reacts with the nitrogen in the amine group of triethylamine to produce cationic compound. The bleach mechanism of these cationic activators is the same, while the bleach performance of TBBC has been found to be better than the

1.3 Problem Statement and Purpose of Thesis

Nowadays, textile wet processes have constraints, being under pressure to be environmentally safe, cost effective and energy efficient. An important aspect in achieving efficient wet processing method is that it should be cost-effective, environmentally friendly and gentle to the textile material. Bleaching is an important and essential textile wet process in pretreatment process of textiles, especially for cotton-based textile materials. The most popular and well-known textile bleaching is performed by using hydrogen peroxide (H_2O_2). Although H_2O_2 is an environmentally acceptable chemical agent, hot peroxide bleaching is a long process and requires large amounts of water, energy, chemicals and time, resulting in increased cost and fiber damage. As an ecofriendly and environmentally benign approach, a number of studies have been conducted to promote more efficient use of energy and to achieve more sustainable and efficient bleaching [16-33].

Considering ecology and sustainability, low temperature bleaching becomes one of the key technologies in textile wet processes. Low temperature bleaching has important ecological and economical advantages such as lower energy and water consumption, higher productivity and lower unit cost compared to conventional bleaching. Industrial energy consumption plays a key role on the overall energy use, hence reduction in the temperature of the bleaching process results in large energy savings to achieve more sustainable production [43]. In addition, bleaching under mild conditions leads to less degreasing of the cotton, which provides reduced weight loss resulting in increased yield. Bleaching at low temperatures also causes less fiber damage (higher polymerization degree) and provides a softer and more voluminous touch.

This thesis focuses on low temperature cotton bleaching, providing an environmentally friendly bleaching system, mainly in terms of energy conservation, by achieving the same or higher bleaching efficiency (whiteness) and maintaining product quality, or minimizing the fiber damage as compared to conventional hot H_2O_2 bleaching system. Attempts to develop more environmentally benign, alternative bleaching processes have focused on new technologies such as bleach activators. The addition of activator in peroxide bleaching bath is an effective way to reduce the temperature of alkaline H_2O_2 bleaching. Nowadays, in the development of new bleach activator ecological and economical points of view must be taken into

consideration. Though there have been many reports on the use of cationic bleach activators for cotton bleaching, yet it has never reached the commercial success due to either production cost on a large scale, environmental concerns and/ or activity. With the aforementioned in mind, this study aims at the development and synthesis of a novel, sustainable based on aliphatic acid chloride and more cost-effective cationic bleach activator, with the aim of reduced production cost, enhanced affinity and bleaching performance, reduced fiber damage for low temperature cotton bleaching to overcome the drawbacks of traditional hydrogen peroxide bleaching and other cationic bleach activators based on aromatic acid chloride. The use of aromatic acid chloride for cationic bleach activators represents a serious pollution problem upon discharge of the effluent. With that in mind, N-[4-(N,N,N)-triethylammoniumchloride-butyryl] caprolactam (TBUCC) and N-[4-(N,N,N)-triethylammoniumchloride- butanoyl] butyrolactam (TBUCCB) were synthesized using butyryl chloride, which is less expensive, sustainable and highly reactive as compared to aromatic ones used in synthesis of cationic bleach activators reported in previous studies [21, 28-29, 32, 51, 67-68, 78, 81]. Newly-synthesized cationic bleach activators were applied for hot peroxide bleaching of cotton and the results were statistically evaluated to optimize the bleaching conditions. DFT calculations were performed to identify the advantages and theoretical limitations of the newly-synthesized cationic bleach activators for low temperature bleaching of cotton.

The objectives of this thesis can be summarized as follows:

- 1) to design and synthesize novel, more sustainable, highly effective cationic bleach activators for low temperature cotton bleaching to overcome the drawbacks of traditional hydrogen peroxide bleaching and other cationic bleach activators based on aromatic acid chloride
- 2) to establish the mechanism of low temperature cotton bleaching with hydrogen peroxide activated by the newly synthesized bleach activators and to optimize the bleaching conditions with the goal of reduced production and energy costs, improved affinity, increased oxidation rates (bleaching performance) and reduced fiber damage (cellulose polymer chains damage or degradation)

3) to identify the advantages and theoretical limitations of newly synthesized bleach activator for hydrogen peroxide bleaching of cotton

4) to elucidate the reaction mechanism of the bleach activator with cotton and to rationalize the superior efficiency of the bleach activator while maintaining the integrity of cellulose polymer chains compared to conventional hot hydrogen peroxide bleaching

1.4 Literature Review

Until date, several studies have been reported on low temperature hydrogen peroxide bleaching for cotton.

Lim et al. (2004) evaluated the performance of a cationic bleach activator, N-[4-(triethylammoniomethyl) benzoyl] caprolactam chloride (TBCC) in a hot peroxide bleaching process. It was observed that temperature had the greatest influence on the whiteness of cotton fabric, followed by the bleach activator concentration, hydrogen peroxide concentration and process time. If hydrogen peroxide is used to bleach cotton at room temperature it typically requires at least an overnight dwell time. By the addition of the cationic bleach activator to a conventional hot bleaching system, a similar level of whiteness was obtained at lower temperature and reduced time with maintaining wettability. The cationic activator was superior to the anionic activator, NOBS, in bleaching the fabric under the optimized conditions used in the study [16].

Lee et al. (2005) investigated hydrolytic stability of a novel cationic bleach activator, TBCC in aqueous solution. It was reported that TBCC is not hydrolytically stable in aqueous solution, therefore it should be stored in solid form and dissolved immediately before use in bleach bath. AvO (available oxygen) of the solution and whiteness of cotton decreased with increase in storage time of TBCC solution, as a result of hydrolysis. Hydrolysis leads to N-4-[triethylammoniomethyl] perbenzoic acid, which has no oxidizing power, resulting in a reduction of AvO. However, the initial rate of decrease in AvO was found to be highly dependent on the pH of the storage solution and the higher pH causes more rapid decrease in initial rate of AvO. This suggests that higher concentration of hydroxyl ions causes greater efficiency of hydrolysis. The AvO of TBCC in solid form was constant over several months, indicating that it is very stable in solid form. A close relationship was found between the reduction of AvO and WI [19].

Lim et al. (2005) have compared and evaluated two activated peroxide systems in cotton bleaching, one with a cationic (TBCC) N-[(triethylammoniomethyl) benzoyl] caprolactam chloride and the other with an anionic (NOBS) nonanoyloxybenzene sulphonate bleach activator. It was shown that the performance of TBCC was superior to that of NOBS, which is due to its higher substantivity toward negatively charged cotton in the bleach bath. The performances of both activators increased with temperature and sodium hydroxide concentration. Also, the performance of the cationic bleach activator improved with activator concentration, while an increase in the concentration of NOBS had a negative effect on the bleach performance [17].

Lavric et al. (2007) used a novel cationic bleach activator, N-[4-(triethylammoniomethyl) benzoyl] butyrolactam chloride (TBBC) in combination with peracetic acid (PAA) to investigate the improvement of cotton bleaching efficiency. The addition of TBBC increased the efficiency of the bleaching process of PAA. In the presence of TBBC, temperature had the greatest effect on PAA performance, followed by the PAA concentration and pH. While increasing concentration of TBBC had the least impact on the whiteness degree, but plays an important role in reducing fiber damage. It was reported that peracid, produced in situ from the reaction between hydrogen peroxide and TBBC, exhibited higher substantivity for the negatively charged surface of cotton than PAA, which leads to a higher level of oxidation on the relevant sites of the fiber in the bleach bath [23].

Shafie et.al. (2009) investigated one-step process for bio-scouring and PAA bleaching of cotton fabrics. Greige cotton fabric was desized either with PAA or ammonium persulphate prior to bio-scouring and PAA bleaching. The results show that desized cotton fabric can be successfully enzymatic scoured and PAA bleached at 60 °C for 90 min in one bath including TAED, sodium perborate, pectinase and non-ionic wetting agent. Desizing with PAA prior to bio-scouring and bleaching improves the whiteness index (WI) and the bleached fabric exhibits higher tensile strength and elongation at break compared with those fabric desizing using ammonium persulphate. It was observed that the desized cotton fabrics bleached with PAA and either cellulase or pectinase enzyme show excellent wettability and acceptable WI, indicating that the combination between PAA and either cellulase or pectinase enzyme did not have any adverse effect on bio-scouring of cotton fabric or low temperature bleaching of cotton fabric [76].

Lee et al. (2010) studied on that the hydrolysis rate of cationic bleach activators including different lactam leaving groups. The bleach activator containing a six-membered lactam ring (γ -valerolactam) was found to have the highest hydrolysis rate constant. The hydrolysis rate of the bleach activators containing 5-, 8-, and 9-membered lactam ring (butyrolactam, ω -heptalactam ω -octalactam, respectively) was lower than that of TBCC (containing 7-membered lactam, caprolactam), indicating higher stability than TBCC in aqueous solution. Although the bleach activator containing the 9-membered ring (ω -octalactam) as a leaving group was found to be the most stable compound in this study, the production cost of this compound is relatively high compared to the other compounds due to the high cost of ω -octalactam [29].

Xu et al. (2010) focused on hydrogen peroxide bleaching of regenerated bamboo in the presence of TBBC as a bleach activator. It was observed that the ratio of TBBC to hydrogen peroxide and pH are critical factors to achieve effective bleaching at low temperature. Using equimolar amounts of TBBC and hydrogen peroxide at 50 °C at pH 7, comparable whiteness and less fiber damage were obtained compared to conventional peroxide bleaching. However, at pH 11.5, TBBC had no effect on whiteness, which may be due to hydrolysis or decomposition [31].

Hou et al. (2010) synthesized and characterized (N-[4 triethylammoniomethyl]-benzoyl) caprolactam chloride (TBCC) as a novel cationic activator for hydrogen peroxide bleaching. Cotton fabric was bleached with hydrogen peroxide at low temperature 60 °C using TBCC. The results show that whiteness index and wettability of the cotton fabric bleached at low temperature were similar to that of conventional bleached cotton fabric. Increasing in NaOH concentration from 0 g/L to 2 g/L provided the whiteness index to increase from 28.9 to 68.3. However, the whiteness index was found to decrease as the NaOH concentration was increased further. Because, liberation of HOO⁻ anion at higher NaOH concentration was so rapid that it became unstable with the formation of oxygen gas, which has no bleaching property. At same time, TBCC could be hydrolyzed and produced the unbleachable compound [26].

Abdel-Halim et al. (2011) prepared peracetic acid by the reaction of hydrogen peroxide with glacial acetic acid in the presence of concentrated sulfuric acid as a catalyst. The results indicate that peracid is not formed in the absence of sulfuric

acid. Because, acetic acid is partially converted to peracetic acid, and the sulfuric acid acts as the acid catalyst needed for the reaction. As concentration of the catalyst sulfuric acid increases, the amount of hydrogen peroxide consumed in forming peracid increases and, consequently the percentage of peracid formation increases. The stability of the peracid decreases at a concentration of sulfuric acid higher than 0.125 mol. At a concentration of 40 ml / l peracetic acid at 70 °C using a liquor ratio of 1:30 at pH 6 for 30 minutes, and then continuing the bleaching process for an extra 30 minutes by increasing the pH to 10.5, satisfactory whiteness index (64) with reasonable loss in tensile properties was achieved [27].

Xu et al. (2013) investigated the TAED-activated peroxide system for bleaching of cotton. It was found that the TAED-activated peroxide system is most effective using stoichiometric amounts of H₂O₂ and TAED under near-neutral pH conditions. Use of H₂O₂ in the TAED-activated peroxide system in excess of the stoichiometric amount had no addition effect on the bleaching performance since H₂O₂ was not active enough to bleach cotton at pH less than 10. No addition effect on bleaching was observed when excessive amounts of H₂O₂ were used under alkaline conditions. This may be attributed to the base-catalyzed bimolecular decomposition of peracetic acid and the nucleophilic attack by H₂O₂ on peracetic acid. NaHCO₃ was found to be more applicable than Na₂CO₃ and NaOH for the TAED-activated peroxide system due to its excellent ability to maintain near-neutral pH [33].

The feasibility of a complete enzymatic one-bath pretreatment of the cotton fabric at low temperature was studied by Spicka et al. (2013). The cotton fabric was enzymatically desized, scoured and bleached with an enzyme mixture of starch degrading enzymes (a mixture of α -amylases, amyloglucosidases and pullulanases), pectinases and glucose oxidases, respectively. Bleaching was performed in the presence TAED at 50 °C and neutral pH (pH 7.5) for two hours. It was concluded that hydrogen peroxide can be efficiently enzymatically produced from the sizing agent and converted with TAED to form peracetic acid to bleach the cotton fabric. While the obtained whiteness was medium, high tensile strength and high polymerization degree were obtained [85].

Zeng et al. (2015) used a novel activator, sodium 4-(2-decanoyloxyethoxycarbonyloxy) benzene sulfonate (DECOBS) for the bleaching of cotton fabric. They performed H₂O₂/DECOBS-activating system under alkaline

medium at low temperature (70 °C) and obtained the same bleaching performance with those of the conventional bleaching at 90 °C, providing energy saving [24].

Fei et al. (2015) analyzed the process factors affecting the bleaching performance of activated peroxide systems on bleaching of cotton fabric such as type of bleach activator, concentration of bleach activator, molar ratio of hydrogen peroxide to bleach activator, type of peroxide stabilizer, concentration of peroxide stabilizer, type of wetting agent, concentration of wetting agent, pH value of bleach bath, bleaching temperature, bleaching time, liquor-to-goods ratio, cotton substrate, and water quality. N-[4-(triethylammoniomethyl)benzoyl]caprolactam chloride (TBCC) and TAED were used as bleaching activators while EDTA (Ethylenediaminetetraacetic acid) and a commercial peroxide stabilizer named DM-1403, which is a polyacrylate-based chelating agent, were used as peroxide stabilizers. Results revealed that an increase in the bleaching temperature caused an increase in the degree of whiteness of cotton fabric. This suggests that the perhydrolysis of bleach activators and oxidative bleaching of cotton fabric with the produced peracids were performed at faster rates as the bleaching temperature increases. Bleaching performance of TBCC was found to be more effective than that of TAED. An increase in pH value of bleach bath led to a reduction in the degree of whiteness of cotton fabric. DM-1403 was more effective than EDTA in improving the bleaching performance. Using in large excess of the stoichiometric amount of hydrogen peroxide to bleach activator decreased bleaching performance as compared to a 1:1 molar ratio (using stoichiometric amount or a slightly excess of stoichiometric amount) of hydrogen peroxide to bleach activator. This is because the peracids produced from the bleach activators were decomposed to a large extent by the attack of excess hydrogen peroxide [84].

Luo et al. (2015) established activated peroxide system for low-temperature bleaching of cotton by incorporating N-[4-(triethylammoniomethyl)benzoyl]caprolactam chloride (TBCC), hydrogen peroxide (H_2O_2) and sodium bicarbonate (NaHCO_3) into an aqueous solution. It was found that the performance of TBCC-activated peroxide system on bleaching of cotton could be improved by increasing temperature, concentration of TBCC and t time. Low-temperature bleaching of cotton was accomplished using a 1:1.1:1.2 molar ratio of TBCC, H_2O_2 and NaHCO_3 , providing equivalent whiteness and slightly inferior water absorbency compared to

conventional bleaching, resulted in no apparent fiber damage. Although NaHCO_3 exhibited no apparent effect on bleaching performance, NaHCO_3 was required for the TBCC-activated peroxide system to maintain the desired pH range [28].

Spicka et al. (2015) bleached a knit fabric from regenerated bamboo fibers with four different PAA bleaching processes: with only PAA, with PAA or H_2O_2 in combination with TAED, and with H_2O_2 in combination with arylesterase enzymes (PAA, PAA/TAED, H_2O_2 /TAED, and H_2O_2 /ENZ). The bleaching processes with PAA were carried out under neutral to slightly alkaline pH at 65 °C. They found that the optimum pH for bleaching with PAA is between 7 and 8. However, the initial pH 8 for the H_2O_2 /TAED bleaching process results in lower bleaching ability. Among the low-temperature bleaching with PAA, the PAA/TAED process has the highest WI (WI=71), followed by the conventional H_2O_2 (WI=70.3), PAA (WI=70), H_2O_2 /ENZ (WI=69), and H_2O_2 /TAED bleaching processes (WI=58). All differently PAA bleached fabrics had higher tenacity compared to the conventionally H_2O_2 -bleached fabric [22].

Chen et al. (2016) reported that the bleaching performance unexpectedly diminished as the TBCC concentration increased over the range of 25–100 g/L. It can be thought that the exchange of TBA on cotton fibers with TBCC and TPA in bleach bath would be prevented to some extent and hence the reduction in the ion activities of TBCC, TPA and TBA will result in a decrease in bleaching performance. However, experimental results show that TBCC-activated peroxide system had a limitation on cold pad-batch bleaching of cotton fabric since padding fabric through a bleach bath requires an extremely high TBCC concentration to ensure sufficient amounts of chemicals loaded on the fabric. It was observed that the degree of whiteness decreased as the TBCC concentration increased in the padding bath. In addition, extending the dwell time was found to have no apparent effect on the degree of whiteness [21].

In Wang et al. (2012) research, the synthesis of eight novel cationic bleach activators were synthesized, four having a caprolactam leaving group and different cationic groups (triethylamine, pyridine, nicotinamide, 1;4-diazabicyclo(2.2.2)octane and 3-picoline) and four having the same varying cationic groups with butyrolactam leaving group. According to obtained results, the activators including 3- picoline

cationic group (PBCC and PBBC) exhibited similar bleaching performance to the current generation of bleach activator, TBBC [51].

Wei et al. (2014) synthesized a series of N-[4 (dimethylalkylammoniomethyl) benzoyl]caprolactam chlorides as cationic bleach activators with various alkyl chain lengths. All these synthesized cationic bleach activators were found to be effective for low-temperature bleaching of cotton fabric under near-neutral pH conditions, but their bleaching performance can be affected by the alkyl chain length. An increase in the alkyl chain length from 2 to 6 carbon atoms could be beneficial in improving bleaching performance, while an increase in the alkyl chain length from 8 to 16 carbon atoms led to a significant reduction in bleaching performance, which may be attributed to the physical interactions between the alkyl chains and cotton fibers [81].

Wang et al. (2017) synthesized three new bleach activator for cotton containing pyridinium (PBBC), nicotinamido (NABBC), and 3-methylpyridinium (3-PBBC) cationic groups. Bleaching results indicated that all of the cotton fabrics treated with the bleach activator showed an improvement in whiteness at a temperature below 95 °C as compared to controlled fabrics bleached without bleach activator. It was reported that 3-PBBC exhibited the best bleaching performance with a similar whiteness index to the prototype bleach activator, TBBC. The chronic toxicity and mutagenicity of TBBC and 3-PBBC were also evaluated. 3-PBBC was found to be less toxic to *D. similis* and *R. subcapitata*, less mutagenic to TA100 as compared to TBBC [67].

Yu et al. (2017) conducted TBCC- H₂O₂ activated bleaching system at a pilot plant scale. It was reported that pilot-plant bleaching with the TBCC-activated peroxide system provided comparable degree of whiteness and a slightly lower water absorbency of cotton fabric with no apparent fiber damage. Cotton fabric bleached with TBCC-activated peroxide system was found to meet requirements for trichromatic reactive dyeing. TBCC-activated bleached samples was found to be dyed into a slightly duller and redder shade of gray, which may be due to a slightly lower degree of whiteness and a higher extractable content of the samples bleached with the TBCC [68].

Liu et al. (2017) investigated pentaacetyl glucose (PAG) as a bleach activator for low temperature cotton bleaching. It was reported that WI and H₂O₂ decomposition rate

strongly increased at 70 °C in the presence of PAG. HO concentration, which was found to be one of the important bleaching species in the H₂O₂/PAG system, increased by 10 times in the H₂O₂/PAG system as compared to conventional H₂O₂ bleaching [86].



2. EXPERIMENTAL STUDY

2.1 Materials

ϵ -Caprolactam (99%), γ -butyrolactam (99 %), triethylamine (99.5%) and 4-chlorobutanoyl chloride (98%) were purchased from Alfa Aesar (USA) to synthesize bleach activator. Hydrogen peroxide (35% w/w) was purchased from Alfa Aesar (USA) and peroxide stabilizer (Ruco-Stab OKM) was provided from Rudolf Group (Germany). 100% single jersey knitted cellulosic greige and scoured fabrics were used in bleaching experiments.

2.2 Instrumentation

The new bleach activator was characterized by Fourier transform Infrared (FTIR), mass spectrometry and proton nuclear magnetic resonance (^1H -NMR). FTIR measurements were performed using Thermo Nicolet Nexus 470 spectrometer. Mass spectra were recorded on Agilent Technologies 1200 SL Liquid Chromatograph with Evaporative Light Scattering (ELS) detector and 6520 QTOF mass spectrometer. Proton nuclear magnetic resonance (^1H -NMR) spectrum was recorded in Methanol- d_4 (CD_3OD) using a 500 MHz BrukerAvance Spectrometer.

All bleaching experiments were conducted using an Ahiba Nuance Infrared Laboratory Dyeing Machine (Datacolor international, USA). The whiteness index of all fabrics was measured using a Datacolor Spectraflash SF600X (Datacolor International, USA). The fluidity of the cotton samples was measured using Ostwald cannon–fenske routine viscometer to calculate the average polymerization degree of the cotton samples.

2.3 Methods

2.3.1 Designing of novel bleach activator

Efficiency of the bleaching system essentially depends on the kinetics of peracid generated, the nature of the leaving group, and hydrolytic stability of bleach

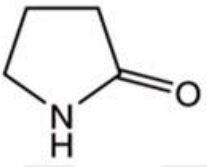
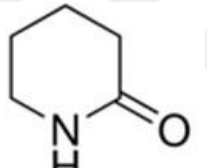
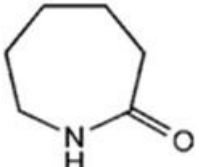
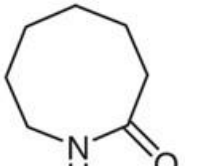
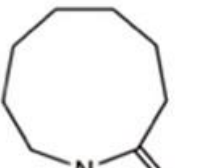
activator. The kinetic potency of the generated peracid is influenced by the nature of the acyl group. In this study, in order to increase the water solubility of the bleach activator and facilitate potential inherent substantivity toward negatively charged cellulosic fibers in aqueous solutions, aliphatic acid chloride was selected.

The polarity of a bond depends on the electronegativities of the bonded atoms. A polar covalent bond exists when atoms with different electronegativities share electrons in a covalent bond. Electronegativity is a measure of the attraction of an atom for bonding electrons in molecules compared to that of other atoms. Large electronegativity values indicate a stronger attraction for electrons than small electronegativity values. Large differences between the electronegativities of the bonded atoms increase the polarity of bonds. Dipole moment indicates the magnitude of the polarity of a bond. TBBC and TBCC compounds consist of six equivalent carbon atoms in an aromatic ring, in which all carbon-carbon atoms are identical. This aromatic ring is a symmetrical molecule that contains only C-C and C-H bonds, and hydrocarbons are nonpolar. C is slightly more electronegative than H (by 0.35 units), so a C-H bond is very slightly polar and has a small dipole moment. However, each C-H bond in the aromatic ring has a partner that points in exactly the opposite direction. Therefore; all the bond dipoles cancel exactly. This makes aromatic ring a nonpolar molecule. In this study, 4-chlorobutyryl chloride, aliphatic acyl chloride (also called acid chloride), was used instead of 4-chloromethyl benzoyl chloride, which is an aromatic acyl chloride, and includes nonpolar aromatic ring, in order to improve the polarity, accordingly, efficiency of the bleach activator. The term acyl chloride describes a functional group containing a carbonyl group (C=O) and a chlorine atom (Cl). Aliphatic acyl chlorides are extremely reactive acylating agents while aromatic acyl chlorides like benzoyl chloride are less reactive [87-90]. In addition, considering the production cost and environmental impact of bleach activator, 4-chlorobutyryl chloride is more cost-effective and more sustainable than 4-chloromethyl benzoyl chloride.

In previous studies, hydrolytic stability of bleach activator (the rate of hydrolysis) was found to be related to the leaving group of the compound. For the synthesis of new cationic bleach activator, lactam-based leaving group was used as a good leaving group. It was reported that bleach activator containing γ -valerolactam has the highest hydrolysis rate constant. Although ω -octalactam based activator was found

to be the most stable in aqueous solution, the synthesis of that activator is not economically feasible compared to other compounds due to the high cost of ω – octalactam. Among these leaving groups, ϵ -caprolactam and γ -butyrolactam are low cost alternatives, which have higher hydrolytic stability than other lactam groups and provide satisfactory bleaching performance [29, 56, 91]. In this study, ϵ -caprolactam and γ -butyrolactam were used as the leaving group. Different lactam-based leaving groups and their hydrolytic stabilities were summarized in Table 2.1.

Table 2.1: Different lactam-based leaving groups and their hydrolytic stabilities [29, 56, 78, 91].

Leaving groups (Lactam based)			
	Structure	Chemical formula	Hydrolytic stability
Butyrolactam (2-Pyrrolidone)		C ₄ H ₇ NO M _w = 85.10	-demonstrating higher hydrolytic stability than ϵ -caprolactam based activator in aqueous solution
δ-Valerolactam		C ₅ H ₉ NO M _w = 99.13	-highest hydrolysis rate constant, demonstrating lowest hydrolytic stability in aqueous solution
ϵ-Caprolactam		C ₆ H ₁₁ NO M _w =113.16	- lower hydrolytic stability than γ - butyrolactam based activator in aqueous solution
ω-Heptalactam		C ₇ H ₁₃ NO M _w =127.19	-demonstrating higher hydrolytic stability than ϵ -caprolactam based activator in aqueous solution
ω -Octalactam		C ₈ H ₁₅ NO M _w = 141.21	-most stable compound -cost of manufacture of this compound is relatively higher than others

2.3.2 Synthesis of bleach activator

In order to achieve effective cotton peroxide bleaching under mild conditions, a novel aliphatic-based cationic bleach activators, N-[4-(N,N,N)-triethylammonium-chloride-butyryl] caprolactam (TBUCC) and N-[4-(N,N,N)-triethylammoniumchloride- butanoyl] butyrolactam (TBUCCB) were developed and synthesized. In an alkaline peroxide bleaching bath, H_2O_2 first dissociates to generate perhydroxyl anion (OH^-). Cationic bleach activator reacts with perhydroxyl anion generating a kinetically potent peracid, as illustrated in Figure 1.3, which rapidly adsorbs, then diffuses into cellulosic fibers, and effectively oxidizes color bodies and renders the fabric significantly whiter. Peracids possess higher oxidizing power than H_2O_2 at lower temperature and efficiently oxidize stains and natural-colored impurities in cotton in a much shorter time.

The synthesis of bleach activators was carried out using a two-step reaction procedure: synthesis of intermediate product by condensation reaction of 4-chlorobutyryl chloride with lactam leaving groups, followed by quaternization step to obtain the cationic bleach activators. The steps for bleach activator synthesis are shown in Figure 2.1.



Figure 2.1: Synthesis of bleach activator.

The byproduct, triethylammonium hydrochloride salt (Et_3N , HCl), must be removed from the intermediate by extraction of the product with a proper solvent. Synthesized intermediate was mixed with different organic solvents such as tetrahydrofuran (THF), ethyl acetate, dichloromethane, acetonitrile and etc. to make Et_3N , HCl insoluble as a white powder in the solution and effectively remove the by-product by filtration.

2.3.2.1 Synthesis of N-[4-(N,N,N)-triethylammoniumchloride-butyryl] caprolactam, TBUCC

TBUCC was synthesized using 4-chlorobutyryl chloride, is an aliphatic acyl chloride, with caprolactam as a leaving group and triethylamine as a cationic group. During the synthesis of bleach activator, the carbonyl carbon of the acid chloride undergoes nucleophilic attack leading to a replacement of the chloride by caprolactam, a better leaving group.

Following the reaction of the aliphatic acid chloride with ϵ -caprolactam, it was quaternized with tertiary amino compound to give the cationic bleach activators (see Figures 2.2 and 2.3). In the first reaction step, 4-chlorobutyryl caprolactam was synthesized. In the second reaction step, N-[4-(N,N,N)-triethylammoniumchloride-butyryl] caprolactam (TBUCC) was synthesized.

Synthesis of the intermediate, 4-chlorobutyryl caprolactam

The first step is to make the intermediate, 4-chlorobutyryl caprolactam. Referring to Figure 2.2 and 2.3, the intermediate was synthesized by the condensation reaction of 4-chlorobutyryl chloride with caprolactam leaving group.

Caprolactam (22.6 g, 0.2 mol) and triethylamine (30.5 g, 0.3 mol) were dissolved in toluene (225 mL) under nitrogen, and heated to reflux. 4-Chlorobutyryl chloride (28.2 g, 0.2 mol) was dissolved in toluene (75 mL) and added slowly to the solution. The solution was refluxed for 6 h, cooled to room temperature and filtered. The filtrate was cooled and stored overnight under the hood. The filtrate was washed with diethyl ether and dried at 40 °C under vacuum overnight.

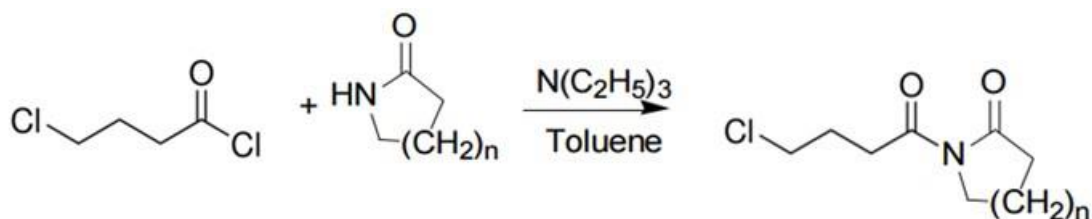


Figure 2.2: Synthesis of 4-chlorobutyl caprolactam (n=3) (Mw=217.5).

Synthesis of final product, N-[4-(N,N,N)- triethylammoniumchloride-butyryl] caprolactam (Quaternization), TBUCC

In the second step, the intermediate was reacted with triethylamine to furnish the final bleach activator, TBUCC. Figure 2.3 summarizes the reaction.

4-Chlorobutyl caprolactam (21.75 g, 0.1 mol) was dissolved in acetonitrile (150 mL) under nitrogen. Triethylamine (0.2 mol) was added drop wise to the solution and the solution was refluxed for 4 h. The solution was cooled to room temperature and the solvent evaporated using a rotary evaporator. The product was washed with diethyl ether and then dried at 40 °C under vacuum overnight.

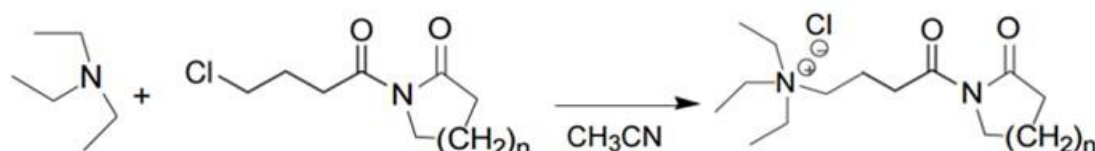


Figure 2.3: Synthesis of N-[4-(N,N,N)-triethylammoniumchloride butyryl]caprolactam (TBUCC) (n=3) (Mw=318.74).

2.3.2.2 Synthesis of N-[4-(N,N,N)-triethylammoniumchloride- butanoyl] butyrolactam (TBUCB)

N-[4-(N,N,N)-triethylammoniumchloride-butanoyl] butyrolactam (TBUCB) was synthesized using a two-step reaction procedure. In the first step, the intermediate was synthesized by the condensation reaction of 4-chlorobutanoyl chloride with butyrolactam to form the corresponding amide (intermediate) and triethylammonium hydrochloride salt as (a byproduct). Butyrolactam (17.2 g, 0.2 mol) was mixed with triethylamine (0.3 mol, 30.5 g) in toluene (225 mL). The mixture was refluxed under

nitrogen. Subsequently, 4-chlorobutanoyl chloride (28.2 g, 0.2 mol) was dissolved in 75 mL of toluene and added slowly to the solution to obtain the intermediate (4-chlorobutanoyl butyrolactam). The solution was refluxed for 6 h, cooled to room temperature. The reaction mixture was dissolved in tetrahydrofuran (instead of acetonitrile) and the salt as a white powder was separated from the reaction mixture by filtration. The filtrate was rotary evaporated to remove tetrahydrofuran, leaving the pure intermediate.

In the second reaction step, 0.1 mol of 4-chlorobutanoyl butyrolactam (intermediate) was refluxed with triethylamine (0.2 mol) in 150 mL acetonitrile for 4 hours to furnish the cationic bleach activator, (TBUCB). The solution was cooled to room temperature and the solvent evaporated using a rotary evaporator to give the cationic bleach activator, (TBUCB) (Figure 2.4).

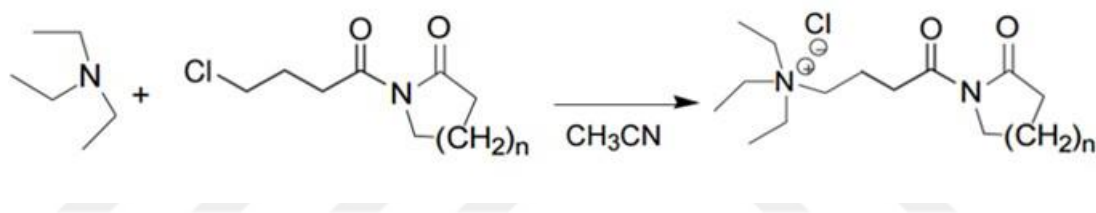


Figure 2.4: Synthesis of N-[4-(N,N,N)-triethylammoniumchloride- butanoyl] butyrolactam (TBUCB), (n=1) (Mw=290.83).

2.3.3 Bleaching method: *Hot peroxide bleaching*

2.3.3.1 Activated bleaching

Hot peroxide bleaching method was applied to evaluate and optimize the bleaching performance of synthesized bleach activators for cotton. An Ahiba Nuance Infrared Laboratory Dyeing Machine (Datacolor International, USA) was used for the hot peroxide bleaching experiments. A bleaching bath was prepared using the desired amount of the bleach activator, hydrogen peroxide and sodium hydroxide at a liquor-to-goods ratio of 20:1. 1 g/L stabilizer and 1 g/L wetting agent were kept constant for all experiments. The bath was heated to target temperature at the rate of 4 °C/min and bleaching was conducted for 30 min. After bleaching, fabric was removed from the bleach bath and rinsed with copious amounts of cold water, then dried under ambient conditions.

2.3.3.2 Conventional bleaching

For comparison, the bleaching was also applied using commercial bleaching recipe for cotton, including 6 g/L H₂O₂ (35 %, w/w), 3 g/L NaOH, 1 g/L wetting agent and 1 g/L stabilizer. Bleaching was conducted at 98 °C for 30 min using a liquor-to-goods ratio of 20:1.

Whiteness index (WI) of unbleached cellulosic fabric was 35.77 while the WI of a conventional bleached fabric (without bleach activators) was 75.77 (Table 2.2).

Table 2.2: Recipe of conventional hot peroxide bleaching.

Conc. of H ₂ O ₂ (g/L), 35% w:w	Conc. of NaOH, 50% w:w	Stabilizer (g/L)	Wetting agent (g/L)	Temp. (°C)	Time (min.)	WI
6	3	1	1	98	30	75.77

2.3.4 Evaluation of bleaching performance

2.3.4.1 Whiteness measurement

The whiteness index (WI) of all fabrics was measured using a Datacolor Spectraflash SF600X (Datacolor International, USA) under illuminant D65 and 100 standard observer, specular included, large area view and UV component included. Test were conducted by using the CIE method according to AATCC Test Method 110 [92]. Measurements were repeated four times by rotating the sample 90° between each measurement and the average of the repetitions was recorded.

2.3.4.2 Water absorbency measurement

Wettability of samples was tested by recording the time required for the droplet to penetrate completely into the fabric according to AATCC Test Method 79 [93].

2.3.4.3 Determination of fiber damage

Degree of polymerization (DP) demonstrates changes in fiber structure and it is an indirect measure of fiber damage. Higher DP values indicate less fiber damage. Average polymerization degree of bleached (by conventional hot peroxide bleaching method and activated bleaching system) and unbleached cotton samples, from viscosity measurements, was calculated using the below equation, in which the

fluidity (F) of a dispersion of samples in cupriethylenediamine (cuen) (0.1 M) solution was measured according to AATCC TM 82 standard [94].

$$DP = 2032 \left[\log \frac{74.35 + F}{F} \right] - 573$$

Ostwald cannon–fenske routine viscometer was used for measuring the fluidity of samples. The experimental set up for viscosity measurement is presented in Figure 2.5.



Figure 2.5: Experimental set up for viscosity measurement (Ostwald cannon–fenske routine viscometer).

Fluidity is calculated in rhes as follows: [92]

$$F = \frac{100}{ctd}$$

Where:

c = instrument constant determined from a liquid of known viscosity;

t = efflux time of the liquid within the ring interval in seconds;

d = density of cuen solution (1.052)

2.3.5 Central composite design and statistical evaluation

Response Surface Methodology (RSM) is a combination of statistical and mathematical methods used to determine the optimum experimental conditions with saving time and cost by reducing the number of experiments. Central composite

design (CCD) (orthogonal blocks) was used with TBUCB to establish an optimized TBUCB-activated hot peroxide-cotton bleaching system since CCD is one of the most favored response surface methodology (RSMs) for process optimization. The experimental design was performed and multiple factors and their interactions were statistically evaluated using Minitab [95]. The order of experiments was arranged randomly. The significance of the process parameters (independent variables) and their interactions were evaluated by means of analysis of variance (ANOVA) with a 95% confidence level.

In this study, independent variables, which are factors that affect the process, are the concentration of activator, molar ratio of activator: H_2O_2 , molar ratio of H_2O_2 :NaOH, temperature and time, while the dependent variable, which is the response /outcome that may change as a result of changes in independent variables, is whiteness index. Slightly higher molar ratio of alkaline to H_2O_2 was used for activating peroxide in bleaching bath. Five levels of each variable were selected, including 7 at center points, 16 at factorial points, 10 at axial points, giving a total of 33 experiments.

2.3.6 Determinination of the limitations of TBUCB at molecular level for cotton: Computational methods

Density functional theory (DFT) calculations were performed at the B3LYP hybrid functional and 6-311+g(d,p) basis set level in the Gaussian 16 Rev. A.03 software package [96-99]. Geometry optimizations were started from different initial structures to obtain lowest energy geometry. Highest occupied molecular orbitals (HOMO), lowest unoccupied molecular orbitals (LUMO), and electrostatic potential surface (ESP) were calculated and mapped onto the optimized geometry of the TBUCB activator. Atomic charges on the activator were calculated by using ESP fitting scheme of Merz-Singh-Kollman (MK) and atomic dipole moment corrected Hirshfeld atomic charges (ADCH) [100-102]. Fukui reactivity indices for the nucleophilic attack sites on the activator were calculated by using finite difference approximation by using the atomic charges based on the MK charges [103]. The geometry of a transition structure and activation barriers are of key importance in describing the reaction mechanism of hydrogen peroxide anion attack at the most susceptible sites for nucleophilic attacks. Free energy profile for the reaction barrier of the perhydroxyl anion attack to the carbonyl groups were calculated at 70 °C. The reaction barrier for the attack to TBUCB is compared with the reaction barrier for

TAED activator. The stationary states were determined by vibrational frequencies where transition states were validated as saddle points by only one imaginary frequency. All calculations were performed in water to mimic the experimental conditions by integral equation formalism polarizable continuum model (IEFPCM) [104].





3. RESULTS AND DISCUSSIONS

3.1 Characterization

3.1.1 Fourier transform infrared spectroscopy (FTIR)

FT-IR spectrum of synthesized bleach activator, TBUCC, was shown in Figure 3.1. Bands at 2979, 2945 and 2881 cm^{-1} were assigned to C–H stretching vibrations of caprolactam (antisymmetric and symmetric- CH_2 -stretching), and at 1686 cm^{-1} , associated with carbonyl (C=O) peak of the amide. The peak observed at 1474 cm^{-1} was due to CH_2 bending, at 1445 cm^{-1} was due to C–H bending and wagging. C–N stretching absorptions are found at 1200–1350 cm^{-1} for aromatic amines and at 1000–1250 cm^{-1} for aliphatic amines. In Figure 3.1, peak at 1332 cm^{-1} was assigned to C–N stretch between the 4-chlorobutyryl chloride and caprolactam, while peaks at 1036, 1072, 1147 cm^{-1} were assigned to C–N stretch between triethylamine and 4-chlorobutyryl chloride. The peak at 1170 cm^{-1} represents CO–N skeletal motion [105-108]. The peaks located at 857 and 851 cm^{-1} belong to C-H out of plane bending.

The most characteristic band in the triethylammonium hydrochloride salt is the N–H bond stretch, and it appears as a weak to medium, somewhat broad band in the range of 3300–3600 cm^{-1} [105-106]. A broad peak centered at 3394 cm^{-1} was found corresponding to N–H bond stretching, indicating the presence of amine salt (triethylamine hydrochloride) produced during the intermediate synthesis. This reaction leads to the production of hydrogen chloride which reacts with triethylamine to form triethylammonium hydrochloride.

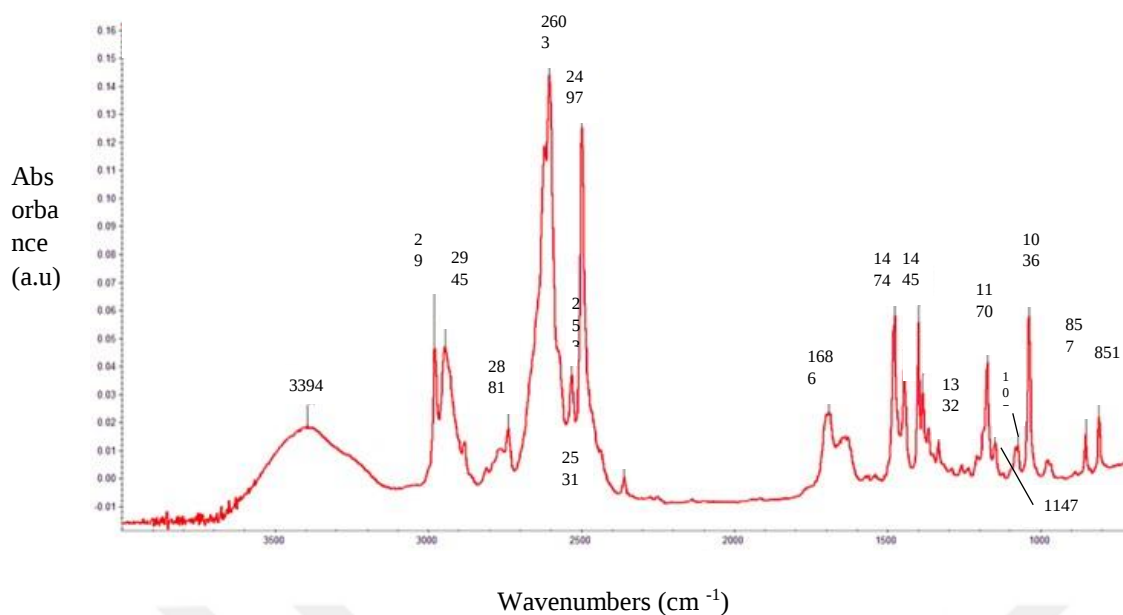


Figure 3.1: FTIR spectrum of synthesized bleach activator (TBUCC).

The byproduct, triethylammonium hydrochloride salt, must be removed from the intermediate by extraction of the product with a proper solvent. To remove the salt, the product was dissolved in acetonitrile and the hydrochloride salt was filtered off. The filtrate was washed twice with diethyl ether and successively dried under vacuum. The diethyl ether and excess triethylamine were removed via rotary evaporation, leaving the pure intermediate. FTIR spectrum of the product (TBUCC) after removal of hydrochloride salt is shown in Figure 3.2. From the FT-IR spectrum in Figure 3.2, it is clearly seen that peak in the range of 3300–3600 cm^{-1} disappeared, indicating hydrochloride salt was mostly removed from the intermediate. The peaks around 3500–4000 cm^{-1} arise from moisture while the peaks around 1700–2400 cm^{-1} come from diamond ATR.

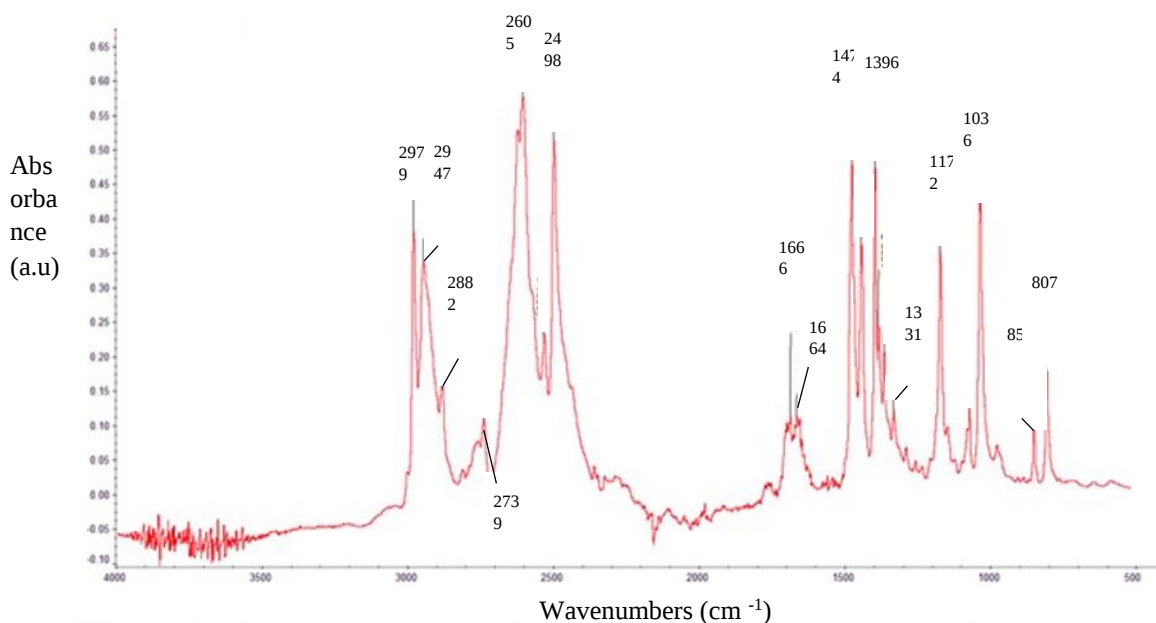


Figure 3.2: FTIR spectrum of the bleach activator (TBUCC) after removal of hydrochloride salt.

FTIR analysis was also conducted to identify the presence of functional groups on the bleached and unbleached fabrics. The FTIR spectra of bleached and unbleached fabrics are presented in Figure 3.3. The peaks at 3333 and 3274 cm^{-1} are characteristic for stretching vibration of the hydroxyl group (OH stretching), including inter- and intra-molecular hydrogen bond vibrations in cellulose. Peak at 2898 cm^{-1} belongs to CH stretching, at 1651 cm^{-1} is due to the C=O stretching. The peak found at 1423 cm^{-1} is assigned to CH_2 scissoring at C(6) and associated with the amount of the crystalline structure of the cellulose. The peak at 1334 cm^{-1} corresponds to OH in plane bending, at 1314 cm^{-1} corresponds to CH_2 wagging. The peak located at 1161 cm^{-1} is attributed to the C-O-C asymmetric stretching [107-114].

With the formation of oxy-cellulose during oxidation, the carboxyl, aldehyde and ketone groups gradually increase, however, oxidation predominantly forms ketone groups. The C=O and C-C-C stretching peaks are the best peaks to use to determine whether a ketone is present in a sample. The absorbance around 1740 cm^{-1} , which is characteristic of carbonyl groups (C=O), and the band around 880 cm^{-1} assigned to the formation of hemiacetal bonds between the aldehyde groups and neighbour hydroxyl groups, increase with increasing degree of oxidation. However, these related peaks were not observed for bleached fabric in Figure 3.3; this may be

because CHO groups in oxycellulose with an oxidation degree of less than 50% are hardly detected and not quantitatively by FTIR. The intensity of the peaks at 3333 and 3274 cm^{-1} decreased, which was attributed to the removal of the hydroxyl groups after bleaching process. However, sharper but lower intensity peaks were detected at 1278, 1108, 1055 and 1030 cm^{-1} , indicating C-O stretching and -C-C-C stretching, which may be due to the presence of ketone groups [111-117].

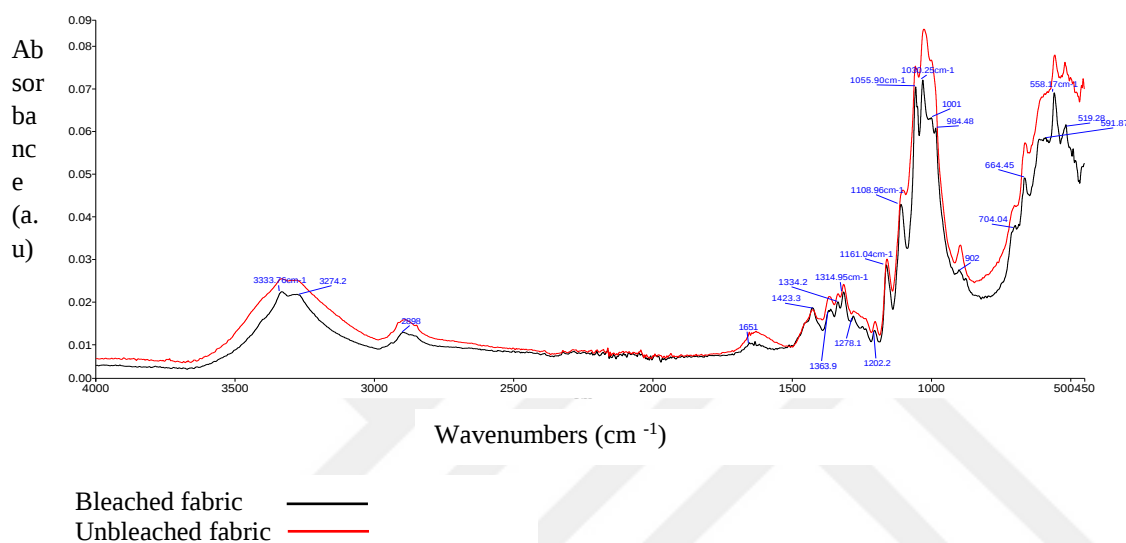


Figure 3.3: FTIR spectrum of the bleached and unbleached fabric.

3.1.2 Mass spectra results

Figure 3.4 shows the mass spectra of synthesized intermediate product for TBUC. Formula of expected compound is $\text{C}_{10}\text{H}_{16}\text{O}_2\text{NCl}$. Similar to the FT-IR results, it was found that $\text{Et}_3\text{N}+\text{HCl}$ was observed as a by-product during the synthesis of intermediate. As shown in Figure 3.3, the 218 signal corresponds to the intermediate.

The 240 corresponds to the sodiated intermediate, which should be $[\text{M} + \text{Na}]^+$. The isotope ratio of ^{35}Cl and ^{37}Cl is about 3:1, which means 218/220 should be 3:1 and 240/242 should be 3:1.

Figure 3.5 shows mass spectrum of synthesized intermediate product after removal of $\text{Et}_3\text{N}+\text{HCl}$. Both 182.1176 and 240.0769 are intermediate: 182 is $[\text{M}-\text{Cl}]^+$, 240 is $[\text{M} + \text{Na}]$.

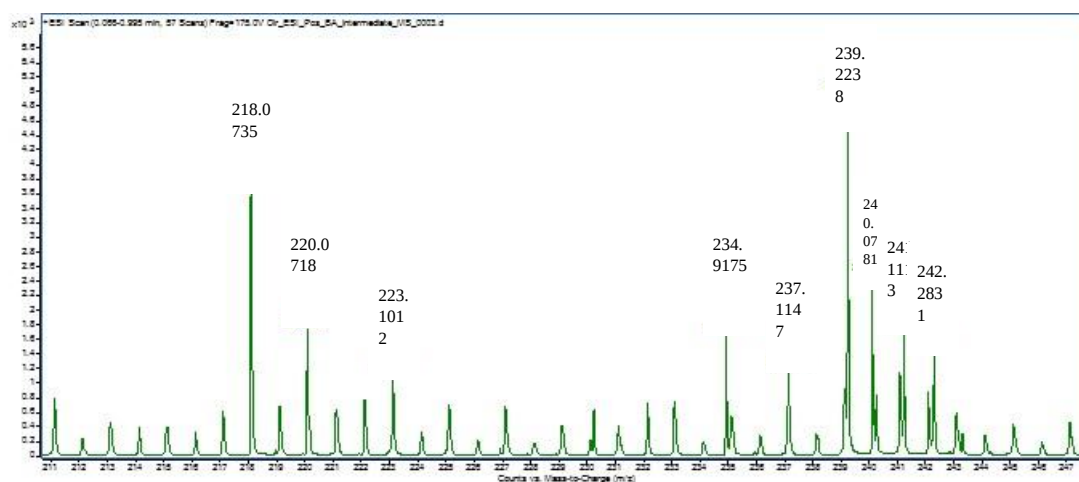


Figure 3.4: Mass spectrum of intermediate product-zoom in.

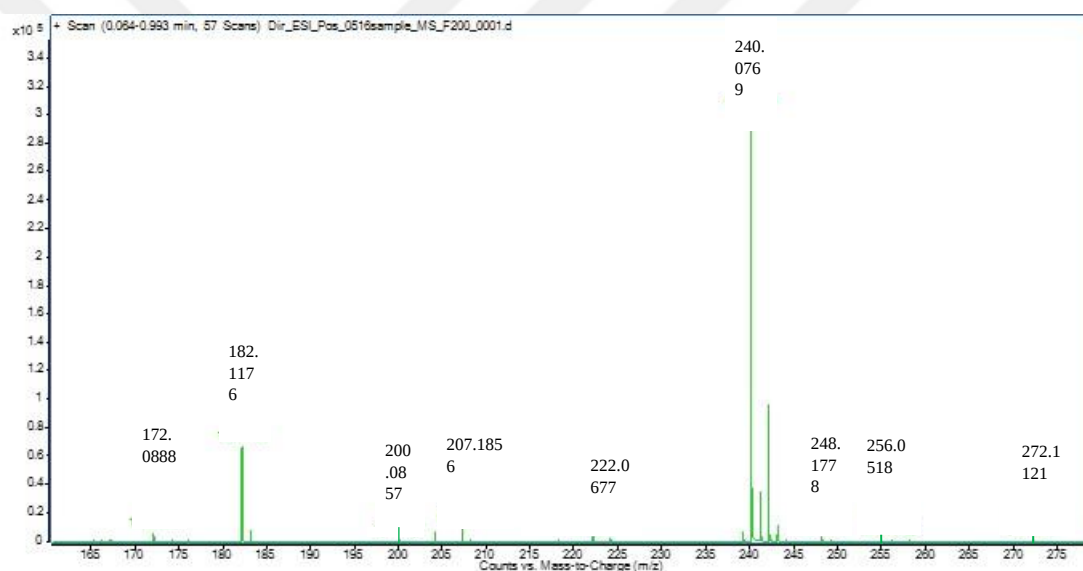


Figure 3.5: Mass spectra of intermediate product after removal of Et₃N+HCl.

Figure 3.6 shows the mass spectrum of final product (after quaternization). Formula of expected compound is C₁₆H₃₁O₂N₂⁺ + Cl⁻. The 283 peak corresponds to the final product.

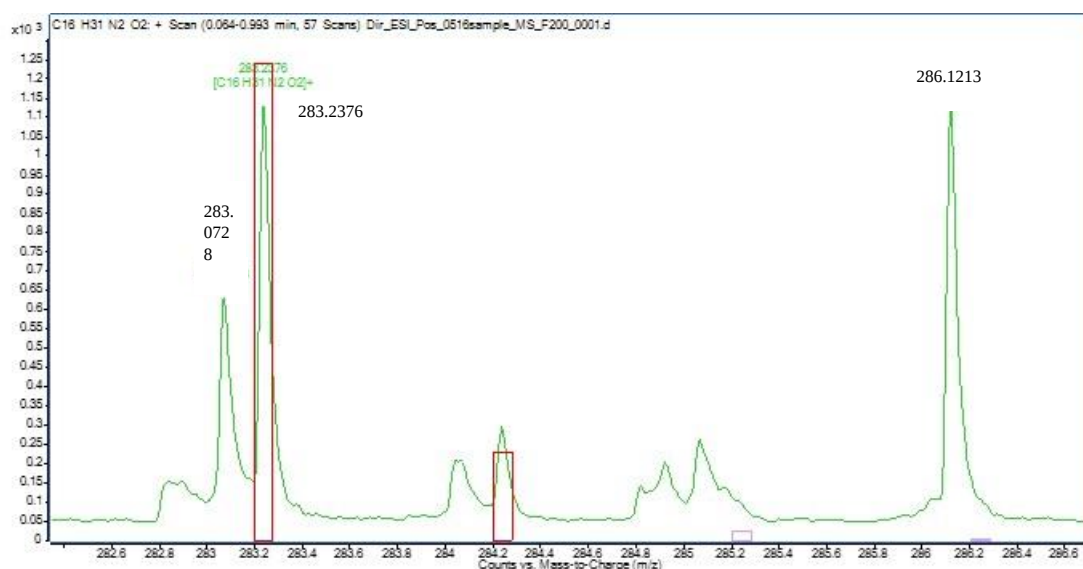


Figure 3.6: Mass spectrum of final product (after quaternization).

3.1.3 ^1H -NMR analysis

Figure 3.7 shows the ^1H -NMR spectrum of TBUCC. ^1H -NMR (500 MHz, CD_3OD , $\delta(\text{ppm})$: 1.2 (t, (3(CH_3), 9H), 1.5–2.35 (m, 4(CH_2), 8H), 3.1–3.5 (m, q and t, 7(CH_2), 14H).

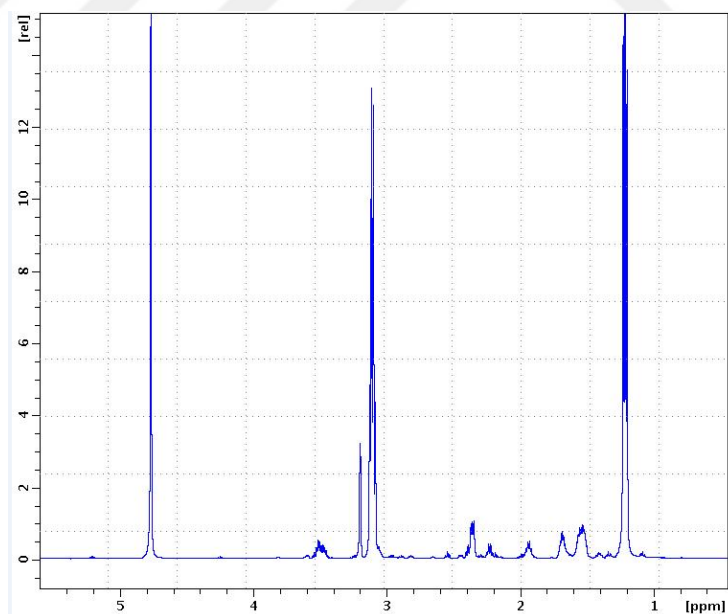


Figure 3.7: ^1H NMR spectrum of TBUCC.

3.2 Bleaching Performance

Bleaching performances of all bleached samples were evaluated in terms of whiteness index, water absorbency and fiber damage (DP).

3.2.1 Whiteness measurement

3.2.1.1 TBUCC-activated peroxide bleaching system

Bleaching experiments in the presence of TBUCC were conducted at 60 °C and 70 °C for 30 min under different process parameters, including concentration of activator (22.7 mmol/L, 36.7 mmol/L), molar ratio of activator:H₂O₂ (1:4, 1:8), molar ratio of H₂O₂:NaOH (1:1.02, 1:1.04).

It can be seen clearly from Table 3.1 that the whiteness index (WI) of bleached samples in TBUCC-H₂O₂ system was improved when 1:8 and 1:10 molar ratio of TBUCC: H₂O₂ was applied at 60 °C for 30 min. Using 1:8 molar ratio of TBUCC: H₂O₂ provided a WI of 69.85-70.11 while Xu et al. (2012) reported that using equimolar amounts of TBBC and H₂O₂ under neutral conditions at 50 °C for 50 min resulted in less WI of 67.01 [118]. It was shown that the effective level of concentration of activator was found to be when higher concentration of peroxide was used, which is an attractive economical advantage.

The optimum pH was found to be 11.5. Increasing the pH beyond 11.5 increases the degree of hydrolysis and decreasing the pH below 11.5 decreases the degree of perhydrolysis and increases the formation of diacylperoxide.

Considering the results given in Table 3.2, TBUCC-H₂O₂ bleaching using 36.7 mmol/L activator was done at 1:10, 1:12 and 1:13 molar ratios of TBUCC: H₂O₂ at 60 °C and 70 °C. Although concentration higher than 1:8 molar ratio of H₂O₂ has no effect on improvement of whiteness at 60 °C, temperature was shown to play a key role on bleaching performance. As the temperature increased from 60 to 70 °C at 1:10 molar ratio of TBUCC to H₂O₂, the WI increased from 70.12 to 75.72. It was also seen that temperature has an interaction with the molar ratio of hydrogen peroxide to activator. As the temperature increased from 60 to 70 °C at 1:12 molar ratio of activator to H₂O₂, the WI increased from 70.86 to 78.97. Molar ratio higher than 1:12 of activator was found to have no considerable effect on WI, indicating that that ratio furnished the optimum peracid concentration that achieved optimum bleaching efficiency.

Table 3.1: Bleaching performances of TBUCC-activated bleached samples under different concentrations of activator, H₂O₂ and NaOH.

Conc. of TBUCC (mmol/L)	Molar ratio of TBUCC:H ₂ O ₂	Conc. of H ₂ O ₂ (g/L)	Molar ratio of H ₂ O ₂ :NaOH	Temp. (°C)	Time (min)	WI	WI- without addition of TBUCC
22.7	1:4	3.1	1:1.02	60	30	62.70	56.93
36.7	1:4	5	1:1.02	60	30	62.38	61.11
22.7	1:8	6.2	1:1.02	60	30	65.23	63.56
36.7	1:8	10	1:1.02	60	30	69.85	64.25
22.7	1:4	3.1	1:1.04	60	30	62.30	57.04
36.7	1:4	5	1:1.04	60	30	62.26	61.29
22.7	1:8	6.2	1:1.04	60	30	64.85	62.35
36.7	1:8	10	1:1.04	60	30	70.11	63.96

From the results shown in Table 3.2, it is clear that the WI increased with the increase of H_2O_2 concentration up to a certain level, after which no remarkable improvement was observed at higher concentration of H_2O_2 . In the presence of TBUCC, WI increased at higher concentration of H_2O_2 up to 1:12, then it started level off. This indicates that the 1:12 molar ratio is the optimum ratio for the generation of optimum peracid concentration in situ by perhydrolysis reaction, achieving the optimum bleaching efficiency, between the TBUCC and perhydroxy anion generated by the disassociation of hydrogen peroxide. This would suggest that the effective concentration of generated PAA depends on the concentration of H_2O_2 up to a certain level.

Table 3.2: Bleaching performances of TBUCC-activated bleached samples using 36.7 mmol/L activator at a large excessive amount of hydrogen peroxide at 60 °C and 70 °C.

Conc. of activator (mmol/L)	Molar ratio of activator: H_2O_2	Temp. (°C)	Time (min)	WI	WI- without addition of TBUCC
36.7	1:10	60	30	70.12	64.37
36.7	1:12	60	30	70.86	62.12
36.7	1:10	70	30	75.72	70.13
36.7	1:12	70	30	78.97	69.95
36.7	1:13	70	30	78.76	70.55

3.2.1.2 TBUCB-activated peroxide bleaching system

The bleach experiments were performed at different concentrations of activator, different molar ratios of H_2O_2 to activator and H_2O_2 to NaOH, different temperature and time as stated in Table 3.3 to optimize the bleaching recipe for TBUCB. Cellulosic fabric was bleached with hydrogen peroxide with the addition of TBUCB at a liquor-to-goods ratio of 20:1 according to recipe given in Table 3.3. NaOH (%50 w/w) was used for alkaline pH (around 11) based on the results of pre-experiments.

Table 3.3: Process parameters and levels of each parameters.

Independent variables	Coded levels and Factor levels				
	-2	-1	0	+1	+2
(A) Conc. of activator (mmol/L)	15.7 (5 g/L)	22.7 7.24 g/L	29.7 9.47 g/L	36.7 11.7 g/L	43.7 (13.93 g/L)
(B) Molar ratio of activator:H ₂ O ₂	1:2	1:4	1:6	1:8	1:10
(C) Molar ratio of H ₂ O ₂ :NaOH	1:1.05	1:1.1	1:1.15	1:1.2	1:1.25
(D)Temp.(°C)	40	50	60	70	80
(E) Time (min.)	30	40	50	60	70

The Response Surface Methodology (RSM) based on Central Composite Design (CCD) was used to evaluate and optimize the hot peroxide bleaching process for newly synthesized TBUCB. Design matrix and bleaching results for TBUCB are given in Table 3.4.

Table 3.4: Design matrix and CCD response data for TBUCB.

Standard order	Run order	A	B	C	D	E	WI
1	30	0	0	0	2	0	79.22
2	25	0	-2	0	0	0	61.42
3	26	0	2	0	0	0	71.37
4	27	0	0	-2	0	0	68.94
5	31	0	0	0	0	-2	69.89
6	29	0	0	0	-2	0	56.45
7	32	0	0	0	0	2	69.53
8	24	2	0	0	0	0	71.11
9	33	0	0	0	0	0	69.10
10	28	0	0	2	0	0	71.55
11	23	-2	0	0	0	0	59.52
12	16	1	1	1	1	1	77.92
13	20	0	0	0	0	0	70.67
14	18	0	0	0	0	0	70.49
15	9	-1	-1	-1	1	-1	66.45
16	19	0	0	0	0	0	69.28
17	4	1	1	-1	-1	1	64.91
18	21	0	0	0	0	0	69.50
19	17	0	0	0	0	0	69.21
20	2	1	-1	-1	-1	-1	57.86
21	13	-1	-1	1	1	1	67.70
22	6	1	-1	1	-1	1	56.92
23	11	-1	1	-1	1	1	69.21
24	5	-1	-1	1	-1	-1	55.60
25	10	1	-1	-1	1	1	70.79
26	3	-1	1	-1	-1	-1	60.42
27	15	-1	1	1	1	-1	68.44
28	8	1	1	1	-1	-1	65.81
29	14	1	-1	1	1	-1	70.66
30	1	-1	-1	-1	-1	1	54.95
31	12	1	1	-1	1	-1	77.53
32	22	0	0	0	0	0	70.17
33	7	-1	1	1	-1	1	60.56

The Analysis of Variance for WI is given in Table 3.5. Coefficients of determination (correlation coefficient) (R^2), ranging from 0% to 100%, indicates the percentage of variation in the response that is explained by the model. The higher the R^2 value, the better the model fits the response data. As can be seen from Table 3.5, the model is adequate to provide an accurate prediction of response function since $R^2 > 0.9$ and lack of fit P value > 0.05 . R^2 is found to be as 99.23%, indicating that 99.23% of the

response variability can be explained by the model. R^2 and Adj- R^2 values are higher than 0.9, providing a high trend between the experimental and the predicted values.

Concentration of activator (A), molar ratio of activator: H_2O_2 (B) and temperature (D) are found to have significant influence on WI due to the higher F-ratio (178.94, 187.78, 869.35, respectively) and the smaller significance level (P value<0.05). Temperature (D), followed by molar ratio of activator: H_2O_2 (B) and concentration of activator (A), respectively, present the highest statistical relevance since a higher F ratio indicates greater relevance of the corresponding factor. Although all the interactions between the factors were analyzed, the interactions between the concentration of activator (A) and the molar ratio of activator: H_2O_2 (B), between the concentration of activator (A) and the temperature (D), between the molar ratio of activator: H_2O_2 (B) and the temperature (D) were statistically significant. In terms of F value, the two-way interaction between the concentration of activator (A) and the molar ratio of activator: H_2O_2 (B) is greater than the other two-way interactions (F= 17.75).

Table 3.5: Analysis of Variance for WI.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Blocks	1	14.70	14.70	14.702	16.29	0.002
Regression	20	1271.10	1271.10	63.555	70.43	0.000
Linear	5	1117.23	1117.23	223.446	247.63	0.000
A	1	161.46	161.46	161.461	178.94	0.000
B	1	169.44	169.44	169.442	187.78	0.000
C	1	1.88	1.88	1.876	2.08	0.177
D	1	784.44	784.44	784.441	869.35	0.000
E	1	0.01	0.01	0.012	0.01	0.911
Square	5	121.54	121.54	24.308	26.94	0.000
A*A	1	55.88	66.26	66.261	73.43	0.000
B*B	1	39.37	44.30	44.299	49.09	0.000
C*C	1	1.02	1.86	1.862	2.06	0.179
D*D	1	20.86	21.87	21.871	24.24	0.000
E*E	1	4.41	4.41	4.409	4.89	0.049
Interaction	10	32.32	32.32	3.232	3.58	0.024
A*B	1	16.02	16.02	16.02	17.75	0.001
A*C	1	0.07	0.07	0.069	0.08	0.787
A*D	1	7.74	7.74	7.742	8.58	0.014
A*E	1	0.50	0.50	0.501	0.55	0.472

Table 3.5 (continued): Analysis of Variance for WI.

B*C	1	0.00	0.00	0.002	0.00	0.965
B*D	1	4.92	4.92	4.917	5.45	0.040
B*E	1	0.02	0.02	0.023	0.03	0.875
C*D	1	0.00	0.00	0.00	0.00	0.998
C*E	1	1.56	1.56	1.556	1.72	0.216
D*E	1	1.49	1.49	1.495	1.66	0.225
Residual Error	11	9.93	9.93	0.902		
Lack-of-Fit	6	7.89	7.89	1.315	3.23	0.109
Pure Error	5	2.03	2.03	0.407		
Total	32	1295.73				

S = 0.949912 PRESS = 138.263

R-Sq = 99.23% R-Sq(pred) = 89.33% R-Sq(adj) = 97.77%

2D contour plots, representing a 3D surface on a two-dimensional plane, illustrate the response function of two factors while keeping all other factors constant for the optimization of process conditions. Figure 3.8 (a)-(j) show the two-way interactions of process parameters on WI while all other parameters are at fixed level. It was observed from Figure 3.8 (a) that a whiteness index higher than 70 was obtained at 9.47 g / L (at 0-level) and higher activator concentrations and at a molar ratio of 1:6-1:10 activator: H₂O₂.

It is seen from Figure 3.8 (b) that the maximum WI can be obtained at 11.7 g/L of activator concentration (at 1-level) and the increase in the activator concentration to a certain value (approximately to 12.8 g/L) either at a low or high level of alkali (NaOH) range used in the study causes a decrease in the WI. Figure 3.8 (c) indicates that WI higher than 80 can be achieved between 11.7 g/L and 13.93 g/L of activator concentrations at a temperature of 80 °C. Similar with the trend of alkali concentration in Figure 3.8 (b), (e) and (h), process time has no significant effect on WI as shown in Figure 3.8 (d) (g) and (j). A whiteness index higher than 75 was obtained at a ratio of 1:6-1:10 activator: H₂O₂ at a temperature of about 68 to 80 °C (Figure 3.8 (f)), indicating that peracid became more active resulting in improved bleaching efficiency.

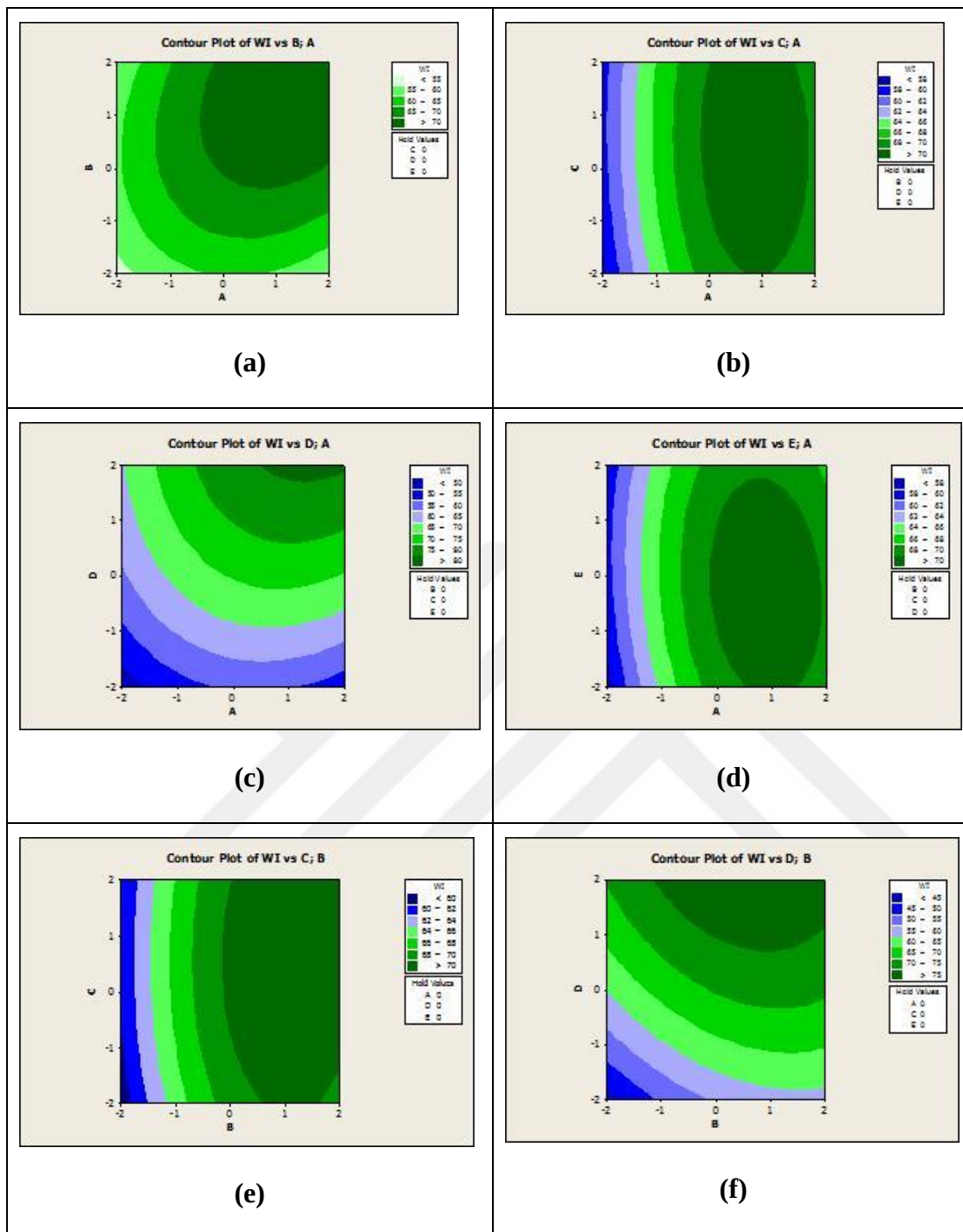


Figure 3.8: Contour plots showing the effect of independent variables on WI.

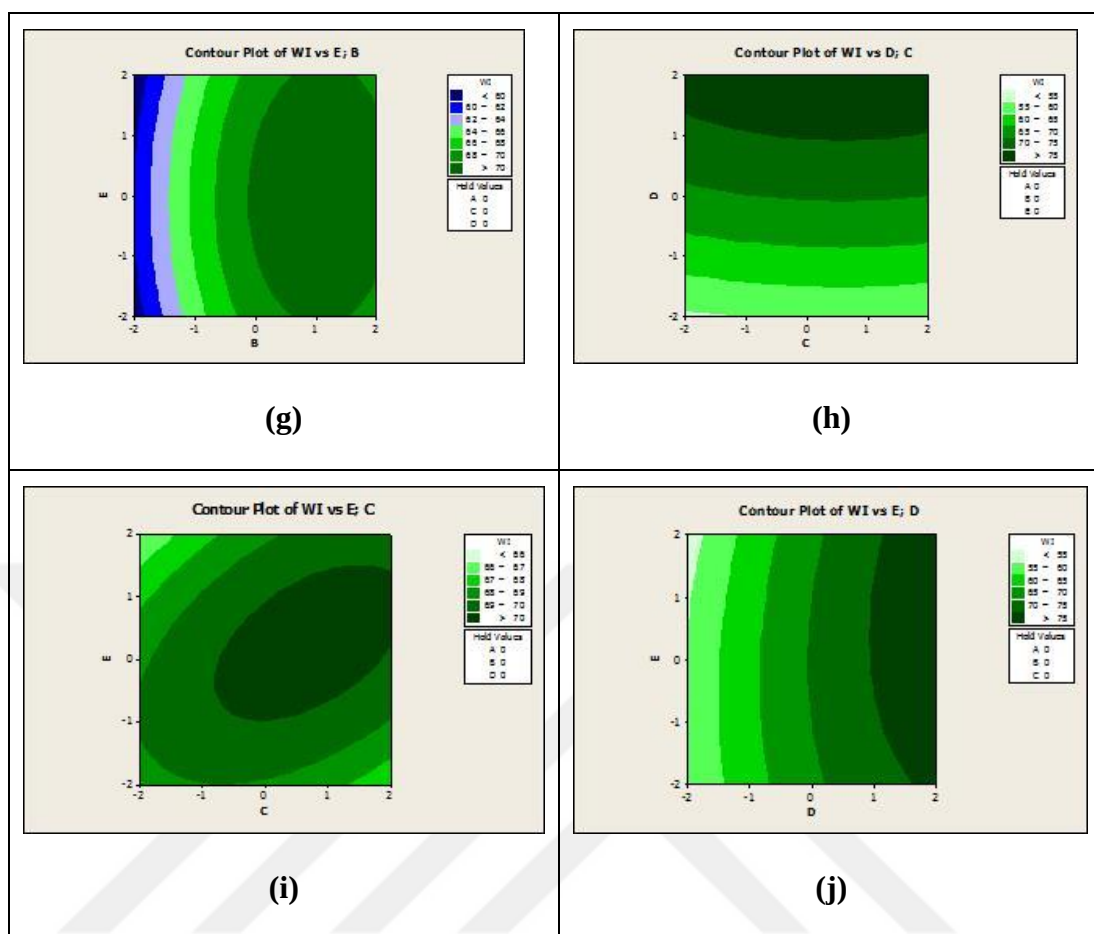


Figure 3.8 (continued): Contour plots showing the effect of independent variables on WI.

3.2.2 Water absorbency

The wetting time of both activated and conventional bleached samples was found to be less than 5 s, indicating good hydrophilicity.

3.2.3 Determination of fiber damage

For the purpose of determination of fiber damage, degree of polymerization (DP) of activated-bleached cotton fabric under optimized bleaching conditions was measured and compared to conventional bleached and untreated fabric. Using 36.7 mmol/L TBUCB and TBUCB at a molar ratio of H_2O_2 around 1:8–1:10 under alkaline pH at 70 °C was found to be the optimum condition for providing satisfactory bleaching performance.

It can be seen clearly from Table 3.6 that comparable whiteness of 75.7–77.5 with conventional bleaching can be obtained at 70 °C with the addition of TBUCB and

TBUCB respectively, providing higher DP of 3350-3410 than the conventional process, which furnished a DP of 3044.

Table 3.6: DP of bleached cotton fabric for activated and conventional peroxide bleaching.

	Bleaching condition	Temp (°C)	Time (min.)	WI	DP (Average)	Reduction in DP (%)
Untreated fabric	-	-	-	35.77	3.780	-
Conventional bleaching	6 g/L H ₂ O ₂ pH:11.5	98	30	75.77	3.044	19.5
TBUCC - H₂O₂ bleaching	36.7 mmol/L Molar ratio of activator: H ₂ O ₂ =1/10 pH= around 11	70	30	75.72	3.350	11.4
TBUCB- H₂O₂ bleaching	36.7 mmol/L Molar ratio of activator: H ₂ O ₂ =1/8 pH= around 11	70	30	77.5	3.410	9.8

3.3 Computational Results

Mapped Surface for the LUMO on the TBUCB activator given in Figure 3.9a is localized on the butanoyl and butyrolactam groups, especially on the carbonyl groups. One can expect the attack of perhydroxyl anion should be directed at these groups because they are the most electron deficient sites in the activator structure. HOMO orbital which has low possibility for the nucleophilic attack is mainly on the chloride anion and partly on the ethyl ammonium groups (Figure 3.9b). ESP surface showed that carbonyl groups on the butanoyl and butyrolactam are the only groups that have both electron rich part, depicted by red color on oxygen which can form a hydrogen bond with perhydroxyl anion, in addition to the electron deficient carbonyl carbon depicted by blue color which can undergo nucleophilic attack by peroxide anion, perhydroxyl (Figure 3.9b). Although there are two carbonyl groups, only the carbonyl carbon of butanoyl is the one that can lead to the formation of peracid (Figure 3.9c). Atomic charges on the carbon atoms were compared by two different methods to determine which one will be preferred for the anion attack. Both ESP charges based on the electrostatic potential fitting method and charges based on the partitioning of the molecular electron density showed higher positive charge on the carbon atom of the butanoyl carbonyl (Figure 3.9d-e), which is the main driving force for the initial diffusion and attack by perhydroxyl anion. At last, Fukui reactivity indices for the nucleophilic attack were compared for the two carbonyl carbons, which showed higher potential of the cationic bleach activation to undergo nucleophilic attack by peroxide anion at butanoyl carbonyl carbon rather than butyrolactam carbonyl carbon (Figure 3.9f). Fukui reactivity indices based on different atomic charge calculation methods gave similar results.

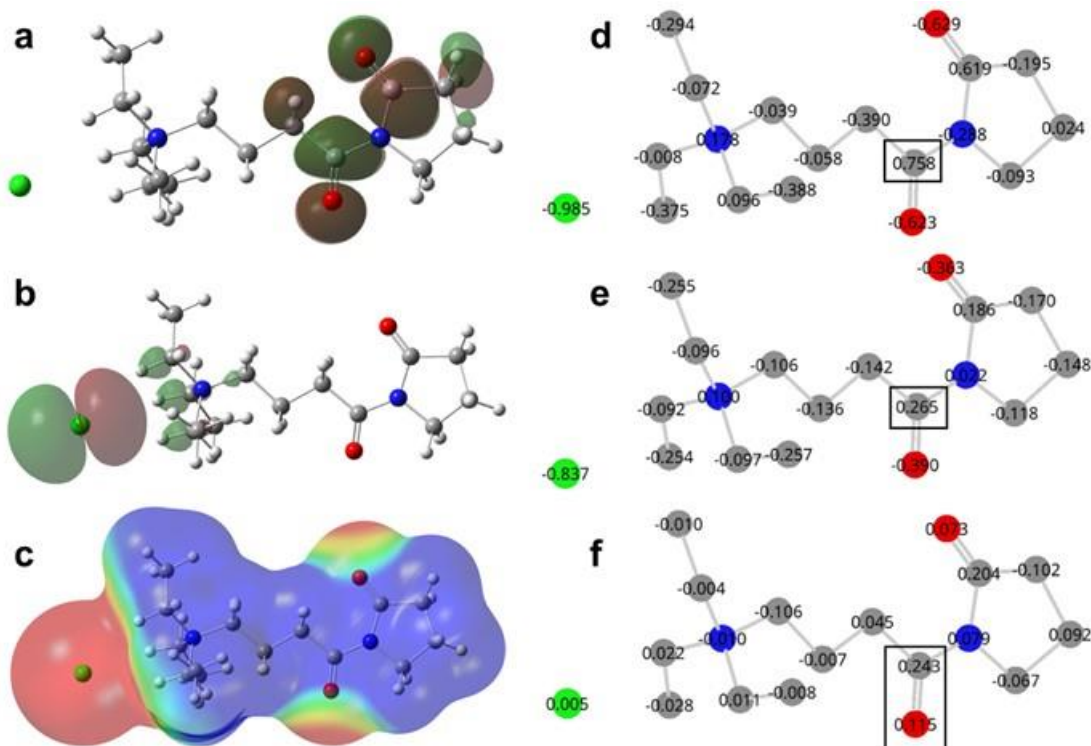


Figure 3.9: a) LUMO and b) HOMO frontier molecular orbital isosurfaces, c) electrostatic potential (ESP) surface mapped on the optimized geometries. Atomic charges based on the d) electrostatic potential fitting method (MK) and e) atomic dipole moment corrected Hirshfeld (ADHC) population analysis f) Fukui reactivity indices showing the most susceptible sites for nucleophilic attack. Highest charges and reactivity indices are marked.

Imaginary frequencies of the transition state of perhydroxyl anion attack and peracid dissociations for TBUCB and TAED are given in Figure 3.10-3.13, respectively.

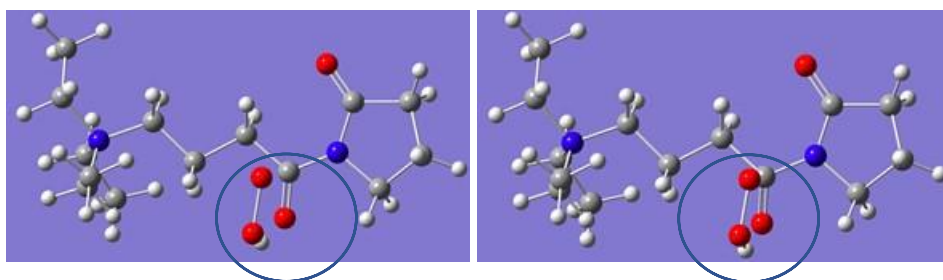


Figure 3.10: Vibration with imaginary frequency for the transition state of perhydroxyl anion attack for the TBUCB.

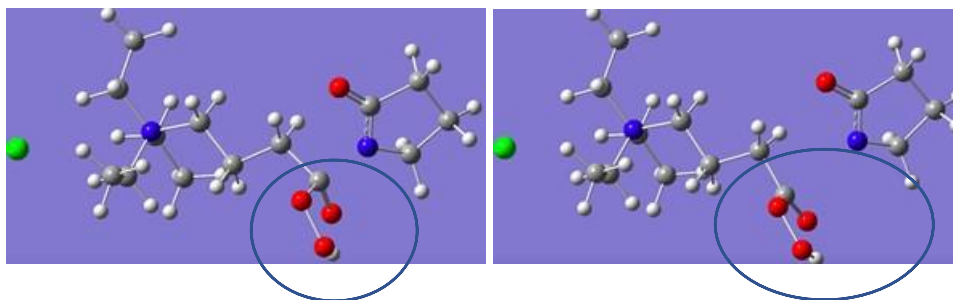


Figure 3.11: Vibration with imaginary frequency for the transition state of peracid dissociation for the TBUCB.

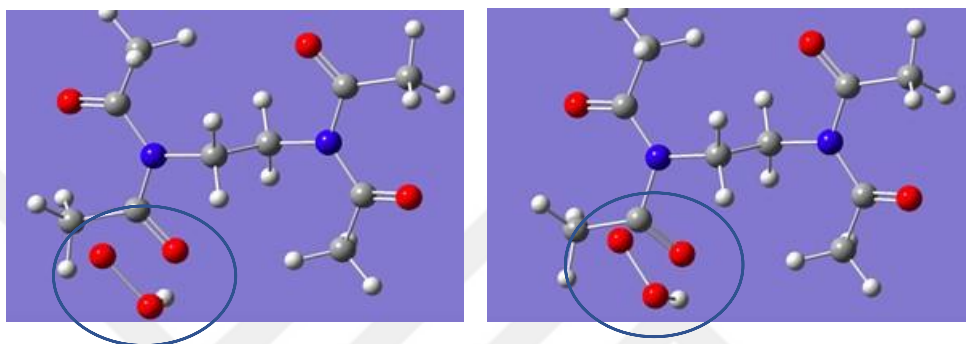


Figure 3.12: Vibration with imaginary frequency for the transition state of perhydroxyl anion attack for the TAED.

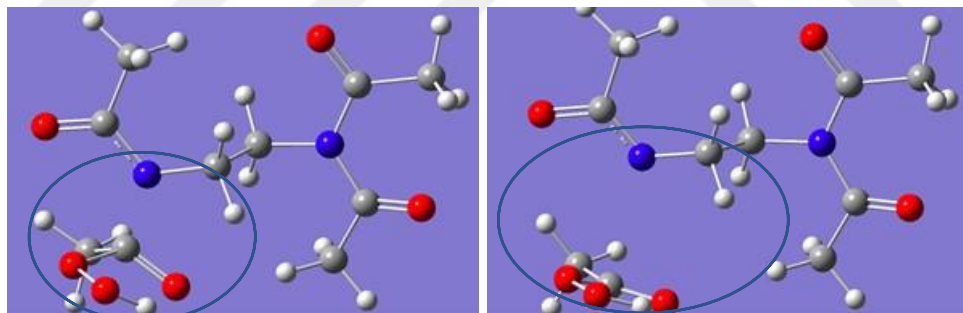


Figure 3.13: Vibration with imaginary frequency for the transition state of peracid dissociation for the TAED.

Reactions were found to follow two step mechanisms, which are perhydroxyl anion attack at the carbonyl carbon and the peracid formation. Transition state characterized by the single imaginary frequency was calculated for the perhydroxyl anion attack at the TBUCB and free energy profile is given in Figure 3.14a. Reaction barrier for the perhydroxyl anion attack at the carbonyl carbon calculated by using sum of electronic and thermal free energies at 70 °C was determined as 12.55 kcal/mol under water solvation effect. This activation barrier was compared with the

TAED activation barrier, and it was determined that perhydroxyl anion attack has lower reaction barrier and higher solubility for TBUCB than TAED determined as 13.72 kcal/mol (Figure 3.14b). There is an interaction between carbonyl carbon and perhydroxyl anion as well as a hydrogen bond formation between the oxygen of the carbonyl and perhydroxyl hydrogen in the transition state. This confirms the importance of initial hydrogen-bonding through these interactions that leads to the nucleophilic attack. Although carbonyl carbon that is part of the butyrolactam has a partial positive charge as a potential site for nucleophilic attack, no transition states for perhydroxyl anion attack at the carbonyl carbon of butyrolactam ring was found, which confirms that there is no reaction happening inside ring, which led to the conclusion that the carbonyl group of butyrolactam is not reactive towards perhydroxyl anion attack to form any peracid. The bond distance between carbonyl carbon of butanoyl and the nitrogen atom of butyrolactam significantly increased after perhydroxyl bonding, followed by bond dissociation and peracid formation in the second step of the reaction. The perhydroxyl anion attack in the first step is the rate determining step, and dissociation of peracid for TBUCB and TAED in the second step occurs with a lower energy barrier at 7.88 and 4.58 kcal/mol, respectively. Cartesian coordinates of atoms for the transition states are given in appendices section.

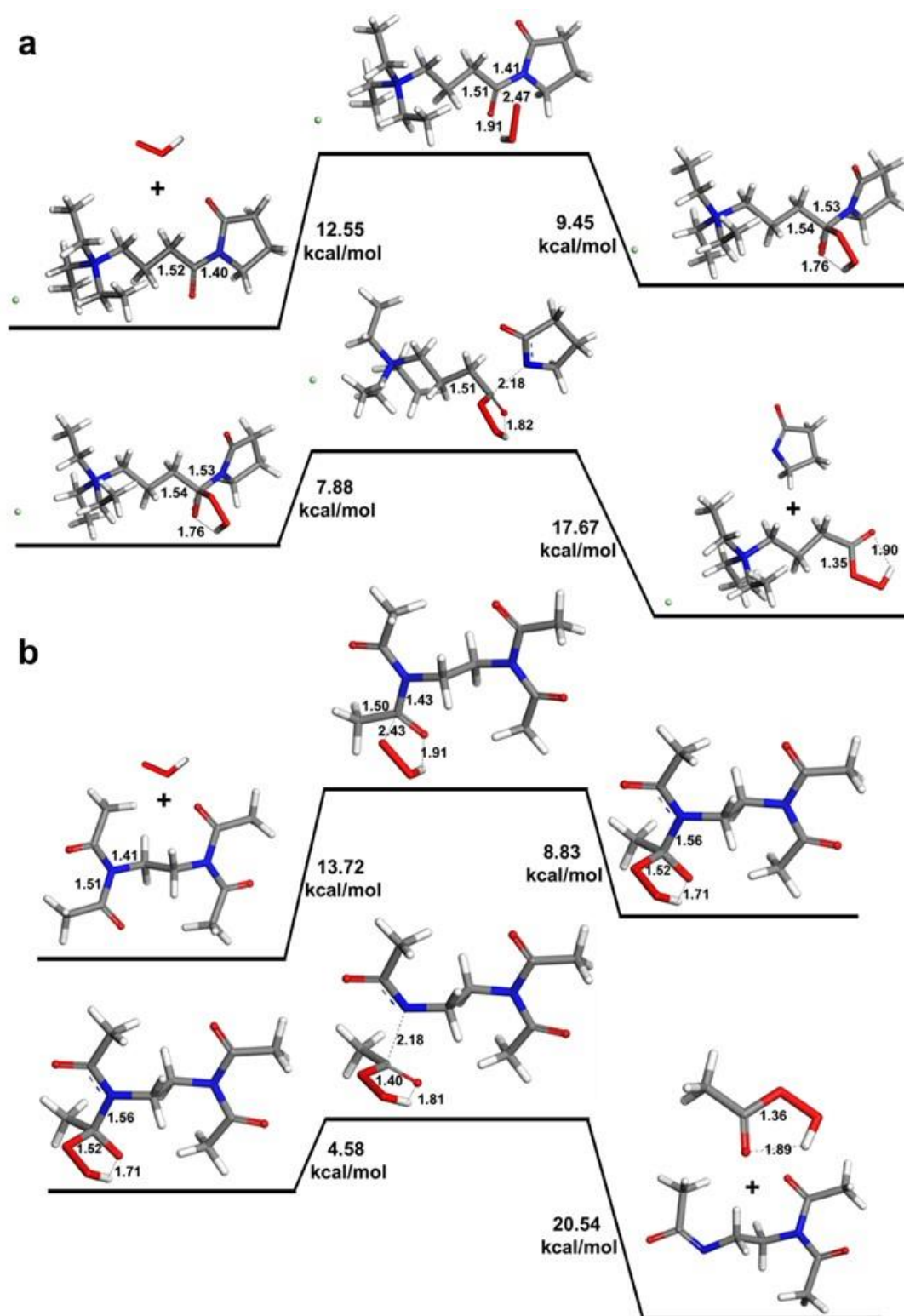


Figure 3.14: Free energy diagrams of the perhydroxyl anion attack and peracid formation for the a) TBUCB and b) TAED. The relative energies are in kcal/mol and distances are in Å.

The main limitation of TBUCB is the conformational freedom due to the alkyl group in butanoyl group. Results showed that positively charged triethyl ammonium group is attracted toward the more negative oxygen atoms of either butanoyl (Figure 3.15a and 3.15c) or butyrolactam (Figure 3.15b and 3.15d) groups, resulting in a bent conformation with decreased reactivity, thereby preventing more peracid formation. In addition, steric interactions cause a barrier for perhydroxyl ion to reach to the activator in bleaching bath for peracid formation. Although all trans coplanar conformation is the lowest energy structure, gauche1 (Figure 3.15a and 3.15c) and gauche2 (Figure 3.15b and 3.15d) conformers of these alkyl groups were easily obtained with less than 2 kcal/mol energy difference. The closest distance between ethylammonium hydrogens and butanoyl oxygen which was 4.51 Å in the lowest energy structure, decreased to 2.51 Å in gauche1 structure. The closest distance between ethylammonium hydrogens and butyrolactam oxygen which was 6.02 Å in the lowest energy structure, decreased to 4.51 Å in gauche2 structure (Figure 3.15c-d).

When phenyl is used in the molecule structure (Figure 3.15e) similar with the structure reported as N-[4-(triethylammoniomethyl)benzoyl]caprolactam chloride (TBCC) in the literature [24, 26, 28], the interaction between triethyl ammonium and the oxygen atoms of the carbonyl group decreased since the butanoyl segment can adopt different conformations while the phenyl group is highly rigid. However, the reactivity of the butanoyl carbonyl towards nucleophilic attacks significantly decreased by phenyl substitution. Alkene modification can be a better alternative to achieve more rigid structure to prevent folding of this aliphatic chain in the future studies (Figure 3.15f). Unlike butanoyl group, rigid conformations of alkene group hinder coplanar structure from intramolecular interaction and keep the plane of molecule parallel to cellulose surface without compromising nucleophilic reactivity. In general, future work of the developments of novel activator should focus on more rigid, linear and coplanar bleach activator/peracid to achieve better substantivity for cellulose, which would mimic the substantivity of direct dyes to cellulose.

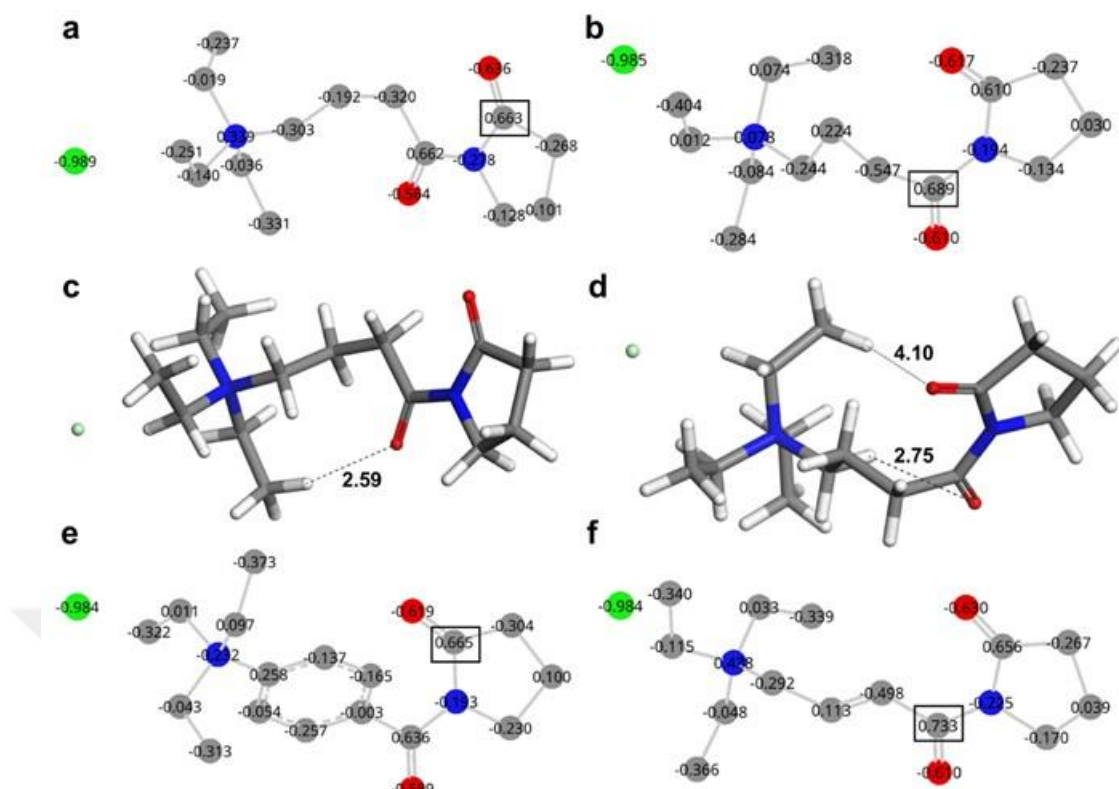


Figure 3.15: Atomic charges for non-coplanar low energy structures of TBUCB in the (a) gauche1 and (b) gauche2 conformations. Ethyl ammonium end group distance to the (c) butanoyl oxygen in gauche1 and (d) butyrolactam oxygen in gauche2 conformations. Atomic charges on the (e) phenyl modified TBUCB and (f) alkene modified TBUCB. Highest positive atomic charges are marked.



4. CONCLUSIONS

There is a growing need for environmentally acceptable and energy efficient cotton bleaching in textile industry. This study aims to develop new economical and ecological bleach activators, providing desired whiteness, absorbency and minimum fiber damage for the textile industry.

In this study, novel, more soluble, more sustainable and cost-effective cationic bleach activators based on aliphatic acid chloride, N- [4-(N,N,N)-triethylammoniumchloride-butyryl] caprolactam (TBUCC) and N-[4-(N,N,N)-triethylammoniumchloride-butanoyl]butyrolactam (TBUCB), were developed and synthesized for low temperature cotton bleaching.

Bleaching results indicated that TBUCC showed the most effective bleaching performance at the molar ratio range of 1:8–1:10 activator to H_2O_2 . Although increasing molar ratio higher than 1:8 at the same temperature had no improvement on bleaching performance, the temperature was found to have a significant effect on improvement of whiteness. It was shown that using 36.7 mmol/L activator (TBUCC) at 1:8–1:10 molar ratio of activator to H_2O_2 under alkaline pH (around 11) at significantly lower temperature (70 °C) provided satisfactory whiteness (WI: 75) and similar water absorbency with significantly reduced fiber damage (DP = 3350) as compared to conventional bleaching, which showed DP = 3044. WI greater than 75 can be achieved up to 78.97 by increasing the molar ratio of H_2O_2 to 1:12. It was also shown that 1:1.02 molar ratio of H_2O_2 to NaOH was the optimum for achieving the highest bleaching bath efficiency for low temperature bleaching with TBUCC- H_2O_2 system. Compared to aromatic-based bleach activator (TBBC), comparable results were obtained in improving whiteness of fabric with the advantage of more sustainable and cost-effective production.

Experimental results (CCD) for TBUCB indicate that the most important factors on WI are temperature, followed by molar ratio of activator: H_2O_2 and concentration of activator, respectively, based on the results of ANOVA. Maximum whiteness index of 77.53 can be achieved at 11.7 g/L (36.7 mmol) at 1:8 molar ratio of activator:

H₂O₂ at 70 °C, providing reduced energy cost and fiber damage (DP= 3410) as compared to conventional hot peroxide bleaching (WI: 75 at 98 °C). With the use of this more sustainable and cost-effective bleach activator in bleach bath, bleaching system can be optimized and WI higher than 80 can be achieved using 11.7 g/L up to about 12.8 g/L activator concentration at 1:8-1:10 molar ratio of activator to H₂O₂ at a temperature of 80 °C.

In order to determine the advantages and theoretical limitations of TBUCB for low temperature bleaching of cotton, density functional theory (DFT) calculations were performed to explain the reaction mechanism through plausible transition state(s) of the nucleophilic attack of perhydroxyl anion (HOO⁻) with different carbonyl carbons. DFT calculations validated the structure, reactivity and peroxide bleaching reaction pathway for the perhydroxyl attack at carbonyl group of the butanoyl segment not at the carbonyl carbon of the butyrolactam, which is consistent with the experimental results.

The use of these newly developed aliphatic acid chloride-based cationic bleach activators, which are more cost-effective, sustainable and highly reactive compared to other cationic bleach activators based on aromatic acid chloride, in hydrogen peroxide bleaching bath offers benefits of energy saving and reduced production cost due to the application of lower temperature (70 °C) over conventional hot peroxide bleaching conducted at 98 °C. Based on the experimental results, TBUCB and TBUCB-activated peroxide bleaching systems provide improved affinity and bleaching efficiency (whiteness index) and reduced fiber damage (higher product quality) compared to the conventional one. The obtained results suggest that the use of novel cationic bleach activators has a promising prospect for industrial application and all these findings will contribute to the commercialization of these novel, more sustainable and effective cationic bleach activators and sustainable bleaching systems. Furthermore, this study also provided key fundamental science principles and suggestions at the molecular level for the design of more efficient bleach activators with higher substantivity for cotton.

Funding

This study is supported by TUBITAK (The Scientific and Technological Research Council of Turkey) for 2214/A – International Research Scholarship Program for Doctorate Student.





APPENDICES

Appendix A: Cartesian coordinates for the transition state of perhydroxyl anion attack for the TBUCB.

Appendix B: Cartesian coordinates for the transition state of peracid dissociation for the TBUCB.

Appendix C: Cartesian coordinates for the transition state of perhydroxyl anion attack for the TAED.

Appendix D: Cartesian coordinates for the transition state of peracid dissociation for the TAED.

Appendix A: Cartesian coordinates for the transition state of perhydroxyl anion attack for the TBUCB.

C	-4.87191800	-0.72130600	0.81959300
C	-6.08895900	-0.18555000	0.05076400
C	-5.72727900	1.27645200	-0.22630300
C	-4.20721000	1.29489700	-0.25368900
N	-3.75918400	0.13324800	0.35759000
H	-4.64882700	-1.76339300	0.60091200
H	-7.01146000	-0.30273500	0.61897200
H	-6.04853900	1.94056900	0.58410100
C	-2.43684600	-0.27878400	0.61259500
O	-2.26674200	-1.23514300	1.36986500
O	-3.51603500	2.19207000	-0.70976800
C	-1.30396500	0.62826000	0.18572100
H	-1.47069400	0.96201300	-0.83563700
H	-1.34913400	1.52769000	0.81422400
C	0.05348900	-0.06470100	0.32877900
H	0.21737600	-0.33728500	1.36907700
H	0.00954400	-0.98311500	-0.25582900
C	1.13990200	0.87569500	-0.19320700
H	1.09000200	1.83968900	0.31287800
H	0.97721100	1.05555100	-1.25608700
N	2.59417500	0.41430900	-0.06220100
C	3.19179300	0.76005600	1.30662600
H	3.11958600	1.84131900	1.39624700
H	4.24544400	0.48908000	1.22204000
C	2.57376700	0.11029900	2.53667700
H	2.57181300	-0.97914900	2.49842600
H	3.19804800	0.40159300	3.38519500

Figure A.1: Cartesian coordinates for the transition state of perhydroxyl anion attack for the TBUCB.

H	1.56502600	0.46656300	2.74200200
C	3.44014000	1.14476700	-1.11539000
H	4.44401000	0.72863500	-1.01641000
H	3.03284000	0.84692700	-2.07831800
C	3.46950400	2.66475100	-1.02372400
H	4.04515100	3.01977500	-1.88188900
H	2.47808000	3.11457200	-1.09107500
H	3.96798100	3.03217000	-0.12694200
C	2.75948900	-1.08735000	-0.29627500
H	2.14875100	-1.58244700	0.45309200
H	3.80809900	-1.29451400	-0.07711400
C	2.39472900	-1.58867900	-1.68845900
H	3.10777400	-1.27434600	-2.45032300
H	2.41783400	-2.68029800	-1.65211300
H	1.39137500	-1.29541500	-2.00080000
Cl	6.62742000	-0.64547000	0.20063100
H	-4.98851400	-0.61602300	1.90208600
H	-6.19992500	-0.72830100	-0.89070800
H	-6.12567700	1.67807500	-1.15818300
O	-1.91096100	-2.90254500	-0.82060900
H	-1.96182900	-2.65217000	0.11948500
O	-2.16404100	-1.59035500	-1.46299000

Figure A.1 (continued): Cartesian coordinates for the transition state of perhydroxyl anion attack for the TBUCB.

Appendix B: Cartesian coordinates for the transition state of peracid dissociation for the TBUCB.

C	-4.75992300	0.17664200	1.32885200
C	-5.92992500	1.14511100	1.03192400
C	-5.34262100	2.04019600	-0.06365000
C	-4.23940200	1.15539700	-0.67974400
N	-3.97392200	0.11508400	0.09776100
H	-5.10877400	-0.81701800	1.62680600
H	-6.26738800	1.68650400	1.91911400
H	-4.87161000	2.94237600	0.34677000
C	-2.21710700	-1.18022600	0.17389800
O	-2.39279300	-1.80916600	1.21674100
O	-3.68144200	1.44940800	-1.77326800
C	-1.22908200	-0.05165000	-0.01413900
H	-1.45038600	0.46030500	-0.95160800
H	-1.39866200	0.65547100	0.79907500
C	0.22250300	-0.57234100	0.02372800
H	0.40345400	-1.04963500	0.98543600
H	0.35188300	-1.33232700	-0.74818200
C	1.16945800	0.60491000	-0.21577200
H	0.93767500	1.42120400	0.46755800
H	1.02717200	0.97619200	-1.23062700
N	2.67026000	0.34784100	-0.06196200
C	3.13516100	0.48829500	1.39308400
H	2.86980300	1.49976700	1.69140100
H	4.22266700	0.41539900	1.34062900
C	2.58765200	-0.50016100	2.41305600

Figure B.1: Cartesian coordinates for the transition state of peracid dissociation for the TBUCB.

H	2.78468700	-1.54163700	2.15818900
H	3.11009400	-0.29434200	3.35072500
H	1.52320400	-0.36925000	2.60436200
C	3.43651900	1.39982300	-0.87852900
H	4.48810200	1.12345800	-0.78625100
H	3.12693400	1.25458800	-1.91049400
C	3.21845400	2.85358600	-0.48050100
H	3.76955100	3.46197700	-1.20159000
H	2.17228600	3.15764400	-0.53417800
H	3.60948400	3.09175400	0.50834900
C	3.08909300	-1.03094000	-0.57240500
H	2.52813700	-1.75608800	0.01027400
H	4.14401900	-1.12190200	-0.30874600
C	2.88747600	-1.27990800	-2.06238900
H	3.58256100	-0.71392600	-2.68206500
H	3.08223600	-2.34017300	-2.23941800
H	1.87012600	-1.07562200	-2.39970100
Cl	6.77881500	-0.15617400	0.34192100
H	-4.14626700	0.55474000	2.16224600
H	-6.78327200	0.58322200	0.63957800
H	-6.06125900	2.36401700	-0.81997000
O	-3.12740300	-3.06936500	-0.82947900
H	-3.08756800	-3.11906500	0.15619700
O	-2.38744300	-1.84532200	-1.03919400

Figure B.1 (continued): Cartesian coordinates for the transition state of peracid dissociation for the TBUCB.

Appendix C: Cartesian coordinates for the transition state of perhydroxyl anion attack for the TAED.

N	-1.54268000	0.57544200	-0.13020900
N	2.20940300	0.00458600	-0.32800700
C	-2.29159900	-0.56213400	-0.56240300
C	2.94418700	1.10027700	0.18059100
C	-2.02667200	1.87971400	-0.11514100
C	2.67479200	-1.32638700	-0.33333500
C	-0.18050100	0.26644800	0.33586100
C	0.84622700	0.32364200	-0.80656700
O	-3.10280700	2.19009200	-0.61132400
O	-1.66272300	-1.57052100	-0.89171300
O	3.71064400	-1.64998900	0.22025800
O	2.38949700	2.18594000	0.26293400
C	4.39066000	0.94495800	0.57166600
C	-1.16575500	2.93464600	0.55364700
C	1.83865600	-2.34617600	-1.07431200
C	-3.76398100	-0.44702300	-0.84930800
H	-0.21358600	-0.72795800	0.77414400
H	0.09890700	0.96206900	1.12176800
H	0.56936000	-0.37352900	-1.58988200
H	0.87747800	1.32111000	-1.23934800
H	4.47801200	0.36532200	1.49138900
H	4.96587300	0.41996200	-0.19008500
H	4.78785500	1.94689600	0.72867800
H	-1.63420100	3.90043800	0.37554700
H	-1.12032900	2.75834200	1.63247300
H	-0.14122300	2.95229700	0.17980600
H	1.83606000	-2.12689100	-2.14598000
H	2.29399600	-3.32108100	-0.91392900

Figure C.1: Cartesian coordinates for the transition state of perhydroxyl anion attack for the TAED.

H	0.80034900	-2.36495000	-0.74014500
H	-4.29393000	0.14305700	-0.10865300
H	-3.90938900	0.02526600	-1.82543100
H	-4.16020400	-1.46107900	-0.88170800
O	-2.09972600	-2.65670300	1.60676500
O	-2.69534400	-1.30404800	1.72057200
H	-1.81450700	-2.64541500	0.67474100

Figure C.1 (continued): Cartesian coordinates for the transition state of perhydroxyl anion attack for the TAED.



Appendix D: Cartesian coordinates for the transition state of peracid dissociation for the TAED.

N	1.38028300	0.69312400	0.08015200
N	-2.31858000	-0.10520800	0.27346800
C	2.55001300	-1.14021600	0.22341600
C	-3.20711300	0.92650200	-0.09696700
C	1.85421700	1.92841000	0.17059800
C	-2.61095000	-1.47522900	0.14022000
C	0.04810600	0.42749500	-0.41477500
C	-0.97583900	0.32934300	0.73361900
O	3.01288000	2.19077400	0.60773900
O	1.72699400	-1.98917100	-0.13003500
O	-3.59219100	-1.87297300	-0.46654800
O	-2.80390300	2.08033300	-0.10097400
C	-4.64692500	0.62066500	-0.42741400
C	1.00346600	3.12662900	-0.28716900
C	-1.65822300	-2.44996900	0.79614800
C	3.03878900	-0.92228100	1.62834400
H	0.06954800	-0.54069400	-0.92771200
H	-0.30526100	1.16379000	-1.14523500
H	-0.61876700	-0.37205400	1.48287300
H	-1.09703600	1.29667100	1.21547900
H	-4.72306500	0.16838800	-1.41701100
H	-5.09305100	-0.07916100	0.27805400
H	-5.18388500	1.56852300	-0.41721100
H	1.47585600	4.04533800	0.06002000
H	0.95378500	3.15969100	-1.38106000
H	-0.02338000	3.09062900	0.08192700
H	-1.63475600	-2.29445600	1.87832800
H	-2.02367700	-3.45387200	0.58904300

Figure D.1: Cartesian coordinates for the transition state of peracid dissociation for the TAED.

H	-0.63638100	-2.34969500	0.42420200
H	3.54577000	0.03653400	1.70856000
H	2.18402700	-0.94110300	2.30223200
H	3.72061100	-1.73895600	1.89075500
O	3.22297300	-1.25437600	-2.00309700
O	3.57386300	-0.81224900	-0.67095900
H	2.45956600	-1.84178400	-1.78371200

Figure D.1 (continued): Cartesian coordinates for the transition state of peracid dissociation for the TAED.





REFERENCES

- [1] **Clark, M.** (2011). *Handbook of Textile and Industrial Dyeing*. Woodhead Publishing, Cambridge, UK ; Philadelphia, PA.
- [2] **Perkins, W.S.** (1996). *Textile Coloration and Finishing*. Carolina Academic Press, Durham, NC, USA.
- [3] **Cockett, S.R. and Hilton K.A.** (1955). *Basic Chemistry of Textile Preparation*. National Trade Press, London.
- [4] **Kamakar, S.** (1999). *Chemical Technology in the Pre-Treatment Processes of Textiles* (1st ed.). Elsevier Science, ebook ISBN: 9780080539478.
- [5] **Tarakçıoğlu, I.** (1979). Tekstil Terbiyesi ve Makinaları, *Tekstil Terbiyesinde Temel İşlemler ve Selüloz Liflerinin Terbiyesi* (Cilt 1). E.Ü Tekstil Fakültesi: İzmir.
- [6] **Zeronian, S. H., and Inglesby, M. K.** (1995). Bleaching of cellulose by hydrogen peroxide, *Cellulose*, 2 (4), 265–272.
- [7] **Coudhury, A. R.** (2006). *Textile preparation and dyeing* (p. 134). Enfield, NH, USA: Science Publishers.
- [8] **Cardamone, J.M., Marmer, W.N.** (1995). Chemistry of the Textiles Industry, *Chapter 2: Whitening of textiles* (pp: 46-101). Springer, Dordrecht.
- [9] **Thiagarajan, P., Selvekumar, N.** (2008). Cotton, pectinolytic enzymes and enzymatic scouring of cotton, *Colourage*, 55 (9), 51-58.
- [10] **Wakelyn, P. J., Bertoniere, N. R., French, A. D., Thibodeaux, D. P., Triplett, B. A., Rousselle, M.-A., Jr., et al.** (2007). Chemical composition of cotton, *In Cotton fiber chemistry and technology* (p. 15). Boca Raton: CRC Press.
- [11] **Choudhury, I., Hashmi, S.** (2020). *Encyclopedia of Renewable and Sustainable Materials* (1st ed.). Elsevier.
- [12] **Gordon, S., Hsieh, Y.L.** (2007). *Cotton: Science and Technology*. Woodhead Publishing Series in Textiles.
- [13] **Mathews, J.** (1999). A new approach to textile bleaching, *J. Soc. Dye. Colour.* 115, 154e155.
- [14] **Vigo, T.L.** (1994). *Textile Processing and Properties: Preparation, Dyeing, Finishing and Performance* (1st ed., Vol.11). Elsevier Science, e-book ISBN: 9780080933986.
- [15] **Lewin, M.** (1984). Bleaching of cellulosic and synthetic fabrics. In M. Lewin, & S. B.Sello (Eds.), *Handbook of fiber science and technology* (pp. 175-228). New York:Marcel Dekker, Inc.

- [16] **Lim, S-H, Gursoy, N.C., Hauser, P.J., Hinks, D.** (2004). Performance of a new cationic bleach activator on a hydrogen peroxide bleaching system, *Color. Technol.*, 120, 114-118.
- [17] **Lim, S.H., Lee, J.J., Hinks D., Hauser, P.J.** (2005). Bleaching of cotton with activated peroxide systems, *Color. Technol.*, 121, 89-95.
- [18] **Rucker, J.** (1989). Low Temperature Bleaching of Cotton with Peracetic Acid, *Textile Chem. Color.*, 21, 19-25.
- [19] **Lee, J.J., Lim, S.H., Hauser, P.J., Hinks, D.** (2005). Stability of a novel cationic bleach activator in aqueous solution, *Color. Technol.*, 121, 37-40.
- [20] **Gursoy, N.C., Lim, S-H., Hinks, D., Hauser, P.J.** (2004). Evaluating Hydrogen Peroxide Bleaching with Cationic Bleach Activators in a Cold Pad-Batch Process, *Textile Res. J.*, 74 (11), 970-976.
- [21] **Chen, W., Wang, L., Wang, D., Zhang, J., Sun, C., Xu, C.** (2016). Recognizing a limitation of the TBLC-activated peroxide system on low-temperature cotton bleaching, *Carbohydrate Polymers*, 140, 1–5.
- [22] **Spicka, N., Forte Tavcer, P.** (2015). Low-temperature bleaching of knit fabric from regenerated bamboo fibers with different peracetic acid bleaching processes, *Textile Research Journal*, 85 (14), 1497–1505.
- [23] **Lavric, P.K., Kovac, F., Forte Tavcer, P., Hauser P.J., Hinks, D.** (2007). Enhanced PAA bleaching of cotton by incorporating a cationic bleach activator, *Color. Technol.*, 123, 230–236.
- [24] **Zeng, H., Tang, R-C.** (2015). Application of a novel bleach activator to low temperature bleaching of raw cotton fabrics, *The Journal of The Textile Institute*, 106 (8), 807–813.
- [25] **Shao, J., Huang, Y., Wang, Z., Liu, J.** (2010). Cold pad-batch bleaching of cotton fabrics with a TAED/H₂O₂ activating system, *Color. Technol.*, 126, 103–108.
- [26] **Hou, A., Zhang, X., Zhou, Y.** (2010). Low temperature bleaching of cellulose fabric with (N-[4-triethylammoniomethyl]-benzoyl) caprolactam chloride as novel cationic activator for H₂O₂ bleaching, *Carbohydrate Polymers*, 82, 618–622.
- [27] **Abdel-Halim, E.S., Al-Deyab, S.S.** (2011). Low temperature bleaching of cotton cellulose using peracetic acid, *Carbohydrate Polymers*, 86, 988–994.
- [28] **Luo, X., Sui, X., Yao, J., Fei, X., Du, J., Sun, C., Xiang, Z., Xu, C., Wang, S.** (2015). Performance modelling of the TBCC-activated peroxide system for low-temperature bleaching of cotton using response surface methodology, *Cellulose*, 22, 3491–3499.
- [29] **Lee, J. J., Hinks, D., Lim, S. H., & Hauser, P.** (2010). Hydrolytic stability of a series of lactam-based cationic bleach activators and their impact on cellulose peroxide bleaching, *Cellulose*, 17 (3), 671–678.

- [30] **Xu, C., Hinks, D., & Shamey, R.** (2010). Bleaching cellulosic fibers via pre-sorption of N-[4-(triethylammoniomethyl)-benzoyl]-butyrolactam chloride, *Cellulose*, 17 (4), 849–857.
- [31] **Xu, C., Shamey, R., Hinks, D.** (2010). Activated peroxide bleaching of regenerated bamboo fiber using a butyrolactam-based cationic bleach activator, *Cellulose*, 17 (2), 339–347.
- [32] **Xu, C., Hinks, D., Sun, C., Wei, Q.** (2015). Establishment of an activated peroxide system for low-temperature cotton bleaching using N-[4-(triethylammoniomethyl)benzoyl]butyrolactam chloride, *Carbohydr Polym.*, 119, 71–77.
- [33] **Xu, C., Long, X., Du, J., Fu, S.** (2013). A critical reinvestigation of the TAED-activated peroxide system for low-temperature bleaching of cotton, *Carbohydr Polym.*, 92 (1), 249–253.
- [34] **Wang, S., Li, S., Zhu, Q., Yang, C.Q.** (2014). A novel low temperature approach for simultaneous scouring and bleaching of knitted cotton fabric at 60 °C, *Ind Eng Chem Res.*, 53 (24), 9985–9991.
- [35] **Xu, C-H., Hinks, D., El-Shafei, A., Hauser, P.J., Li, M., Ankeny, M., Lee, K.** (2011). Review of Bleach Activators for Environmentally Efficient Bleaching of Textiles, *Journal of Fiber Bioengineering & Informatics*, 4 (3), 209–219.
- [36] **Ponnusamy, S.K., Gunasundari, E.** (2018). Green Chemistry in Textiles. In: Muthu S. (eds), *Sustainable Innovations in Textile Chemistry and Dyes* (pp:53-73). Springer, Singapore.
- [37] **Alghamdi, A.A., Abdel-Halim, E.S., Al-Othman, Z.A.** (2016). Low-Temperature Bleaching of Cotton Cellulose using an Ultrasound-assisted Tetraacetylenediamine / Hydrogen Peroxide/Triethanolamine System, *BioResources*, 11 (1), 2784-2796.
- [38] **Hofmann, J., Just, G., Pritzkow, W., & Schmidt, H.** (1992). Bleaching activators and the mechanism of bleaching activation, *Journal für Praktische Chemie/Chemiker- Zeitung*, 334 (4), 293–297.
- [39] **Tzanov, T., Costa, S., Guebitz, M., Cavaco Paulo, A.** (2001). Dyeing in catalase treated bleaching baths, *Color Technol.*, 117, 1–5.
- [40] **James, A.P., Markirdy, I.S.** (1990). The Chemistry of peroxygen bleaching, *Chem Ind. London*, 641-645.
- [41] **Brooks, R.E., Moore, S.B.** (2000). Alkaline hydrogen peroxide bleaching of cellulose, *Cellulose*, 7, 263-286.
- [42] **Winkler, J., Smith, E.R., Compton, R.G.** (1997). A Study of the Mechanism of Bleaching Cotton Using Peracids and Hydrogen Peroxide as Model Systems, *J. Colloid Interface Sci.*, 195, 229-240.
- [43] **Hauthal, H.G., Schmidt, H., Scholz, H.J., Hofmann, J., Pritzkow., W.** (1990). Studies concerning the mechanism of bleaching activation, *Tenside Surfact Det* 27, 187–193.

- [44] **Kabir, S.M.F., Chakraborty, S., Hoque, S.M.A. Mathur, K.** (2019). Sustainability Assessment of Cotton-Based Textile Wet Processing, *Clean Technol.*, 1, 232–246.
- [45] **Topalovi, T.** (1972). *Catalytic Bleaching of Cotton: Molecular And Macroscopic Aspects* (Ph.D. Thesis). University of Twente, the Netherlands.
- [46] **Fu, S., Farrell, M.J., Ankeny, M.A., Turner, E.T., Rizk, V.** (2019). Hydrogen Peroxide Bleaching of Cationized Cotton Fabric, *AATCC J. Res.*, 6 (5), 21-29.
- [47] **Wang, M., Long, X., Du, J., Sun, C., Fu, S., Xu, C.** (2014) X-ray photoelectron spectroscopy analysis of cotton treated with the TBBC/H₂O₂/NaHCO₃ system, *Text. Res. J.*, 84 (20), 2149-2156.
- [48] **Cai, J.Y., Evans, D.J., Smith, S.M.** (2001). Bleaching of natural fibers with TAED and NOBS activated peroxide systems, *AATCC Rev.*, 1 (12), 31–34.
- [49] **Wang, J., and Washington, N.M.** (2002). Hydrophobic bleach systems and textile preparation: a discontinuity in fabric care, *AATCC Rev.*, 2 (6), 21–24.
- [50] **Grime K. and Clauss, A.** (1990). Laundry bleaches and activators, *Chem. Ind.*, 15 (20), 647-653.
- [51] **Wang, G.** (2012). *Synthesis of Bleach Activators with Varying Cationic Group* (Master of Science Thesis). Graduate Faculty of North Carolina State University, USA.
- [52] **Mistik, S.I., Yukseloğlu, S.M.** (2005). Hydrogen peroxide bleaching of cotton in ultrasonic energy, *Ultrasonics*, 43, 811–814.
- [53] **Abdul, S. B., Narendra, G.** (2013). Accelerated bleaching of cotton material with hydrogen peroxide. *Journal of Textile Science and Engineering*, 3, 1–4.
- [54] **Deyou, Y., Wu, M., Junxiong, L., Jintao, Z.** (2018). Economical Low-Temperature Bleaching of Cotton Fabric Using an Activated Peroxide System Coupling Cupric Ions with Bicarbonate, *Fibers and Polym.*, 19 (9), 1898-1907.
- [55] **Steiner, N.** (1995). Evaluation of Peracetic Acid as an Environmentally Safe Alternative for Hypochlorite, *Textile Chem. Color.*, 27, 29-32.
- [56] **Hickman, W.S.** (2002). Peracetic acid and its use in fibre bleaching, *Rev. Prog. Color.*, 32, 13- 27.
- [57] **Usluoglu A., Arabaci, G.** (2014). Bleaching of Cotton/polyamide fabrics with enzymes and peracetic acid, *Asia-Pac. J. Chem. Eng.*, 9, 364–367.
- [58] **Bulut M.O.** (2016). Low temperature bleaching for reactive dyeing and top white knitted cotton fabric, *J. Clean. Prod.*, 137, 461-474.
- [59] **Ibrahim, N.A., Sharaf, S.S., Hashem, M.M.** (2010). A novel approach for low temperature bleaching and carbamoylethylation of cotton cellulose, *Carbohydrate Polymers*, 82, 1248-1255.

- [60] **Rucker, J., and Cates, D.** (1988). 2,2'-Bipyridine catalyzed bleaching of cotton fibers with peracetic acid, Part:II: Bleaching mechanism, *Textile Res. J.*, 58, 198-210.
- [61] **Inamdar, U.Y., Pervez, M., Navik, R.G., Peng X., Cai, Y.** (2017). Low-temperature bleaching of cotton fabric by activated peroxide system, *Emerging Materials Research*, 6 (2), 387-395.
- [62] **Hebeish, A., Hashem, M., Shaker, N., Ramadan, M., El-Sadek, B., Hady, M.A.** (2009) New development for combined bioscouring and bleaching of cotton-based fabrics, *Carbohydr Polym.*, 78 (4), 961–972.
- [63] **Scarborough, S.J., Mathews, A.J.** (2000). Using TAED in bleaching fiber blends to improve fiber quality. *Text Chem Color Am Dyest Rep.*, 32 (3), 33–37.
- [64] **Indi, Y.M., Wasif, A., Patel, A.A.** (2017). Activated bleaching with sodium perborate and potassium persulphate, *Indian J. Fibre Text. Res.*, 42, 235-240.
- [65] **Long, X., Xu, C., Du, J., Fu, S.** (2013). The TAED/H₂O₂/NaHCO₃ system as an approach to low-temperature and near-neutral pH bleaching of cotton, *Carbohydr. Polym.*, 95 (1), 107–113.
- [66] **Cai, J.Y., Evans, D.J.** (2007). Guanidine derivatives used as peroxide activators for bleaching cellulosic textiles. *Colo Technol.*, 123 (2), 115–118.
- [67] **Wang, G., Umbuzeiro, G.D.A., Vendemiatti, J.A., Oliveira, A.C.D., Vacchi, F.I., Hussain, M., Hauser, P.J., Freeman, H.S., Hinks, D.** (2017). Synthesis, characterization, and toxicological properties of new cationic bleach activators, *J Surfact Deterg.*, 20 (1), 277-285.
- [68] **Yu, J., Shao, D., Sun, C., Xu, C., Hinks, D.** (2017). Pilot-plant investigation on low-temperature bleaching of cotton fabric with TBCC-activated peroxide system, *Cellulose*, 24, 2647–2655.
- [69] **Beck, R.H.F., Koch, H., Mentech, J.** (1996). *Carbohydrates as organic raw materials III*, Bekkum, H.V., Röper, H., Voragen, A.G.J. (Eds., pp.295-306). Wiley VCH: New York.
- [70] **Altay, P., Hauser, P.J., Gursoy, N.C., El-Shafei, A.** (2019). Facile synthesis of a novel, highly effective, more sustainable and cost-effective cationic bleach activator for cotton: N-[4-(N,N,N)-triethylammoniumchloride-butanoyl] caprolactam, *Cellulose*, 26, 2849–2860.
- [71] **The Procter & Gamble Company.** (2005). *Dual-compartment laundry composition containing peroxyacids*, US Patent No: WO 2005035707 A1.
- [72] **Abdel-Halim, S.E., Al-Deyab, S.S.** (2013). One-step bleaching process for cotton fabrics using activated hydrogen peroxide, *Carbohydr. Polym.*, 92 (2), 1844–1849.
- [73] **Malik, S.K., Das, M.** (2006). Low temperature bleaching of cotton using TAED activated peroxide bath, *Indian J. Fiber Text. Res.*, 31, 588-590.

- [74] **Xu, C., Hinks, D., Shamey, R.** (2011). Development of a Novel Bleaching Process for Cotton, *AATCC Review*, 73-77.
- [75] **Kumbasar, E.P., Korlu, A.E., Can, C.** (2011). The effects of activator on whiteness and hydrophilicity during the hydrogen peroxide bleaching, *Tekstil Konfeksiyon*, 1, 50e57.
- [76] **Shafie, A.E., Fouda, M.M.G., Hashem, M.** (2009). One-step process for bioscouring and peracetic acid bleaching of cotton fabric, *Carbohydr. Polym.*, 78, 302–308.
- [77] **Horvath, A.T., Horvath, A.E., Lindstrom, T., Wagberg, L.** (2008). Diffusion of cationic polyelectrolytes into cellulosic fibers, *Langmuir*, 24, 10797–10806.
- [78] **Hauser, P.J., Hinks, D., Lee, J.J., Lim, S.H.** (2007). *Cationic bleach activator with enhanced hydrolytic stability*, US Patent No: WO2007081724 A2.
- [79] **Gosselink, E.P., Miracle, G.S., Willey, A.D., Burns, M.E., Kott, K.L., Sivik, M.R., Taylor, L. F.** (1995). *Multiple-substituted bleach activators*. US Patent No. 5460747.
- [80] **Willey, A.D., Miracle, G.S., Kott, K.L., Burns, M.E., Baillely, G.M.A., Guedira, N-E., Hardy, F.E., Taylor, L.F., Sivik, M.R.** (1997). *Quaternary substituted bleach activators*. US Patent No. 5686015.
- [81] **Wei, D., Sun, C., Wang, M., Du, J., Xu, C.** (2014). Synthesis of N-[4-(dimethylalkyl- lammoniomethyl) benzoyl]caprolactam chlorides as cationic bleach activators for low-temperature bleaching of cotton fabric under near-neutral pH conditions, *Color. Technol.*, 130, 432–436.
- [82] **Li, M., Hinks, D.** (2012). An environmentally benign approach to cotton preparation: On bath enzymatic desizing, scouring and activated bleaching, *AATCC Review*, 46-51, Charlotte, USA.
- [83] **Gursoy, N.C., Hauser, P.** (2010). An investigation of dyeing properties of bleached knitted cotton fabrics using novel cationic bleaching activators, *Tekst. Konfeksiyon*, 20 (2), 155-161.
- [84] **Fei, X., Yao, J., Du, J., Sun, C., Xiang, Z., & Xu, C.** (2015). Analysis of factors affecting the performance of activated peroxide systems on bleaching of cotton fabric, *Cellulose*, 22 (2), 1379–1388.
- [85] **Spicka, N., Forte Tavcer, P.** (2013). Complete enzymatic pre-treatment of cotton fabric with incorporated bleach activator, *Textile Research Journal*, 83(6) 566–573.
- [86] **Liu, K., Zhang, X., Yan, K.** (2017). Low-temperature bleaching of cotton knitting fabric with H₂O₂/PAG system, *Cellulose*, 24, 1555–1561.
- [87] **Clayden, J., Greeves, N., Warren, S.** (2012). *Organic chemistry* (2nd ed.). Oxford University Press, Oxford.
- [88] **Brown, W.H., Poon, T.** (2016). *Introduction to organic chemistry* (6th ed.). Wiley, Hoboken.

- [89] **Ouellette, R., Rawn, J.D.** (2015). *Principles of organic chemistry* (1st ed.). Elsevier, Amsterdam.
- [90] **Robert, J.D., Caserio, M.C.** (1977) *Basic Principles of Organic Chemistry* (2 ed.). W. A. Benjamin, Inc., Menlo Park, CA. ISBN 0-8053-8329-8.
- [91] **Sigma-Aldrich** (2021). Retrieved January 2021, from <https://www.sigmaaldrich.com/united-states.html>.
- [92] **AATCC.** (2009). *Test method 110: Whiteness of textiles*. American Association of Textile Chemists and Colorists Technical Manual.
- [93] **AATCC.** (2009). *Test method 79: Absorbency of textiles*. American Association of Textile Chemists and Colorists Technical Manual.
- [94] **AATCC TM 82.** (2009). *Fluidity of dispersions of cellulose from bleached cotton cloth*. American Association of Textile Chemists and Colorists Technical Manual.
- [95] **Montgomery, D.C.** (2005). *Design and Analysis of Experiments* (6th ed.). John Wiley and Sons, New York, NY.
- [96] **Stephens, P.J., Devlin, F.J., Chabalowski, C.F., Frisch, M.J.J.** (1994). Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields, *Phys Chem.*, 98, 11623–11627.
- [97] **Becke, A.D.** (1993). Density-Functional Thermochemistry. III. The role of exact exchange. *Chem. Phys.* 98, 5648–5652. Doi: 10.1063/1.464913
- [98] **Lee, C., Yang, W., Parr, R.G.** (1998). Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys Rev B.*, 37, 785–789.
- [99] **Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Fox, D.J.** (2016). *Gaussian 16, Revision A.03*. Gaussian, Inc., Wallingford CT.
- [100] **Besler, B.H., Merz, K.M., Jr Kollman, P.** (1990) Atomic charges derived from Semiempirical Methods, *J Comput Chem.*, 11, 431–439.
- [101] **Lu, T., Chen, F.** (2012). Atomic Dipole Moment Corrected Hirshfeld Population Method, *J. Theor. Comput. Chem.*, 11 (1), 163. <https://doi.org/10.1142/S0219633612500113>
- [102] **Lu, T., Chen, F.** (2012) Multiwfn: A multifunctional wavefunction analyzer, *Comput Chem.*, 33, 580-592.
- [103] **Reed, A.E., Weinstock, R.B., Weinhold, F.** (1985). Natural Population Analysis, *J Chem Phys.*, 83, 735–746. <https://doi.org/10.1063/1.449486>
- [104] **Tomasi, J., Mennucci, B., Cancès, E.** (1999). The IEF version of the PCM solvation method: an overview of a new method addressed to study molecular solutes at the QM ab initio level, *J. Mol. Struct THEOCHEM.*, 464, 211-226.
- [105] **Sigma-Aldrich** (2021). Retrieved January 2021, from <https://www.sigmaaldrich.com/technical-documents/articles/biology/ir-spectrum-table.html>.
- [106] **Coates, J.** (2000). Interpretation of infrared spectra, a practical approach, *Encyclopedia of analytical chemistry*, 12, 10815-10837.

- [107] **Lingegowda, D.C., Komal Kumar, K., Devi Prasad, A.G., Zarei, M., Gopal, S.** (2013). FTIR spectroscopic studies on cleome gynandra – comparative analysis of functional group before and after extraction, *ROMANIAN J. BIOPHYS.*, 22 (3–4), 137–143, BUCHAREST.
- [108] **Faix, O.** (1992). *Fourier transform infrared spectroscopy*, In: LIN, S.Y.; DENCE, C.W. (ed.) *Methods in lignin chemistry*. Springer-Verlag: Germany.
- [109] **Ben Ticha, M., Meksi, N., Drira, N. Mhenni, M.F.** (2015). Clean Process: Reducing indigo by using environmentally friendly 3-hydroxybutanone on dyed cotton modified with Denitex BC 200%, *RJTA*, 19 (2).
- [110] **Lojewskaa, J., Miskowieca, P., Lojewskia, T., Proniewicz, L.M.** (2005). Cellulose oxidative and hydrolytic degradation: In situ FTIR approach, *Polym. Degrad. Stab.*, 88, 512e520.
- [111] **Haule, L. V., Carr, C. M. and Rigout, M.** (2016). Investigation into the supramolecular properties of fibres regenerated from cotton based waste garments, *Carbohydr. Polym.*, 144, 131-139.
- [112] **Spedding, H.** (1960). Infrared spectra of periodate-oxidised cellulose, *J. Chem. Soc. (London)* 628, 3147–3152.
- [113] **Calvini, P., Gorassini, A., Luciano, G., Franceschi, E.** (2006). FTIR and WAXS analysis of periodate oxycellulose: Evidence for a cluster mechanism of oxidation, *Vibrational Spectroscopy*, 40, 177–183.
- [114] *The Carbonyl Group, Part I: Introduction* (2021). Retrieved May 2021, from <https://www.spectroscopyonline.com/view/carbonyl-group-part-i-introduction>.
- [115] **Xu, F., Yu, J., Tesso, T., Dowell, F. and Wang, D.** (2013). Qualitative and Quantitative Analysis of Lignocellulosic Biomass Using Infrared Techniques: A Mini-Review, *Applied Energy*, 104, 801-809. <https://doi.org/10.1016/j.apenergy.2012.12.019>
- [116] **Hospodarova, V., Singovszka, E., Stevulova, N.** (2018). Characterization of Cellulosic Fibers by FTIR Spectroscopy for Their Further Implementation to Building Materials, *American Journal of Analytical Chemistry*, 09 (06), 303:310.
- [117] **Carrillo, F., Colom, X., Sunol, J. J., & Saurina, J.** (2004). Structural FTIR analysis and thermal characterisation of lyocell and viscose-type fibres, *European Polymer Journal*, 40 (9), 2229–2234.
- [118] **Xu, C., Shamey, R., Hinks, D., El-Shafei, A.** (2012). Cotton bleaching optimization using a butyrolactam-based cationic bleach activator, *AATCC Rev.*, 12 (1), 66-70.

CURRICULUM VITAE

Name Surname : Pelin Altay

EDUCATION :

- **B.Sc.** :2008, Ege University, Textile Engineering Department
- **M.Sc.** :2010, Ege University, Textile Engineering Department

PROFESSIONAL EXPERIENCE AND SCHOLARSHIP:

- Research Asisstant, Istanbul Technical University/Faculty of Textiles Technologies and Design/Textile Engineering Department, Istanbul/Turkey
- February 2016-February 2017. TUBITAK (The Scientific and Technological Research Council of Turkey) for 2214/A – International Research Scholarship Program for Doctorate Student. North Carolina State University/College of Textiles-USA.

PUBLICATIONS & PRESENTATIONS ON THE THESIS:

- **Altay, P.**, Gursoy, N.C. (2013). Low Temperature Bleaching with Cationic Activators. International R&D Brokerage Event of “Innovative and Functional Textiles, June 1st, 2013 Istanbul, Turkey.
- **Altay, P.**, Hauser, P.J., Gursoy, N.C., and El-Shafei, A. (2019). Facile synthesis of a novel, highly effective, more sustainable and cost-effective cationic bleach activator for cotton: N-[4-(N,N,N)-triethylammoniumchloride-butanoyl] Caprolactam, *Cellulose*, 26:2849–2860.
- **Altay, P.**, Yildirim, E., Gursoy, N.C., Hauser, P.J., and El-Shafei, A. (2021). Synthesis of Novel Cationic Bleach Activator, N-[4-(N,N,N)-triethylammoniumchloride- butanoyl] butyrolactam, for Cellulose : Optimization and Theoretical Limitations, *Cellulose*, Preprint has been published online on May 2021.

OTHER PUBLICATIONS AND PRESENTATIONS:

- Korkmaz, S., Özcan, G., **Altay, P.** (2014). Reactive dyeing of organic cotton knitted fabrics using ultrasound technology, *International Journal of Engineering & Technical Research (IJETR)*, ISSN: 2321-0869, Volume 2, Issue 9, 316-322.
- **Altay, P.**, Cavdar, Z.B., Ucar, N., Yavuz, N.K. (2016). Analysis of Carbon and Activated Carbon Nanofiber Web, *International Journal of Environmental Engineering– IJEE*, ISSN: 2374-1724, Volume 3, Issue 1, 84-88.
- Ucar, N., Cavdar, Z., Yavuz, N.K., **Altay, P.**, Kizildag, N. (2016). SO₂ Adsorption Capability of Activated Carbon Nanofibers Produced By Different Activation Process Parameters, *Tekstil ve Konfeksiyon Dergisi*, 26 (4), 407-413.
- Kalaycı, B., İlkiz, B.A., Budak, E.H., **Altay, P.**, Gürsoy, N.C. (2017). Design of Automatic Textile Airing program: An Approach to Sustainable Laundering, *Tekstil ve Konfeksiyon Dergisi*, 27(4), 393-399.
- **Altay, P.**, Özcan, G., Tekçin, M., Şahin, G. Çelik, S. (2018). Comparison of Conventional and Ultrasound Method for Dyeing of Spunbond Polyester Nonwoven Fabric, *Ultrasonics – Sonochemistry*, Volume 42, 768–775.
- Ucar, N., Alptöğ, Ö., Önen, A., Karatepe, N., **Altay, P.** (2019). Improvement of SO₂ adsorption capacity of fiber web surface produced from continuous graphene oxide fiber, Volume 110, No 3, 358–367.
- Yüksek, I.O., Alptöğ, Ö., **Altay, P.**, Karatepe, Önen, A., Uçar, N. (2018). Effect of PVA Addition on SO₂ Adsorption Properties of GO Fibers, *IOP Conf. Series: Materials Science and Engineering*, IOP Conf. Series: Materials Science and Engineering 460, 012050.
- Eryuruk, S.H., Kayaoglu, B.K., **Altay, P.** (2019). Thermal comfort properties of nonwoven fabrics used in surgical gowns, *IOP Conf. Series: Materials Science and Engineering* 459, 012039.
- **Altay, P.**, Alptöğ, Ö., Önen, A., Karatepe, N., Uçar, N. (2019). The Effect of PH, Coagulation Bath and Reduction on Characteristic Properties of Continuous Graphene Oxide Fiber, *Materials Performance and Characterization*, 8 (1), 503-515.
- Arat, R., Başkan, H., Özcan, G., **Altay, P.** (2020). Hydrophobic silica-aerogel integrated polyacrylonitrile nanofibers, *Journal of Industrial Textiles*.
<https://doi.org/10.1177/1528083720939670>
- **Altay, P.**, Atakan, R., Özcan, G. (2021). Silica Aerogel Application to Polyester Fabric for Outdoor Clothing, *Fibers and Polymers*, 22, pp: 1025-1032, 2021.
- Selver, E., Karaca, N., Önen, A. Uçar, N., **Altay, P.** (2020). Morphological/Alignment Properties of Thermoplastic Polyurethane Nanofiber Affected by Processing Parameters, *Journal of Elastomers and Plastics*. <https://doi.org/10.1177/0095244320969849>
- Fung, F., Kalaoglu, F., **Altay, P.**, Hes, L., Bajzik, V. (2020). Measuring movement ease for clothing pattern by means of special made shirt, *Fibres and Textiles Vlakna a Textil*, 27(2), pp. 43–48.
- Selver, E., Öztaş, B., Uçar, M., Uçar, N., Baydoğan, M., **Altay, P.**, Geygel, B. (2021). Mechanical and Thermal Properties of Glass/Epoxy Composites

Filled with Silica Aerogels, Plastics, Rubber and Composites: Macromolecular Engineering.
<https://doi.org/10.1080/14658011.2021.1903142>

- Bekiroğlu, E., Özcan, G., **Altay, P.** (2021). Improvement in pilling property of viscose/PET blended knitted fabric after garment dyeing, The Journal of the Textile Institute. <https://doi.org/10.1080/00405000.2021.1912953>
- Özcan, G., **Altay, P.**, Tekçin, M., Şahin G., Çelik, S. (2014). Dyeability of Spun Bond Polyester Nonwoven Fabric in Ultrasound Bath, 14th AUTEX World Textile Conference, Bursa, 26-28 Mayıs 2014.
- De Mey, G., Ozcelik, M., Schwarz, A., Kazanı, I., Hertleer, C., Van Langenhove, L., **Altay, P.**, Gursoy, N. (2014). Designing of Thermal Comfortable Bed Systems, 7-8 Eylül 2014 Tampere, Finland.
- **Altay, P.**, Ozcan, G., Kübra, Y., Gürbüz, A., Karaağaç, D.M. Design of Chameleon Like Photochromic Cotton Woven Fabric, Ambience14&10i3m, 7-9 Eylül 2014 Tampere, Finland. Poster presentation.
- Tüfekçi, F., Kılıç, H., Memnun, K., **Altay, P.**, Ozcan, G. (2015). Prototype Development of Fully Automatic Printing Paste Preparation System, 5th International Istanbul Textile Congress 2015: Innovative Technologies: “Inspire to Innovate”, 11-12 Eylül 2015.
- **Altay, P.**, Olmez, M., Onen, A., Ucar, N. (2017). The Effect of Dispersion Concentration on the Properties of Graphene Oxide Fiber, III. International Symposium on Multidisciplinary Studies (ISMS), 10-11 November 2017, Ankara, Turkey.
- **Altay, P.**, Alptöğ, Ö., Yüksek, I.O., Onen, A., Karatepe, N., Ucar, N. Investigation on SO₂ Adsorption Capacity of Graphene Oxide Fibers with Activated Carbon Particles and Metal Salt, 8th International Istanbul Textile Conference on Evolution of Technical Textiles (ETT 2018), 14-16 April 2018, Tüyap Fair and Exhibition Center, Istanbul, Turkey.
- Ucar, N., **Altay, P.**, Yüksek, I.O. (2018). Morphological Analysis of Continuous Graphene Oxide Fibers incorporated with CNT and MnCl₂, ICAMNN 2018 : 20th International Conference on Advanced Materials, Nanoscience and Nanotechnology, 7-8 September 2018, Istanbul/Turkey.
- **Altay, P.**, Atakan, R., Ozcan, G., Coban, M.E., Ozcan, I. (2019). Optimization of scouring process for wool fleece, ICONWOOLF 2019: International Congress on Wool and Luxury Fibers, 19 April 2019, Çorlu, Tekirdağ/Turkey.
- Özcan, G., Eryürük, S.H., Yüksek, I.O., **Altay, P.**, Atakan, R. Development of Boron Additive, Flame Retardant and Antibacterial Textile Surfaces from Cotton Textile Wastes, 6th MEMTEK Symposium on Membrane Technologies and Applications, 18-20 November 2019, Istanbul/Turkey. Poster presentation.
- **Altay, P.**, Karaca, N., Onen, A., Ucar, N., Baydoğan, M. (2020). Thermoplastic Polyurethane/ Polystyrene Composite Nanofibers: Improvement of surface area and porosity, 7th International Fiber and Polymer Research Symposium (7. ULPAS), 25-26 September 2020.
- Yüksek, I.O., **Altay, P.**, Filiz, Ş.Y., Gursoy, N.C. (2020). Kas Hastaları için Denim Pantolon Tasarımı, İTÜ Ulusal Tekstil Kongresi ve II.Ar-Ge Günü, Akademi Sanayi Buluşması 11-12 Kasım 2020.

- Eryürük, S.H., Kalaoğlu, F., **Altay, P.**, Şahin, E., Yıldırım, A., Sağlam Y. (2020). Çok katmanlı termal koruyucu giysilerin nem yönetimi özelliklerinin incelenmesi, İTÜ Ulusal Tekstil Kongresi ve II.Ar-Ge Günü, Akademi Sanayi Buluşması 11-12 Kasım 2020.

